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Atmospheric Measurement Techniques
Discussions

Interactive comment on "The use of NO_2 absorption cross section temperature sensitivity to derive NO_2 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 #1 for his/her thorough review and recommendations.

Main concern:

The method seems to work well at the four selected sites. However, to my opinion, its validity is not fully demonstrated in the paper. In order to achieve that, comparisons

with correlative data sets would be helpful. A comparison between retrieved and modelled stratospheric NO2 VCD is presented in Fig. 10 for the WSU/Pullman site but since at Cabauw and WSU/Pullman almost coincident MAX-DOAS observations exist, I wonder why you did not use these data to verify your tropospheric NO2 columns. In a first attempt, you could use the MAX-DOAS tropospheric NO2 columns derived by the geometrical approximation. Moreover, if you have twilight zenith-sky observations at these both stations, you could also derive stratospheric NO2 columns and convert them to the DS measurement times using your GMI model in order to validate/verify your TESEM stratospheric columns.

Response:

We have not included co-incident MAX-DOAS/zenith measurements because the profile inversion algorithms for MAX-DOAS and DS-DOAS measurements, developed by E. Spinei, has not been described in the literature before and an extensive discussion of these methods would be required to convince the reader that the comparisons were valid. Thus, to include the results in this paper would require such extensive discussion of the method that we believe it is not appropriate for this paper. However, we like the idea of the referee to compare tropospheric columns from MAX-DOAS (30° elevation angle) data using geometrical approximation since it does not require lengthy description. To address the question of the method validity we added the following discussion: "To demonstrate validity of TESEM to DS measurements we compare total, stratospheric and tropospheric columns with time coincident measurements. MFDOAS direct sun total NO2 columns were validated using a high resolution (∼0.001 nm) Fourier Transform Ultraviolet Spectrometer (FTUVS) over JPL-TMF (Wang et al., 2010) that retrieves absolute columns and does not require Langley-type calibration. The total VCD derived by the MFDOAS and FTUVS instruments agreed within (1.5 ± 4.1)%. Even though this comparison was done on the data over a clean site, similar results are expected over a polluted site with a long-term record of measurements. We applied a modified version of TESEM to MAX-DOAS (30° elevation angle) and zenith sky data to derive tropospheric and stratospheric VCD without the need to subtract zenith sky dSCD. We convert SCD into tropospheric VCD using a geometrical approach where AMF $\approx$ 2 for 30° and $\approx$ 1 for zenith sky at SZA < 75° (range of MAX-DOAS applicability). The tropospheric columns agree within 30% and stratospheric within 50%. An extensive discussion of stratospheric columns derived from twilight zenith sky and DS, and tropospheric columns from multi-axis, DS and zenith sky DOAS measurements over Cabauw during CINDI are presented in Spinei et al., 2014."

Specific comments:

1. Abstract: The abstract is a bit too long to my opinion. I suggest to move the paragraph on the traditional NO2 fitting in the Introduction.

We have removed the paragraph on the traditional NO2 fitting.

2. Page 5705, line 6: Please replace T0=0C by T0=273K in order to be consistent with Fig. 3. corrected

3. Page 5707, lines 20-21: please add a reference for the MLE method.

We added “Herman et al., 2009”

4. Page 5711, Sect. 5: The error sources are briefly discussed here. I think it would be interesting to provide an error budget on the retrieved tropospheric and stratospheric NO2 columns. I suggest to include a table with the different error sources and their corresponding uncertainties. Also related to this point, I think it would be interesting to see error bars in Fig. 10.

We added Fig. (6) showing the estimated errors from different sources on VCD as a function of SZA. We have left out the error bars from Fig. 10 to reduce “clutter” of the data, but refer the reader to the error analysis section (5)

5. Page 5719, lines 15-25: You applied your method only to mid-latitude sites in late spring/summer. Do you expect larger uncertainties in fall/winter ? What about the ap-

plication of your method to highly polluted sites, e.g. in or in the vicinity of megacities? Please clarify the possible limitation(s) of your method.

To demonstrate applicability of TESEM to Fall/Winter measurements we added to the paper Winter results for GSFC and Fall results for WSU locations. For middle latitude sites minimum daily SZA in Fall/Winter are typically larger than in summer so using summer reference spectrum is desirable to maximize ΔSCD if residuals stay reasonably small. Separation between stratospheric and tropospheric columns is impacted by higher uncertainty in stratospheric NO2 effective temperature in winter. To deal with this issue we modified TESEM for winter months where daily Tstrat is fitted to produce a linear fit as a function of time at SZA < 75°. The errors are larger for winter months than for summer due to larger errors in dSCD/dSCDT and larger uncertainty in Tstrat. In general, higher pollution results in higher accuracy of the retrieval. This method should work very well in megacities especially since most of them are located in warm climates with small seasonal variations in stratospheric temperatures. The two main limiting factors (assuming high quality measurements) are difference between stratospheric and tropospheric columns and accuracy in estimation of stratospheric and tropospheric temperatures. These conditions in megacities with warm climates are optimized for TESEM. Another requirement is availability of long term measurements to ensure presence of the same pollution levels as in reference spectrum for MLE method. Note, MLE does not require low pollution, it requires some time periods with constant VCD as a function of AMF. The major issue comes from estimating SCDref and Tref. To evaluate this effect we separated clean days and polluted days from the GSFC data and applied MLE to the two datasets separately. We have found that MLE performs almost equally well if sufficient number of measurements exists.

Technical corrections:

1. Page 5697, line 16 and page 5707, line 5: the use of Ts for the plural of T is confusing, please try to avoid that.

corrected

2. Page 5703, line 7: T should be in italic.

corrected

3. Page 5707, lines-20-21: ‘(MLE, Eq. (7)’ should be replaced by ‘(MLE, see Eq. (7))’.

corrected

4. Page 5727, step 2, second column: ‘SCDref’ instead of ‘SDCref’.

corrected

5. Page 5740, Fig. 10: Right y-axis are missing in the second and third right plots. Could you please put the dates on the upper left corner of the plots to avoid a mixing with the axis legends. Similar comment for Fig. 8.

corrected

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 5695, 2014.