MAX-DOAS measurements of nitrogen dioxide at the high altitude sites Zugspitze and Pico Espejo

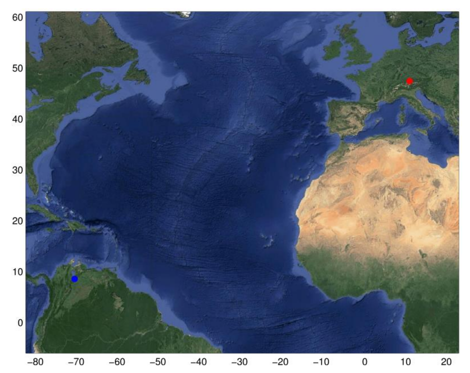
Stefan F. Schreier*, Andreas Richter, Folkard Wittrock, and John P. Burrows

Institute of Environmental Physics/Remote Sensing, University of Bremen, Germany

* Email: schreier@iup.physik.uni-bremen.de

Location, instrumentation, and motivation

Zugspitze (Germany):
- 2962 m a.s.l., 47.42°N, 10.99°E
- MAX-DOAS measurements from February to July 2003
- suitable for measurements of NO_2 in the free troposphere (FT) at mid-latitudes
- polluted boundary layer air is occasionally uplifted and transported to the FT



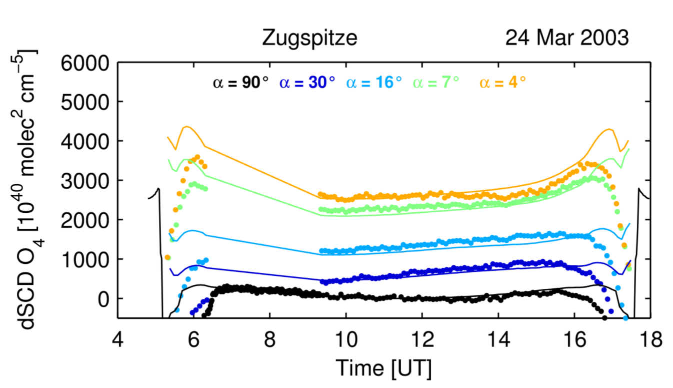
Pico Espejo (Venezuela):
- 4765 m a.s.l., 8.53°N, 71.06°W
- March 2004 to February 2009
- facilitating measurements in the stratosphere and/or free troposphere
- tropical region that is generally unperturbed by tropospheric pollution (sometimes long-range transport from fires)

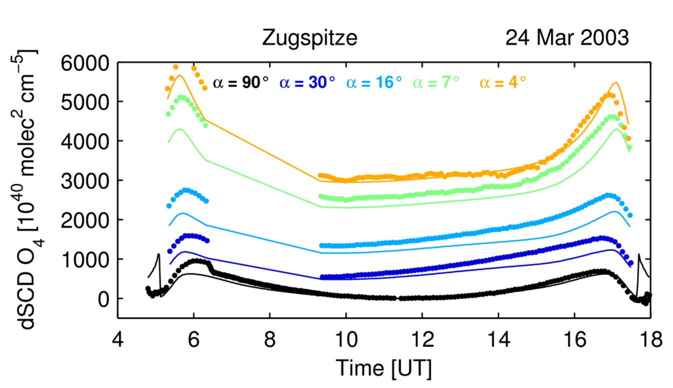
Instrumentation:
- the MAX-DOAS system consisted of a temperature stabilized grating spectrometer (wavelength range: 321-410 nm) equipped with a cooled CCD detector
- the instrument was connected to a telescope unit
- several viewing directions were included

Motivation:
- long-term data sets from two mountain MAX-DOAS systems in the tropics/mid-latitudes can be used for the retrieval of NO_2
- elaborate on the method by *Gomez et al. (2014)*
- analysis of NO_2 mixing ratio in the free troposphere

Synthetic vs. measured O_4 dSCDs

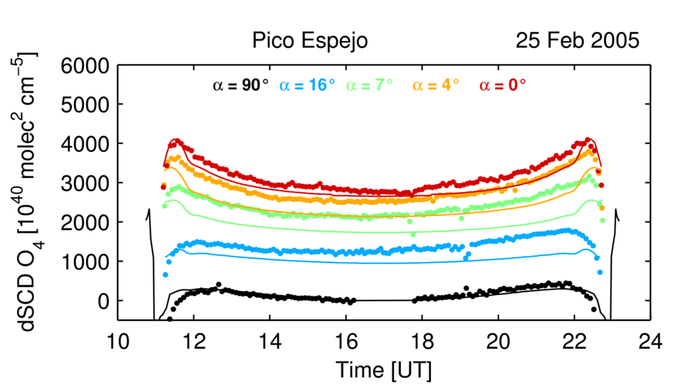
- time series of O_4 dSCDs as retrieved from measured (dotted line) and synthetic (solid line) spectra using Fit A (left) and Fit B (right) are shown for single days with clear sky conditions at Zugspitze (upper) and Pico Espejo (lower)
- best agreement between O_4 dSCDs is found for the zenith direction (α = 90°)
- for the off-axis directions (α = 0°, 4°, 7°, 16°, and 30°), the agreement is reasonable (within 20% for SZAs < 70°)
- these findings support the use of O_4 dSCDs from MAX-DOAS measurements for the estimation of NO_2 mixing ratios in the free troposphere applying the modified geometrical approach

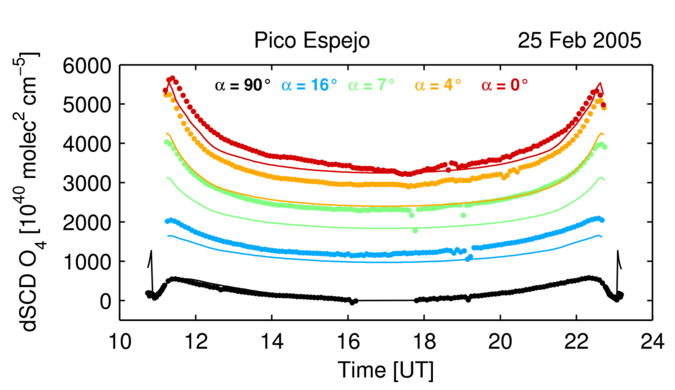




Zugspitze

Fit A (338-357 nm) Fit B (346-372 nm)





Pico Espejo

Acknowledgements

Backward trajectories were calculated with the HYSPLIT online tool from NOAA (National Oceanic and Atmospheric Administration)

GFASv1.0 fire radiative power (FRP) data have been provided by MACC (Monitoring atmospheric composition & climate)

Selected References

Gomez, L., Navarro-Comas, M., Puentedura, O., Gonzalez, Y., Cuevas, E., and Gil-Ojeda, M.: Long-path averaged mixing ratios of O_3 and NO_2 in the free troposphere from mountain MAX-DOAS, Atmos. Meas. Tech., 7, 3373-3386, doi:10.5194/amt-7-3373-2014, 2014.

Richter, A., et al.: SCIAMACHY validation with ground-based DOAS observations, DLR Project (final report), 2005.

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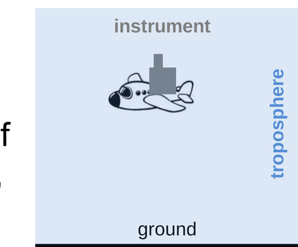
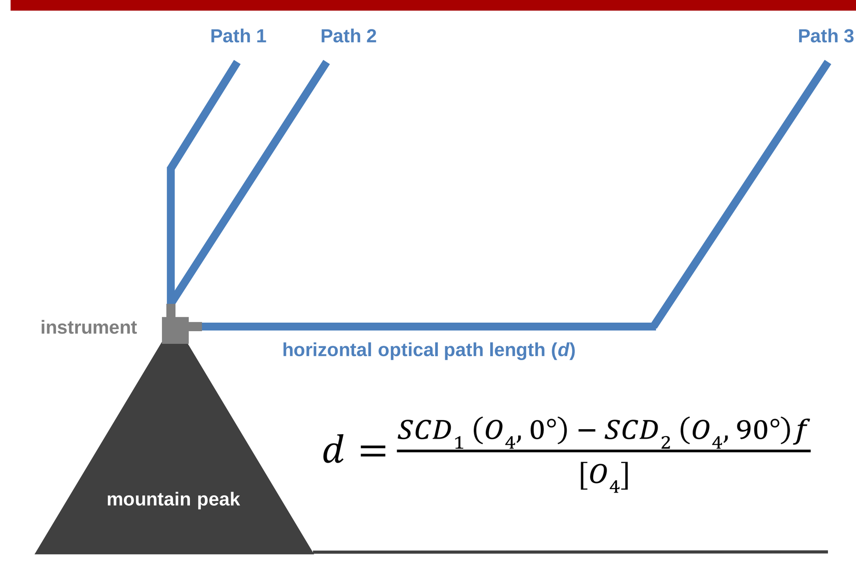
Simulation of synthetic spectra

	SCIATRAN input
RTM mode	Intensity/radiance
RTM type	Spherical atmosphere
Extraterrestrial solar flux	Sun_kurucz_10
Wavelength range	330-410 nm (UV)
Wavelength step	0.04 nm
Forward model trace gases	NO_2, O_3, O_4, BrO, HCHO, NO_3, OClO, SO_2, and ClO
Aerosols	No aerosols
Clouds	No clouds
Albedo	0.05

- the radiative transfer model SCIATRAN is used for the computation of synthetic spectra
- the geometry in SCIATRAN is modified in a way to account for the atmosphere below (the instrument is "flying" at the altitude of Zugspitze/Pico Espejo, see right figure)



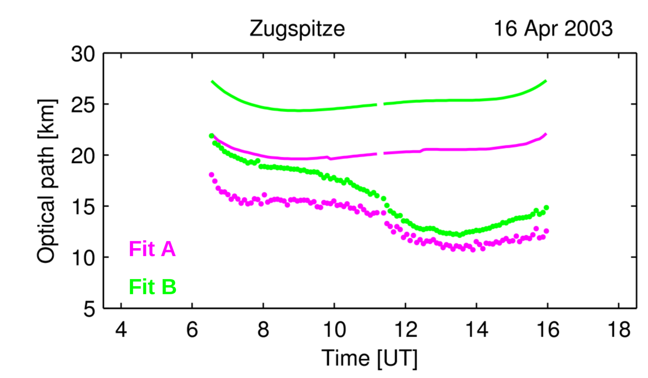
Horizontal optical path length



$$d = \frac{SCD_1(O_4, 0°) - SCD_2(O_4, 90°) f}{[O_4]}$$

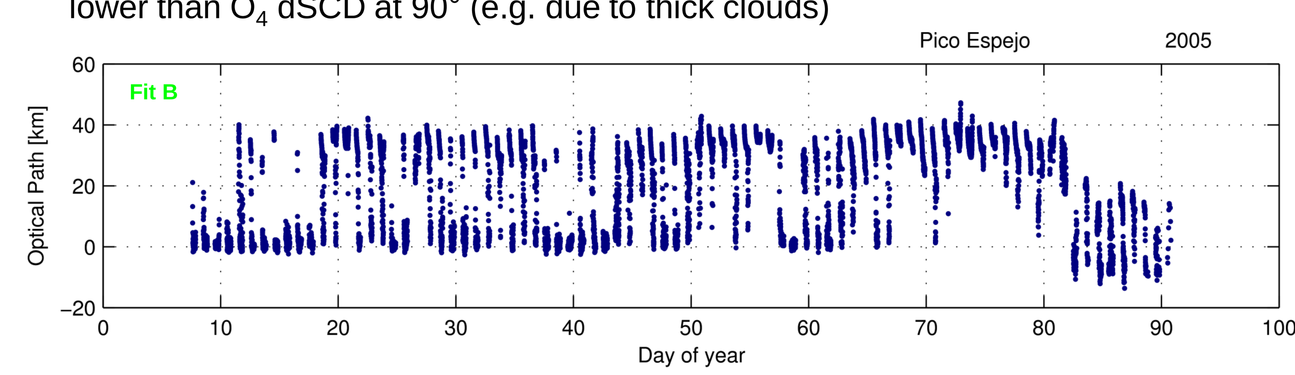
adapted from *Gomez et al. (2014)*

- the following assumptions are made for the modified geometrical approach (MGA):
  - single scattering geometry
  - scattering point altitude close to the instrument

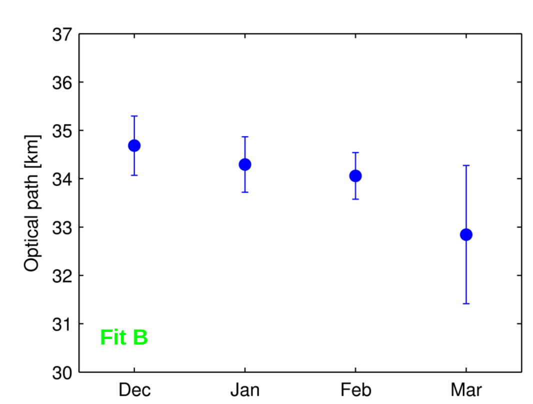


- in the figure below, *d* is presented for Pico Espejo during a typical dry season (January, February, and March)
- the optical path length varies between 0 (thick clouds) and 50 km (no clouds, low aerosol amounts)
- negative values arise when the retrieved O_4 dSCD at 0° is lower than O_4 dSCD at 90° (e.g. due to thick clouds)

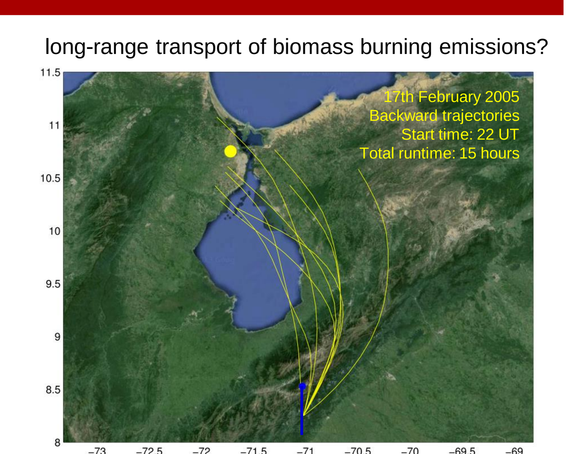
- in the figure above, *d* is shown for a single day at Zugspitze (16th April 2003)
- the optical path length as derived from the synthetic spectra (solid line) is larger than *d* as estimated from the measured spectra; a possible explanation could be an increase in aerosol amounts; the NO_2 dSCDs also rise throughout the day (see right figure)

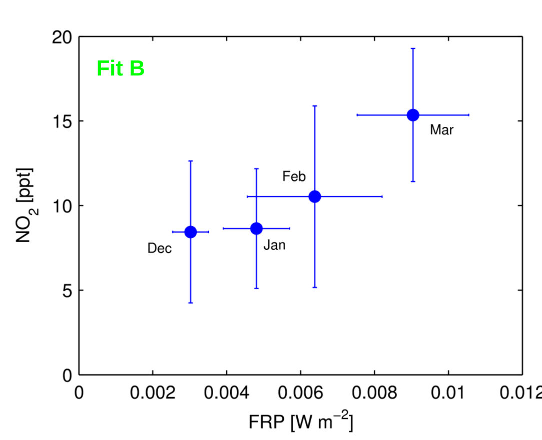


NO_2 from biomass burning in the FT?



- the multi-year averaged (2004-2009) optical path length for clear sky conditions (*d* > 30 km) at Pico Espejo is shown for December, January, February, and March (left figure)
- clearly, *d* is decreasing towards the end of the dry season (probably because of increasing aerosol loads due to increased fire activity)





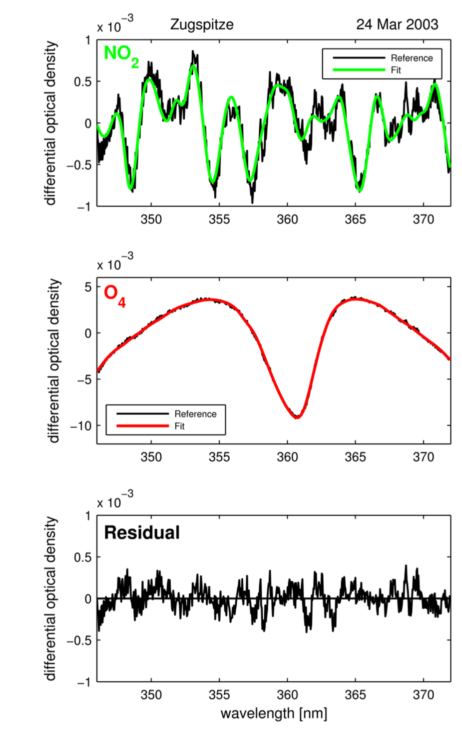
- in the left figure, multi-year monthly means of NO_2 mixing ratios are plotted against multi-year monthly means of fire radiative power (FRP)
- FRP has been spatially averaged (5°-10°N, 75°-65°W)
- clearly, NO_2 mixing ratios increase towards the end of the dry season

- although the long-path averaged NO_2 mixing ratios at Pico Espejo were measured at an altitude of almost 5000 m a.s.l., and thus, clearly above the boundary layer, it seems that the FT is affected by biomass burning emissions in this region

DOAS retrieval of dSCDs

- the measured and synthetic spectra are analyzed using the Differential Optical Absorption Spectroscopy (DOAS)
- the retrieval of NO_2 and O_4 differential slant column densities (dSCDs) is performed in the spectral window 338-357 nm (Fit A) and 346-372 nm (Fit B)

Cross sections	Data source
O_3	O3_SERDYUCHENKO_223K_AIR.RAW
NO_2	NO2_220K_VANDAELE.RAW
O_4	O4_HERMANS_WEB.RAW
BrO	BrO_223K_FLEISCHMANN.RAW
HCHO	H2CO_297K_MELLER.RAW
Ring	RING_SCIATRAN_UV.RAW
Reference	ZS_FILE
Polynomial	4th degree

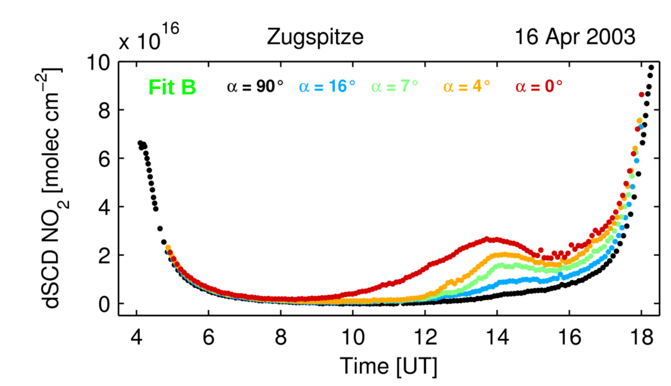


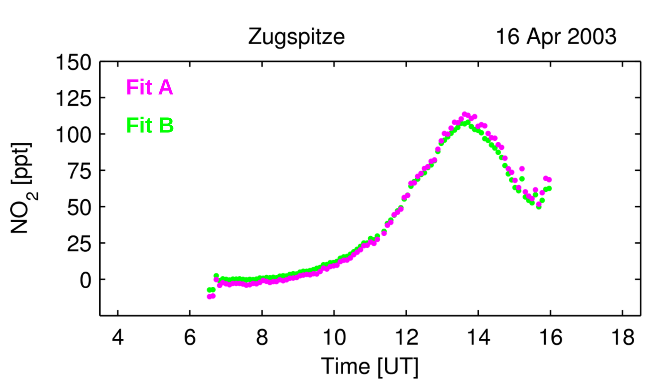
- in the left figure, an example of the spectral DOAS analysis is shown
- the spectrum was measured at Zugspitze on 24th March 2003 (SZA = 68.8°, α = 4°)
- here, a spectrum in zenith direction taken around noon (SZA = 46.06°) is used as a reference
- as the spectrum was taken at almost 3000 m a.s.l., the differential optical density of NO_2 (upper) is rather low
- the DOAS analysis performed on synthetic spectra yields similar results (not shown)

Long-path averaged NO_2 mixing ratios

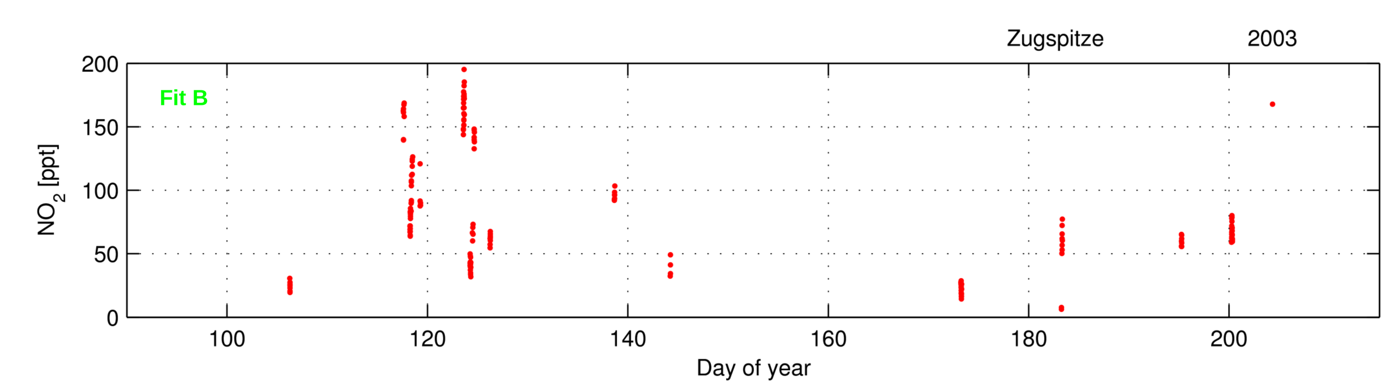
$$[NO_2] = \frac{SCD_1(NO_2, 0°) - SCD_2(NO_2, 90°) f}{d}$$

- NO_2 mixing ratios, averaged over the horizontal optical path, are estimated using the left formula
- here, *f* is a correction factor to take into account the difference in SZA between α = 0° and α = 90°

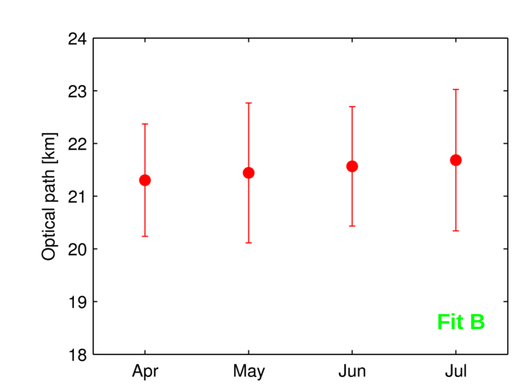




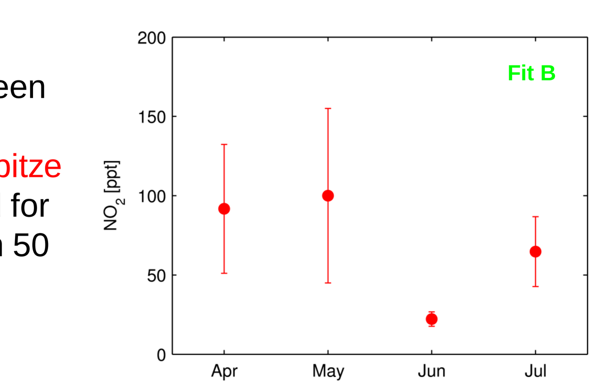
in the left figures, NO_2 dSCDs and NO_2 mixing ratios are shown for an exemplary day at Zugspitze with increased pollution



mixing ratios of NO_2 (for cases with *d* > 20 km) are shown for Zugspitze (April, May, June, and July 2003 (left figure)



- monthly means of optical path lengths can reach values between 20 and 23 km during clear sky conditions (*d* > 20 km) at Zugspitze
- mixing ratios of NO_2 as derived for clear sky conditions range from 50 to 150 ppt (see right figure)
- due to prevailing cloudiness in June, only few values remain



Summary and conclusions

- two long-term MAX-DOAS data sets have been analyzed for NO_2 and O_4 dSCDs at two different high altitude stations in the tropics and mid-latitudes
- the comparison of O_4 dSCDs (synthetic vs. measured) showed reasonable agreement
- the modified geometrical approach (*Gomez et al., 2014)* has been used for the calculation of optical path lengths and NO_2 mixing ratios in the free troposphere
- averaged horizontal optical path lengths during clear sky conditions are 21.5 km (Zugspitze) and 34 km (Pico Espejo) and averaged mixing ratios of NO_2 are 70 ppt (Zugspitze) and 11 ppt (Pico Espejo)