Atmospheric
Measurement
Techniques

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Discussions

Interactive comment on "The use of NO₂ absorption cross section temperature sensitivity to derive NO₂ profile temperature and stratospheric/tropospheric column partitioning from visible direct sun DOAS measurements" *by* E. Spinei et al.

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We would like to thank reviewer #2 for his/her thorough review and recommendations.

Minor comments:

1. Abstract. This comment is related only to nomenclature: In the first paragraph of the abstract the magnitudes that can be obtained by using TESEM method are presented,

they are: total vertical NO2 column and the slant NO2 profileweighted temperature (T). In my opinion is not clear if T from here is the profile weighted Temperature of the slant NO2 profile-weighted temperature. Specially when in the second paragraph of the abstract a new magnitude, total column NO2 T, is defined. How should this magnitude be interpreted, as a total NO2 column profile-weighted temperature? Still I cannot understand very well what is a slant column profile-weighted temperature. Later on in the text (lines 9 and 10 pg 5704) these concepts are clarified, but in my opinion this should be clarified in the abstract as well.

— We apologize for the confusion. All the T refer to the slant NO2 profile weighted temperature along the photon path unless specifically stated that it is a vertical NO2 profile weighted temperature. We have shortened the abstract and removed this ambiguity both from the abstract and the text.

2. Line 14 pg 5697. Here is stated that DS measurements have the same sensitivity to stratospheric and tropospheric absorption for solar zenith angles below 75deg but later on in the text (line 2 pg 5701) this magnitude is changed to SZA<80deg. Please unify criterion.

— We have unified to SZA < 80° to be consistent with Cede et al., 2006

3. Line 16 pg 5697. Please avoid the use of plural of magnitudes as "Ts".

— We have corrected all the instances of using plural tense with T, SCD, and VCD

4. One of the most interesting characteristics of TESEM is that does not need any external information to extract T. This talks by itself, in my opinion the explanation about the traditional fitting of NO2 should be in the introduction, but not in the abstract (this is lines 25-28 pg 5697 and lines 1 to 3 pg 5698).

— This information is removed from the abstract

5. Figure 1. This figure would be more clear if x axis were solar zenith angle instead time.

— We assume that the reviewer refers to Fig 2 and 4. We found plotting Heff or Teff vs SZA for mid-latitude location to be less informative due to relatively large SZA around noon especially in winter. If plotted vs. SZA the figures are mainly populated on the edges and no information in the middle. We have combined Fig. 2 and 4 in one and added a separate panel for SZA vs. local time.

6. Line 27 pg 5699. Seasonal variability of NO2 in the stratosphere is a well-known issue; authors should indicate that is not a result from GMII-CTM model but an expected behaviour.

— We have rephrased the sentence to: "As expected, GMI-CTM model predicts maximum stratospheric NO2 columns in summer and minimum in winter."

7. Line 20 pg 5700 The referente of Hendrick et al., 2011 is for ozone measuerements, but there are loads of references about NDACC data of NO2: Hendrick, F., Mahieu, E., Bodeker, G. E., Boersma, K. F., Chipperfield, M. P., De Mazière, M., De Smedt, I., Demoulin, P., Fayt, C., Hermans, C., Kreher, K., Lejeune, B., Pinardi, G., Servais, C., Stübi, R., van der A, R., Vernier, J.-P., and Van Roozendael, M.: Analysis of stratospheric NO2 trends above Jungfraujoch using ground-based UVvisible, FTIR, and satellite nadir observations, Atmos. Chem. Phys., 12, 8851-8864, doi:10.5194/acp-12-8851-2012, 2012. Gil, M., Yela, M., Gunn, L. N., Richter, A., Alonso, I., Chipperfield, M. P., Cuevas, E., Iglesias, J., Navarro, M., Puentedura, O., and Rodríguez, S.: NO2 climatology in the northern subtropical region: diurnal, seasonal and interannual variability, Atmos. Chem. Phys., 8, 1635-1648, 2008. Pinardi, G. and Lambert J.C., O3M SAF VALIDATION REPORT, SAF/O3M/IASB/VR/NO2/095. 2011.

— We have replaced Hentrick et al. 2011 with: Hendrick, F., Mahieu, E., Bodeker, G. E., Boersma, K. F., Chipperfield, M. P., De Mazière, M., De Smedt, I., Demoulin, P., Fayt, C., Hermans, C., Kreher, K., Lejeune, B., Pinardi, G., Servais, C., Stübi, R., van der A, R., Vernier, J.-P., and Van Roozendael, M.: Analysis of stratospheric NO2 trends above Jungfraujoch using ground-based UVvisible, FTIR, and satellite nadir

observations, Atmos. Chem. Phys., 12, 8851-8864, doi:10.5194/acp-12-8851-2012, 2012.

8. Line 24 pg 5701, Please change MAX by MAXDOAS and zenith by Zenith sky DOAS.

— We have replaced: "DS, multi-axis and zenith sky DOAS"

9. Line 1 pg 5702. In an ideal case, cross sections must be fitted taken into account the temperature of atmosphere, but usually this not the case (specially because usually the T profile is not known and TESEM method haven't been developed till now), but for its purposes DOAS works relatively well as well only using two different temperatures. In my opinion the sentence should be "cross section should be fitted: " instead "cross sections must be fitted".

— Corrected

10. Line 6 pg 5705. Just for homogeneity in the notation through the entire work, please use T in K instead degC.

— Corrected

11. Line 10 pg 5705 and line 16 pg 5706. In the formula of line 10 there are two different T profiles; T of measurements and TREF. The main assumption of the method until now seems to be that REF contribution to dDSCD is negligible, and then it is not necessary calculate TREF, but later on it is demonstrated that TREF can be calculated as well. Please explain this in this point of the text, otherwise that seems that it is a limitation of the method.

— We do not believe we make any assumptions about SCDREF prior to Line 10 pg 5705. To clarify this point we add the following: "SCDREF and TREF are not known beforehand but can be approximated from the DS DOAS measurements themselves (see Section 3.1)"

12. Line 2 pg 5706. Maybe this is only a misunderstanding from my part, but I don't understand very well the mean of dDSCD T. This is the difference between SCD x T and SCDREF x TREF?. In the definition of this line it seems that T and TREF are the same. Please explain.

— It is correct: $\Delta SCDT\alpha$ = SCD*T - SCDREF*TREF T and TREF might or might not be the same. We removed this line to avoid ambiguity

13. Line 23 pg 5706. To apply this approximation the place should be in principle unpolluted and measurement taken at large solar angles, but if I have understood well, this method is limited to SZA < 75°. This same explanation is given in lines 1 to 3 pg 5708. What large solar angles are involved here? Or, in other words, what is the SZA range of applicability of TESEM.

— We greatly appreciate this question since we have not realized how ambiguous the description appears. We have removed Eq. (3b) and its discussion from Section 2.3. We have introduced Section 3.1 that focuses on determination of SCDREF and TREF: "SCDREF can be estimated from DS measurements using Minimum Langley extrapolation method (MLE, Herman et al., 2009, see Eq. (7)). Where the slope of the smallest ΔSCD in each ΔAMF bin versus ΔAMF is determined to approximate VCD at the reference time (VCDREF). MLE is a statistical modification of the Langley plot method that relies on availability of long-term measurements. The main assumption of MLE is that there are time periods at each SZA when VCD $\approx$ VCDREF (ΔVCD $\approx$ 0), and the change in smallest ΔSCD at each ΔAMF bin is only caused by the change in AMF. This method is applicable to polluted or unpolluted sites. Due to strong changes in stratospheric NO2 VCD at SZA > 75° only measurements at SZA < 75° are used to derive VCDREF. To avoid errors associated with seasonal variability of NO2 VCD MLE should be applied to data collected during the same season. One month of data is typically sufficient. TREF is harder to estimate since it requires prior knowledge of stratospheric and tropospheric NO2 SCD in the reference spectrum. These columns can also be estimated from the DS data used in MLE analysis. For conditions when MLE assump-

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tions apply (VCD $\approx$ VCDREF and T $\approx$ TREF) Eq. (3) simplifies to T=ΔSCDTα/ΔSCD. Then stratospheric SCD in the reference spectrum can be approximated using Eq. (5), (6) and Langley Plot method. TREF can be determined, knowing stratospheric and tropospheric NO2 profile T at the reference time"

Please note, that SZA < 75° limitation applies only to determination of SCDREF and TREF to comply with Minimum Langley Method that requires that constant VCD compared to VCDREF exists as a function of SZA. This is done to avoid known changes in NO2 column due to photochemistry after sunrise and before sunset. After SCDREF and TREF are estimated, Eq. (3a) is used to determine T. There is no limitation on SZA here. At SZA > 87°, however, the uncertainty in AMF becomes more pronounced as well as the uncertainty in TSTRAT. In addition, SNR of the DS measurements at SZA > 85° reduces.

14. Formula (4). Please add χSTRAT+χTROP=1.

— Added

15. Line 3 pg 5708 large SZA and low levels of pollution. Please add "low".

— We have removed this sentence and introduced Section 3.1 (see above).

16. line 14 pg 5708, Once all parameters have been calculated using some approximations as low solar zenith angles and unpolluted measurements, calculated magnitudes have been used to calculate other magnitudes affected by these approximations out of the range of applicability of such assumptions. This does not seem consistent to me, because calculated SCDSTRAT and SCDTROP are valid only for previously made assumptions, and could not be used out of the range of assumptions. Please clarify this point.

— Estimation of SCDREF and TREF are done using valid assumptions and under valid conditions for Langley-type methods. SCDREF and TREF are physical quantities at a specific reference time, place and observation geometry. They do not have an

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ability to change as a function of other measurements. After these "constants" are estimated they can be used to calculate T from Eq. (3a) which has no assumptions at all about SZA or pollution levels. SCDSTRAT and SCDTROP are then recalculated for all measurement conditions using Eq. (5) and (6) that do not have any limitations posed by SZA or pollution level. We believe Section 3.1 makes this point more clear now.

17. Figure 7. Residuals are really low, but it would be nice if their dependence with lambda would be shown here as well as the fits. Really good fits by the way. I would expected better fits for unpolluted place (lower residuals) than for NASA/GSFC site, maybe this behaviour is due to the low NO2 column at JPL, is this place at midday representative of free troposphere?

— Residuals are now added to the figure. The main reason for better residuals over GSFC compared to JPL is a design change (implemented in 2010) that increased number of collected direct sun photons. The rsidual OD RMS are slightly smaller over Pullman compared to GSFC for the same MFDOAS configuration (as the reviewer suggests). JPL-TMF is representative of free troposphere on most mornings and days with easterly winds.

18. Line 21 pg 5715. Table 3 is Table 4 actually

— Corrected

19. Line 7 pg 5716. Please explain what means "more 'dynamic' meteorology" in order to explain the different behaviour of stratospheric NO2 from different sites. Differences in the column could be attributed to different season, but I do not understand very well what means "dynamical meteorology". Is it possible to support this fact using any kind of observation?

— Thank you for pointing out the confusion of using this explanation. We believe that the following is more appropriate:

"More variability in stratospheric NO2 over NASA/GSFC can be partially explained by more variability in solar actinic flux in May 2013 compared to measurement days in July 2007 (JPL-TMF) and in July-August 2011 (WSU/Pullman) (daily solar flux data are available from ftp://ftp.geolab.nrcan.gc.ca/data/solar_flux/daily_flux_values/). However it cannot fully explain large changes in T27km (6 – 8K) over NASA/GSFC in May 2013 from day to day compared to no more than 3K over the two other sites. "

20. Figure 10, axis are missing in some plots. It would be nice if these plots could be larger, it's difficult to see NO2 amounts specially in the first row.

— Corrected

21. Last paragraph of conclusions. Have authors applied TESEM method to MAX-DOAS or zenith sky measurements? In that case, does the method work as well as for DS measurements?

— Yes, we have applied TESEM for calculation of ΔSCDs from MAX-DOAS and zenith sky measurements. It allows for separation of tropospheric and stratospheric columns without the need to subtract zenith sky measurements. We now have a discussion of comparison of TESEM tropospheric and stratospheric columns from MAX-DOAS and zenith sky with the DS data (please see response to main concern by reviewer #1)