MAX-DOAS measurements of African continental pollution outflow over the Atlantic Ocean

Lisa K. Behrens[1] (lbehrens@iup.physik.unibremen.de), Andreas Hilboll[1,2], Enno Peters[1,3], Andreas Richter[1], Leonardo M. A. Alvarado[1], Folkard Wittrock[1], John P. Burrows[1], and Mihalis Vrekoussis[1,2]

[1] IUP - Institut für Umweltphysik, University Bremen, Germany
[2] MARUM, Bremen, Germany
[3] DLR - Deutsches Zentrum für Luft und Raumfahrt, Bremerhaven, Germany

1 Project & Ship Cruise

Figure 1: Research vessel Maria S. Merian
A MAX-DOAS instrument was installed on board of the research vessel for the COPMAR project in October 2016.

Motivation:
- enhanced levels of atmospheric key pollutants can be identified over the Atlantic Ocean in global trace gas maps retrieved from satellite measurements
- the aim of this project was to validate these enhanced values by using ship-based MAX-DOAS (Multi-AXis Differential Optical Absorption Spectroscopy) measurements

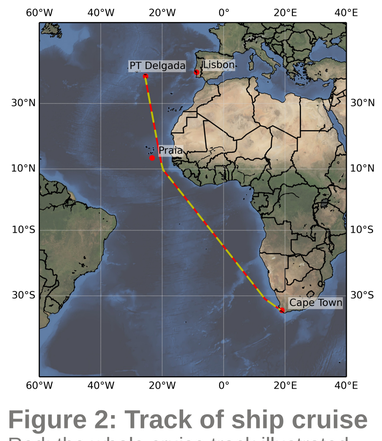

Figure 2: Track of ship cruise
Red: the whole cruise track illustrated.
Yellow: the measurement periods (day).
Start: on 8 October 2016 on the Azores.
End: on 25 October 2016 in Cape Town.

Project:
COPMAR - Continental Outflow of Pollutants towards the Marine TRoposphere:
- conducted in October 2016 on the research vessel Maria S. Merian (MSM)
- cruise track from Ponta Delgada (Azores) to Cape Town (South Africa, Figure 2)
- the campaign was part of the cruise MSM58/2

Data:
- elevation angles from 0° (horizon) to 90° (zenith) are used for the anaylsis - one scan took ~10 min
- the instrument was continuously scanning a vertical plane towards the African continent
- measurements which might be contaminated by the vessel plume are excluded (measurements with a relative wind direction between 90° and 270°)
- the data are corrected for the ship's movement (roll and pitch)

2 Method

DOAS: Differential Optical Absorption Spectroscopy (Figure 3)
- based on Lambert Beer's law: $I(\lambda,s) = I0\exp(-\sigma(\lambda)\rho s)$
  - method to calculate the absorption of light (UV/vis) travelling through the atmosphere
- amount of trace gases can be derived from absorption ⇒ slant column densities (SCDs)
  - retrieved with a least square fit
- SCDs can be converted to vertical column densities (VCDs) by using air mass factors (AMF), calculated with the radiative transfer model (RTM) SCIATRAN: SCD = AMF * VCD
- for pollution close to the ground → the highest SCDs are expected for the lowest elev. angles

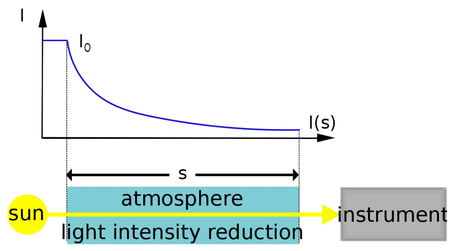

Figure 3: Illustration of the DOAS method
I: reduced intensity
I_0: intensity of the light directly from the sun
s: light path
λ: wavelength
σ: absorption cross-section
ρ: concentration of absorbers

3 Measurement validation with stratos. NO_2

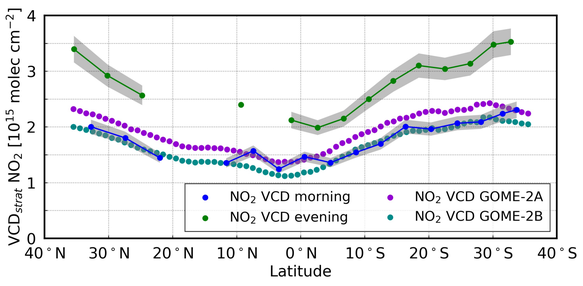

Figure 4: Lat. dependency of stratos. NO_2
IUP-UB GOME2-A and GOME2-B data (equator crossing time: ~9:30 LT) are averaged between 10°W - 40°W. MAX-DOAS VCDs are averaged between 88° - 92° solar zenith angle (SZA), because of the higher sensitivity to the stratosphere. A fix reference spectrum (17.10.16) is used for the analysis.

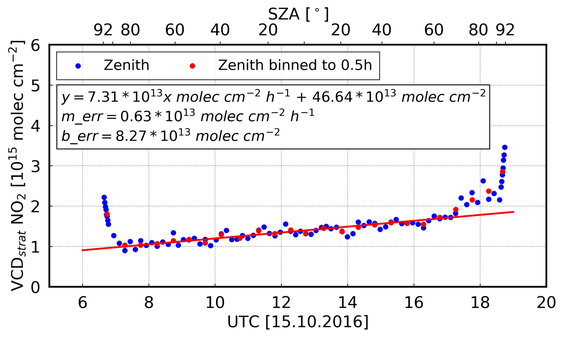

Figure 5: Diurnal cycle of stratos. NO_2
The diurnal cyle of stratospheric NO_2 is shown for 15.10.16. During twilight in the morning the NO_2 values are smaller than during twilight in the evening (see also Figure 4).

- potential small tropos. contribution from outflow is ignored for this analysis
- MAX-DOAS data agree well with satellite data (Figure 4)
  - due to the diurnal cycle of stratos. NO_2, the satellite measurements are closer to the morning values (Figure 5)
  - previous studies found a similar latitudinal dependency over the Atlantic Ocean (Kreher et al, 1995 and Senne et al, 1998) and over the Pacific Ocean (Peters et al, 2012).
- the increase during the days is due to photochemistry in the stratosphere

⇒ instrument performed well, further weaker absorbers are analysed

4 Continental outflow of HCHO & CHOCHO

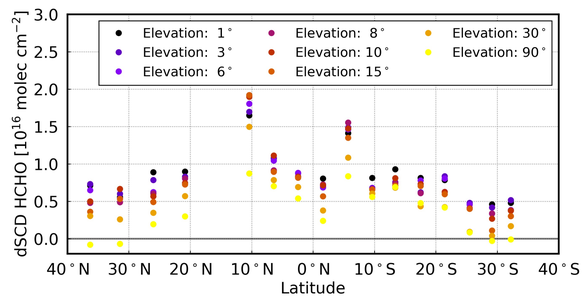

Figure 6: Elevation angle dependency of HCHO
The elevation angle with the highest daily mean dSCDs depends on the lat. This is expected from RTM calculations, because the continental outflow is expected to be in the free troposphere. A fix ref. spec. (23.10.16) is used for the analysis.

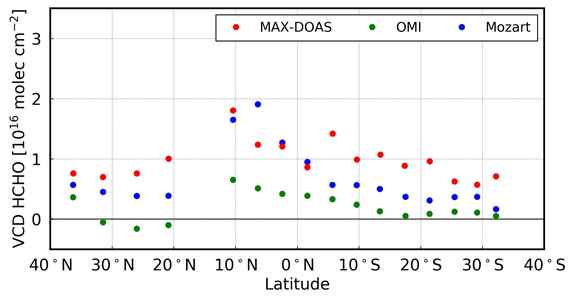

Figure 7: Comparison to model and sat. data
Model data are Mozart-4 (~1.9° x 2.5°, 6h), and satellite data are from the Ozone Monitoring Instrument (OMI). Correlation coefficients are 0.73 (MAX-DOAS - MOZART-4) and 0.69 (MAX-DOAS - OMI).

- SCDs: close to Azores and Cape Town, pollution is found close to the ground
  - ~10°N (HCHO & CHOCHO) and ~5°S (HCHO): highest values are found for elev. angles between 6° -10° ⇒ pollution is in higher layers in the atm.
- latitudinal dependency of VCDs (HCHO & CHOCHO) is clearly visible in daily mean MAX-DOAS measurements, model data, and OMI data
  - HCHO:
    - satellite data are always lower than MAX-DOAS and model data
    - MAX-DOAS and model results show a good agreement
  - CHOCHO
    - wider spread of OMI VCDs than for model and MAX-DOAS VCDs
    - OMI VCDs are close to the detection limit
    - satellite data are mostly higher than MAX-DOAS data, MAX-DOAS data are slightly higher than model data in the area of expected outflow

⇒ continental outflow of HCHO (3 days) and CHOCHO (1 day) can be detected

5 Measurements of tropospheric NO_2

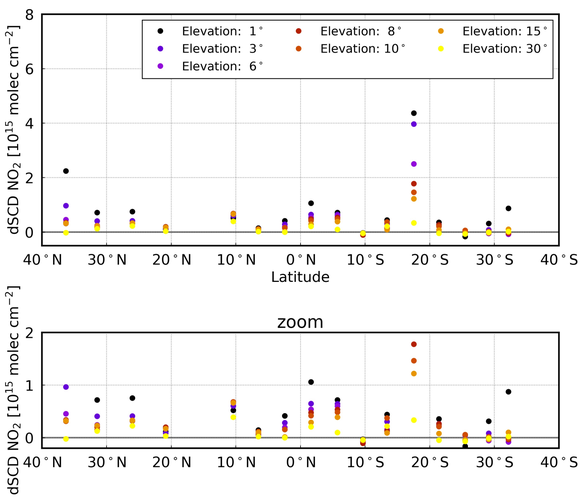

Figure 6: Elevation angle dependency of tropospheric NO_2
The elevation angle with the highest daily mean differential SCDs depend on the latitude. The closed reference spectrum is used for the analysis.

- close to the Azores and Cape Town: pollution is found close to the ground
- ~10°N: highest values are found for elevation angles of ~10° ⇒ pollution is in higher layer in the atmosphere, although the values are small

⇒ possibly detection of continental outflow of NO_2 at 2 days

- ~18°S: container vessel was in front of MSM
  - high NO_2 values are detected during the whole day
  - large spread of elevation angles with highest NO_2 close to the surface

⇒ plume from the vessel is in the lowest layers for the atmosphere

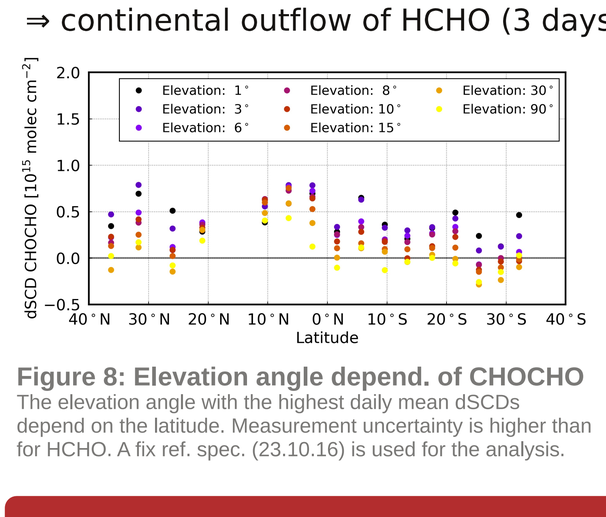

Figure 8: Elevation angle depend. of CHOCHO
The elevation angle with the highest daily mean dSCDs depend on the latitude. Measurement uncertainty is higher than for HCHO. A fix ref. spec. (23.10.16) is used for the analysis.

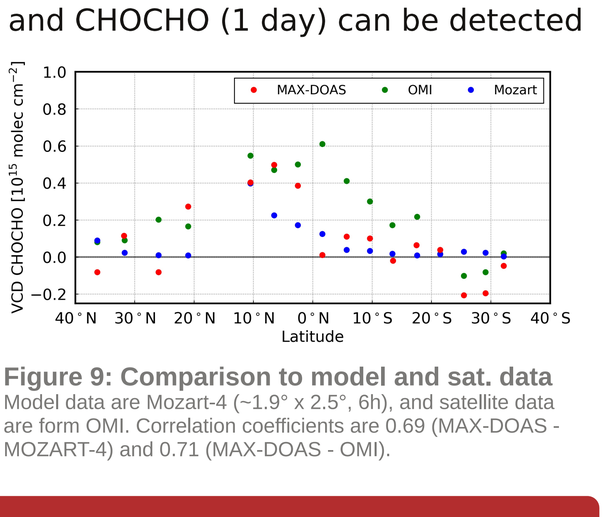

Figure 9: Comparison to model and sat. data
Model data are Mozart-4 (~1.9° x 2.5°, 6h), and satellite data are form OMI. Correlation coefficients are 0.69 (MAX-DOAS - MOZART-4) and 0.71 (MAX-DOAS - OMI).

6 Summary & Outlook

Summary
- COPMAR was a measurement campaign in Oct. 2016 in the Atlantic Ocean
- stratospheric NO_2 was successfully observed
  - latitudinal dependency and diurnal cycle are clearly visible
- at one day: high tropo. NO_2 data are observed, because the Maria S. Merian was sailing behind a container vessel
- outflow of HCHO, NO_2, and CHOCHO from the African Continent can be observed at one to three days depending on the trace gas
  - ship-based measurements agree well with model and satellite data

⇒ enhanced values in HCHO, NO_2 and CHOCHO as indicated from satellite data are confirmed by our ship-based measurements

Outlook
- investigation of the altitude for the outflow ⇒ calculation of trajectories

Acknowledgements & References

- Peters, E., Wittrock, F., Großmann, K., Frieß, U., Richter, A., and Burrows, J. P.: Formaldehyde and nitrogen dioxid over the remote western Pacfic Ocean: SCIAMACHY and GOME-2 validation using ship-based MAX-DOAS observations, Atmospheric Chemistry and Physics, 12, 2012.
- Kreher, K., Fiedler, M., Gomer, T., Stutz, J., and Platt, U.: The latitudinal distribution (50°N - 50°S) of NO_2 and O_3 in October/November 1990, Geophysicak Research Letters, Vol. 22, No. 10, 1995.
- Senne, T., Stutz, J., and Platt, U.: Meaurements of the latitudinal distribution of NO_2 column density and layer height on Oct. / Nov. 1993, Geophysicak Research Letters, Vol. 23, No. 8, 1996.
- Rozanov, V., et al.: Radiative Transfer through Terrestrial Atmosphere and Ocean: Software Package SCIATRAN, J. Quant. Spectrosc. Rad. Transfer, 133, 13–71, doi:10.1016/j.jqsrt.2013.07.004, 2014.

- This study has been funded by the University of Bremen, and by the DFG-Research Center / Cluster of Excellence "The Ocean in the Earth System".
- Thanks for financial support from Postgraduate International Programme in Physics and Electrical Engineering (PIP).
- We further thank the "DFG Senatskommission für Ozeanographie" for the travelling time at Maria S. Merian and the "Leitstelle Deutsche Forschungsschiffe" for the logistic support.
- GOME-2 lv1 data were provided by EUMETSAT.
- We acknowledge use of Copernicus Atmosphere Monitoring Service (CAMS) Information as well as of MOZART-4 global model output (available at http://www.acom.ucar.edu/wrf-chem/mozart.shtml).