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Supplement of

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

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TESEM application to DS-DOAS data collected during Fall/Winter months

Separation of stratospheric and tropospheric columns during winter months at middle latitudes from DS-DOAS measurements is more challenging for TESEM due to: 1) smaller stratospheric columns (greater effect of DOAS fitting error and cross correlation between $\sigma(NO_2)$ and $\alpha(NO_2)$), and 2) greater uncertainty in assumed NO_2 effective stratospheric and tropospheric temperatures. Nonetheless, in addition to summertime measurements when TESEM is mostly accurate, we here present results for observations taken over GSFC/NASA during November 2012 – February 2013, and over WSU/Pullman in October 2011.

1. DOAS fitting

Direct sun measurements collected during the late fall/winter months (cold temperatures) over GSFC/NASA and WSU/Pullman require fitting O_2O_2 cross sections at two temperatures (203 and 293K, Thalman and Volkamer (2013)). This is to eliminate residual structure that becomes present around 477 nm if only the Hermans et al. cross section at 296K is fitted (see Spinei et al. 2014).

Using the summer reference spectrum is beneficial due to more "predictable" NO_2 T^{STRAT} and T^{TROP} for VCD^{ref} and T^{ref} calculation, as well as higher retrieved dSCD coming from the difference in the observation SZA between summer and winter. On the other hand, stratospheric VCD^{REF} can be 2-4 times larger in summer than winter. As a result, 10% error in summer VCD^{REF} can correspond to 20-40% error in winter VCD^{REF}. In addition, a summer reference spectrum produces a slightly larger DOAS fitting residual OD.

2. Results and discussion

Figure S1 shows NO_2 T, stratospheric, tropospheric, and total columns using TESEM analysis for three days in December 2012 and February 2013 over GSFC/NASA. The days were chosen to demonstrate the effect of inaccurate T^{TROP} estimation caused by temperature inversion. The main assumption of TESEM – that T^{TROP} can be estimated by T at the surface – does not hold during temperature inversion events. This is because even within the lowest 400 m, the temperature aloft can be 5-10K warmer than at the surface. As a result, $T_{0km} < T^{TROP}$ and the stratospheric fraction become underestimated. This is evident from the data collected in the morning on 14 December 2012 when TESEM calculated T as 8K larger than T at the surface. Examination of the atmospheric sounding temperature profile shows a strong inversion at 12:00 UTC (7:00 LT), with a temperature difference of ~ 9K between the surface and at 280 m. This results in a negative stratospheric fraction and VCD (-3.85 x 10^{15} molecules cm^{-2}). The absolute value of underestimation depends on the error in T^{TROP}. NO_2 T is larger than T_{0km} through most of the day on 14 December 2012. At 16:00, when NO_2 T approached T_{0km}, VCD^{STRAT} approached 0 molecules cm^{-2}. Temperature inversion was still present at 19:00 LT. On 10 February 2013, the stability had changed, with strong inversion in the morning and no temperature inversion within the first 1 km later in the day. TESEM tracked the conditions by underestimating VCDS^{TRAT} in the morning and gradually "recovering" later in the afternoon to the more expected columns of 2 x10^{15} molecules cm^{-2}). On 12 February 2013, the conditions had again changed and VCD^{STRAT} is within the expected error. TESEM results improved when the T^{TROP} estimated from the surface measurements was adjusted by the difference between sonde T at 0.1 km and 0.4 km. While TESEM is not reliable enough to be used to separate stratospheric and tropospheric NO_2 columns during stagnation events, it can be reliably used to identify such events in data.

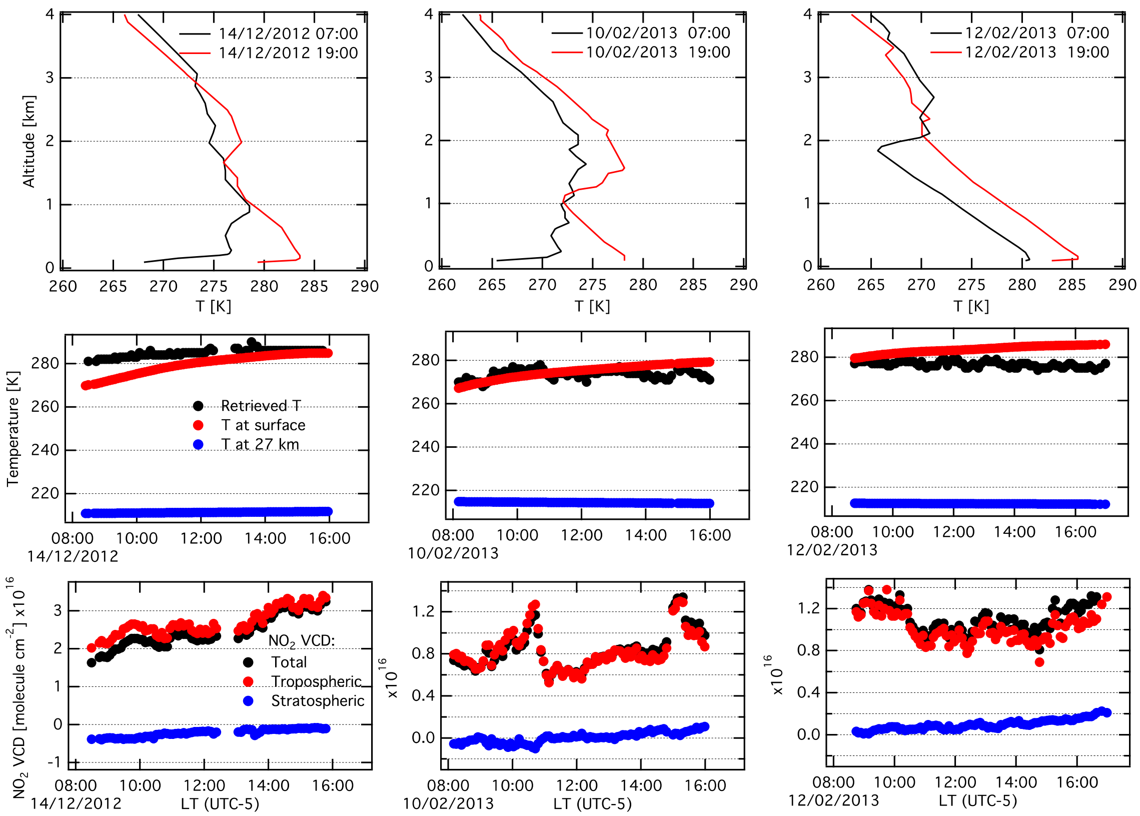

Figure S1 NO_2 *T*, stratospheric, tropospheric, and total columns calculated from DS data collected over GSFC/NASA on 14 December 2012, and 10 and 12 February 2013, using TESEM. Temperatures at the surface and at 27 km, and atmospheric sounding temperature profiles are also shown. No averaging of data is performed.

The data shown in Figure S1 has some contamination of VCD^{STRAT} by VCD^{TROP} due to cross correlation between $\sigma(NO_2)$ and $\alpha(NO_2)$. Four-hour VCD^{STRAT} averaging eliminates this contamination effect.

Analysis of the spectra collected over WSU/Pullman in October 2011 shows that TESEM "struggles" to separate stratospheric and tropospheric columns under low pollution conditions and higher uncertainty in the estimation of T^{STRAT} and T^{TROP}. On average, the retrieved VCD^{STRAT} is 5 x 10^{14} molecule/cm^2 lower than the GMI predictions. Figure S2 shows an example of the retrieved total, stratospheric, and tropospheric columns for 29 October 2011 over Pullman, WA, in comparison to the GMI estimations.

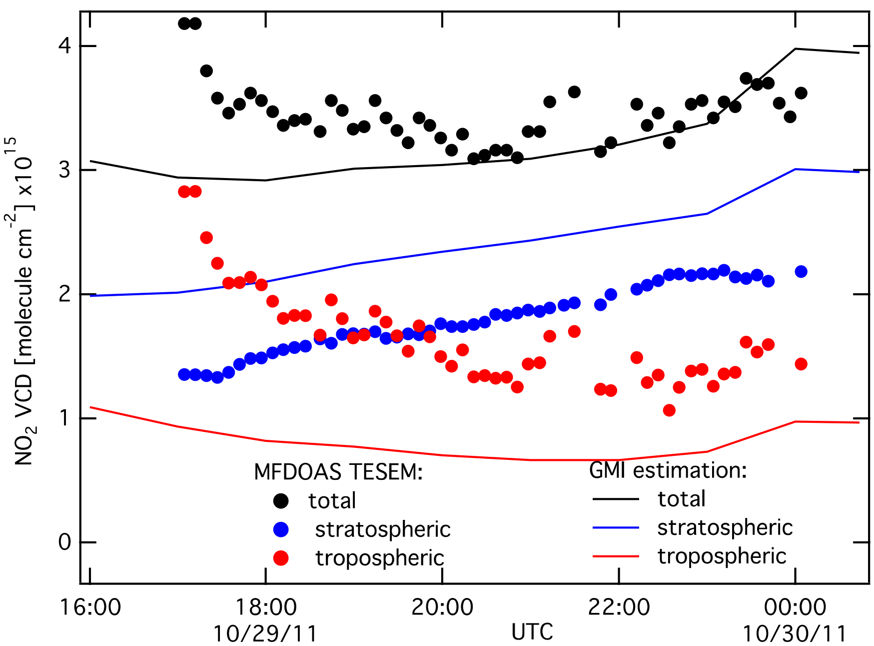

Figure S2. NO_2 *T*, stratospheric, tropospheric, and total columns calculated from DS data collected over WSU/Pullman on 29 October 2011, using TESEM and GMI estimations.

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Table **S1** MFDOAS measurement sites, observation periods, and estimated stratospheric and tropospheric vertical NO_2 profile weighted temperatures.

Site name and location	Elev [m]	Dates	Source of temperature at 27 km*	Mean T at 27 km [K]	Mean T at surface [K]	Pollution level
WSU, Pullman, WA Lat: 46.7325° N Lon: 117.169° W	764	October, 2011	Atm. soundings from Spokane, WA (47.68° N, 117.63° W)	219.26 ± 2.25	282.01 ± 4.75	low
NASA/GSFC Greenbelt, MD Lat: 38.993° N Lon: 76.839 ° W	~90	November, 2012-February, 2013	Atm. soundings from Sterling, VA (38.98° N, 77.46° W)	215.69 ± 5.04	276.67 ± 5.29	moderate - high

*Atmospheric soundings (http://weather.uwyo.edu/upperair/sounding.html) launched from nearby locations.

Table **S2** MFDOAS measurement sites, observation periods, and estimated total, stratospheric, and tropospheric NO_2 effective temperatures.

Site name	Dates	Est. mean NO_2 T [K]	Measured mean NO_2 T [K]	NO_2 ($T-T_{27km}$) [K]
WSU, Pullman, WA 46.73° N, 117.17° W	October, 2011	234	243.48 ± 10.84	23.69 ± 10.98
NASA/GSFC, Greenbelt, MD 38.99° N, 76.84 ° W	November, 2012-February, 2013	270	278.02 ± 6.59	61.61± 9.54