Temperature effects in MAX-DOAS observations of NO$_2$

A. Richter, F. Wittrock, E. Peters, A. Schönhardt and J. P. Burrows
Institute of Environmental Physics/Remote Sensing, University of Bremen
FB 1, P.O. Box 330440, D-28334 Bremen, Germany
Email: Andreas.Richter@iup.physik.uni-bremen.de

Temperature Dependence of NO$_2$

- The NO$_2$ absorption cross-section is temperature dependent
- The temperature dependence of the differential structures is to good approximation linear (see Figure 1)
- Using an inappropriate temperature in the retrieval will result in errors in the columns
- It also reduces fitting quality although not much (as deviations from linear scaling are small)

Errors from NO$_2$ T-dependency

- Tropospheric NO$_2$ retrievals from MAX-DOAS observations have to use cross-sections at tropospheric temperatures
- As temperature changes over the day and over the season, biases are introduced which should be corrected with measured or modelled atmospheric temperatures
- For NO$_2$ profile retrievals, height dependent errors are introduced if the effect is not accounted for
- T-effect: 0.36%/K
- Standard used: 298K
- 2% - 13% from annual cycle in mid-latitudes (-10°C to 30°C)
- ~ 5% during individual days
- ~ 11% for elevated NO$_2$ layer at 3 km

Fig. 1: Temperature dependence of the differential NO$_2$ cross-section in the 425 - 450 nm fitting window. Left: absolute values, middle: values scaled to 221K, right: scaling parameters as a function of temperature

Retrieval of NO$_2$(T) signature

- As tropospheric NO$_2$ is warmer than stratospheric NO$_2$, the temperature dependence of the NO$_2$ cross-section can potentially be used to separate the two components in zenith-sky measurements
- To maximize the signal, a spectral region with large T-effect has to be selected
- Based on analysis of the orthogonalised T-dependence (see Figure 2), the spectral region 450 - 480 nm was selected

Fig. 2: Orthogonalised T-dependence of the NO$_2$ cross-section

- In MAX-DOAS measurements with very good signal to noise ratio, the signature of the temperature dependence of NO$_2$ can be retrieved
- Differential optical depths are small (of the order of 2x10$^{-5}$) peak-to-peak
- In measurements during the CINDI campaign, periods of tropospheric NO$_2$ pollution can be identified in the zenith-sky measurements as enhanced values
- During these times, also the fitting coefficient of the temperature correction is enhanced

Fig. 3: Example fits of the NO$_2$ 220K signal (left) and the temperature dependence (298 - 220 K) (right) for one observation during CINDI

Application to more days

- Method works well on many days
- Values at large SZA are questionable (no off-axis observations available for comparison)
- On some days (example June 19), offsets are observed during some times which could point at enhanced tropospheric NO$_2$ in the zenith measurements (reducing 30% observations)
- During short periods of high NO$_2$, 30° observations show different behaviour as T-signal with even negative values as large NO$_2$ values in the zenith reference measurement occur and offset results from the differential nature of T-signal absorption
- Offset can be fitted or directly be taken from the 30° values

Fig. 4: Slant column retrieved for NO$_2$ (red) and the T-dependence (blue) in one day of zenith-sky measurements during CINDI

Fig. 5: Tropospheric NO$_2$ for June 17, 2009. Top: 30° elevation and zenith-sky, both with noon zenith-sky reference, middle: 30° relative to closest zenith-sky compared to T-signal from zenith, bottom: same as middle but with ad-hoc offset for T-signal

Conclusions

- Over the range of typical atmospheric temperatures, the T-dependence of the NO$_2$ absorption cross-section leads to uncertainties in the order of many per cent in tropospheric NO$_2$ columns derived from MAX-DOAS observations
- The effects are systematic with respect to diurnal variation, seasonal variation, and vertical distribution
- Correction is possible using a simple scaling approach and temperature measurements
- In the presence of large NO$_2$ pollution and with low noise measurements, the spectral signature of the temperature dependence can be used to estimate tropospheric NO$_2$ absorption from zenith-sky observations alone
- This was demonstrated for several days of measurements during the CINDI campaign
- Comparison to off-axis observations shows good agreement
- Compared to other methods of tropospheric NO$_2$ retrieval, this is of more academic interest

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Selected References


see also: www.iup.uni-bremen.de/doas