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Temperature effects in MAX-DOAS observations of NO_2

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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

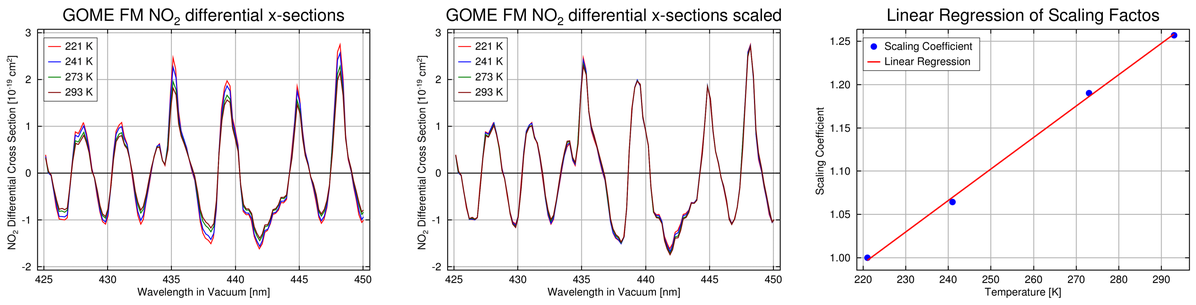
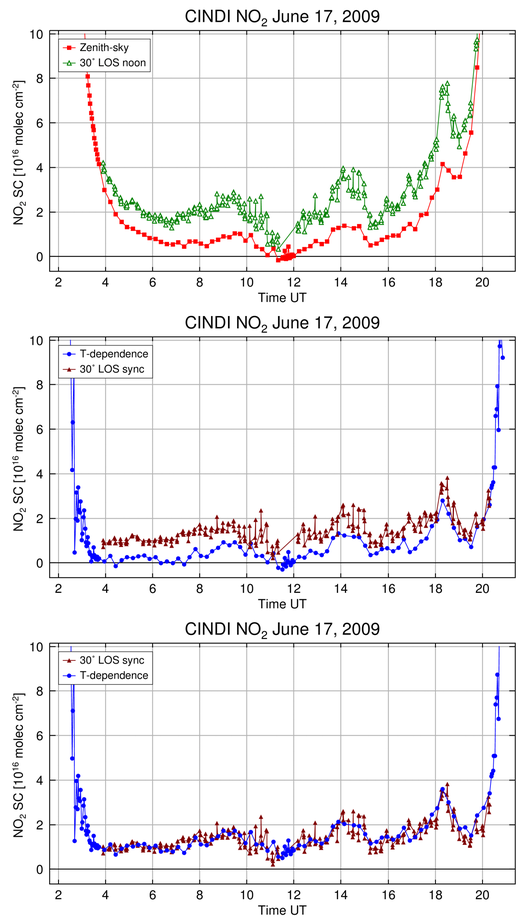


Fig. 1: Temperature dependence of the differential NO_2 cross-section in the 425 - 450 nm fitting window. Left: absolute values, middle: values scaled to 221K, right: scaling parameters as a function of temperature

Retrieving tropospheric NO_2



- measurements at lower elevation angles carry more information on tropospheric absorption
- comparison to zenith-sky values highlights episodes of tropospheric pollution
- measurements were taken in different azimuthal directions
- scatter in 30° elevation measurements results from horizontal gradients
- using the closest in time zenith-sky measurement as background isolates the tropospheric signal

- comparison to T-signal from zenith-sky measurements shows good agreement but offset
- offset results from the differential nature of T-signal which is relative to the effective temperature in the noon spectrum used as background
- offset can be fitted or directly be taken from the 30° values

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

Retrieval of NO_2(T) signature

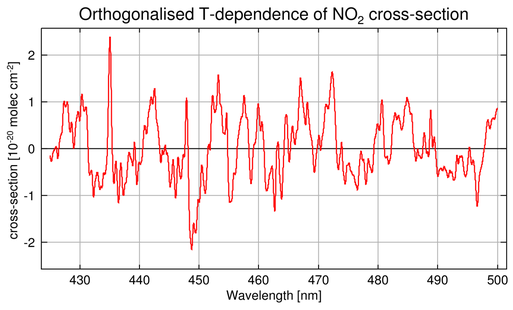


Fig. 2: Orthogonalised T-dependence of the NO_2 cross-section

- 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 Fig. 2), the spectral region 450 - 480 nm was selected

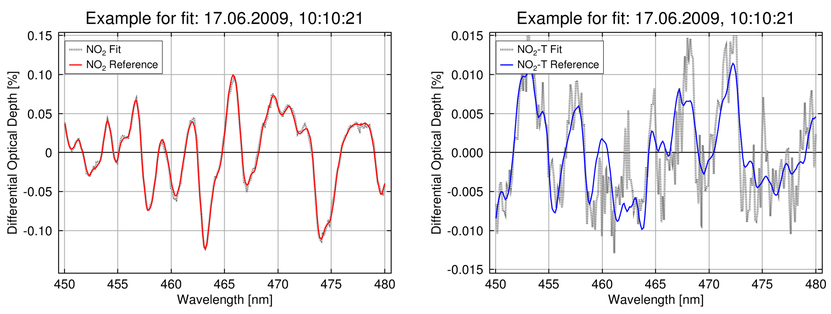


Fig. 3: Example fits of the NO_2 220K signal (left) and the temperature dependence (298 - 220 K) (right) for one observation during CINDI

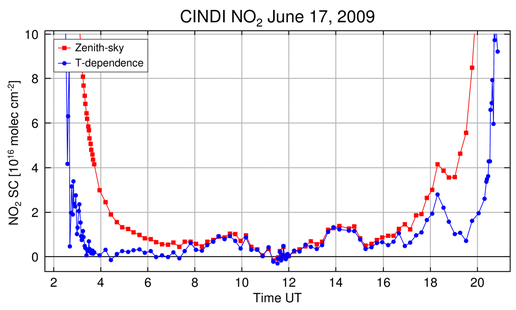


Fig. 4: Slant column retrieved for NO_2 (red) and the T-dependence (blue) in one day of zenith-sky measurements during CINDI

- 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 $2x10^{-4}$ 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

Application to more days

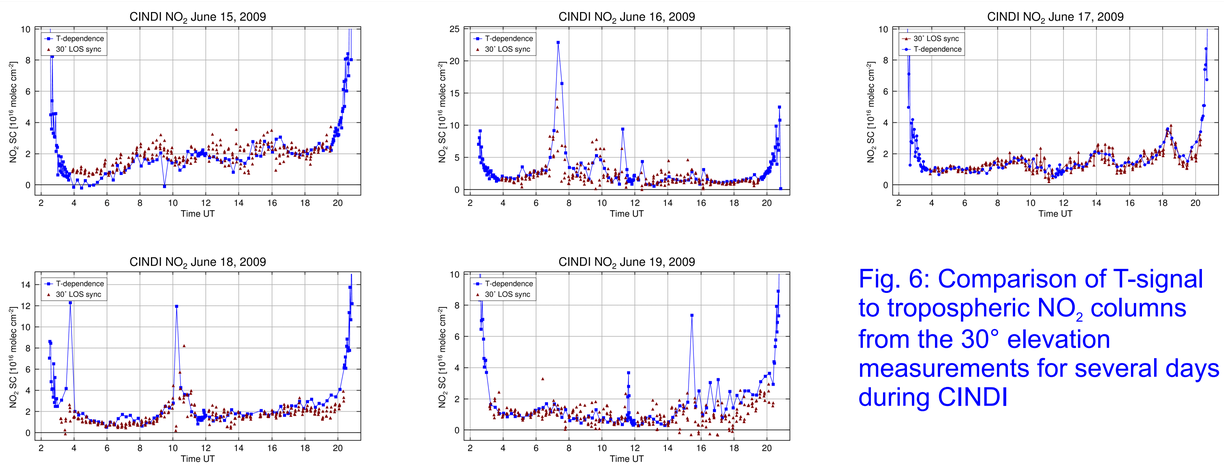


Fig. 6: Comparison of T-signal to tropospheric NO_2 columns from the 30° elevation measurements for several days during CINDI

- 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 influence 30 measurements taken a few minutes later (see June 18 and 19)
- the problem of air mass factors (effect of multiple scattering in clouds and aerosols) remains for both methods

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

Acknowledgements

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