MAX-DOAS measurements of atmospheric composition over the Atlantic Ocean

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1 Project & Ship Cruise

Figure 1: Research vessel Maria S. Merian

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 measurements

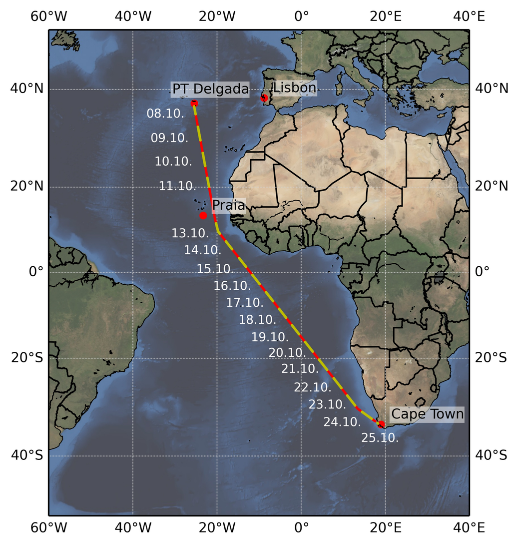

Figure 2: Track of ship cruise
Red: the whole cruise track illustrated.
Yellow: the measurement periods (day).

Cruise and instrument details:
- the project: COPMAR (Continental Outflow of Pollutants towards the Marine TRoposphere)
  - took place from Ponta Delgada (Azores) to Cape Town (South Africa, Figure 2)
  - from 08 October 2016 to 25 October 2016
  - the campaign was part of the cruise MSM58/2
  - the ship sailed at nearly constant speed
- a MAX-DOAS (Multi-AXis Differential Optical Absorption Spectrometer) was installed on board of the research vessel Maria S. Merian
  - for the campaign an Avantes spectrometer was used; wavelength range: 288 nm - 550 nm; one scan took ~ 15 min
  - the instrument was continuously scanning a vertical plane, towards the African continent

2 Method & Data Selection

Method:
- DOAS: Differential Optical Absorption Spectroscopy (Figure 3)
  - based on Lambert Beer's law: $I(\lambda,s) = I_0 \exp(-\sigma(\lambda)\rho s)$
    - λ: wavelength; σ: absorption cross-section; ρ: concentration of absorbers
    - method to calculate the absorption of light travelling through the atmosphere
  - can be used for ultra violet (UV) and visible (vis) light
  - amount of trace gases can be derived from the absorption ⇒ slant column densities (SCDs) can be calculated and converted to vertical column densities (VCDs)

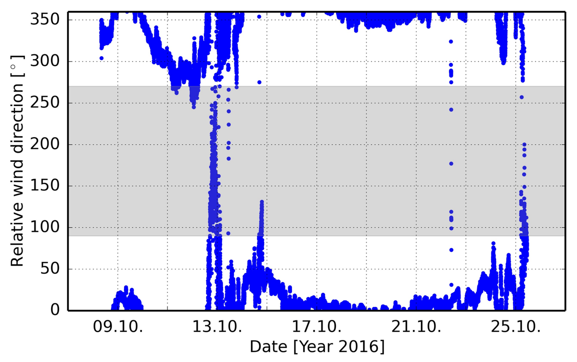

Figure 4: Relative wind direction during the cruise
Because of the rather high speed, headwinds dominated during the campaign, shifting either side of the bow. The gray shaded wind directions are excluded, because of possible contamination by the vessel plume.

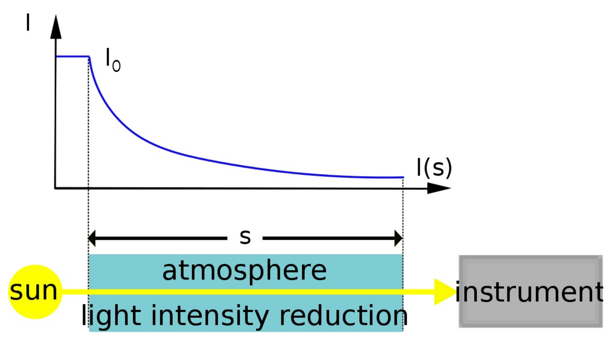

Figure 3: Illustration of the DOAS method
I: intensity at the detector
I_0: intensity of the light directly from the sun
s: light path

Data Selection:
- elevation angles: 1° steps from -3° to 8°, 10°, 15°, 30° and 90°
- they are corrected for the ship's movement (roll and pitch)
- elevation angles from 0° to 90° are used for the anaylsis; azimuth angle: 90° relative to the ship
- measurements which might be contaminated by the vessel plume are excluded (measurements with a relative wind direction between 90° and 270°, Figure 4)

3 Investigation of stratospheric NO_2

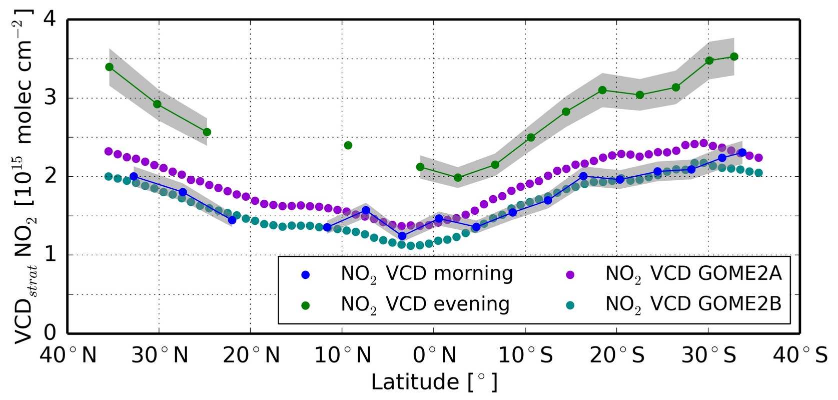

Figure 5: Latitudinal dependency of strat. NO_2
The latitudinal dependency of stratopheric NO_2 over the Atlantic Ocean shows a local minimum near the equator and an increase towards the poles. The MAX-DOAS data agree well with the IUP-UB GOME2-A and GOME2-B satellite data (equator crossing time: ~9:30 LT). Due to the diurnal cycle of stratospheric NO_2, the satellite measurements are closer to the morning values (see Figure 6). 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).

MAX-DOAS retrieval
- the DOAS fit RMS is nearly constant; therefore, a fixed reference spectrum is used to analyse the data (17.10.2016, noon)
- a reference SCD (SCD_0=2.1*10^{15}molec cm^{-2}) is calculated for the 17.10.2016 and added to all SCDs to get total SCDs
- stratospheric air mass factors (AMF) are calculated with the radiative transfer model SCIATRAN to yield total VCDs
- the potential small tropospheric contribution from outflow is ignored for this analysis

Latitudinal dependency
- the satellite data are averaged between 10°W and 40°W and multiplied by a stratospheric AMF to get VCDs
- MAX-DOAS: the VCDs are averaged between 88° - 92° solar zenith angle (SZA), because of the higher sensitivity to the strat.

Diurnal cycle
- the increase during the days due to photochemistry is clearly visible (Figure 6)

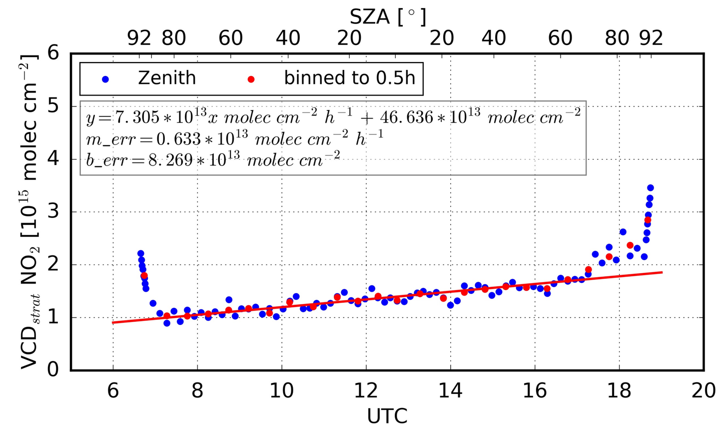

Figure 6: Diurnal cycle of strat. NO_2
The diurnal cyle of stratospheric NO_2 is exemplary shown for 15.10.2016. Data with a SZA smaller than 92° are shown. Also, all other days show a similar increase during the day. As shown in Figure 5, during twilight in the morning the NO_2 values are smaller than during twilight in the evening.

4 Continental outflow of HCHO

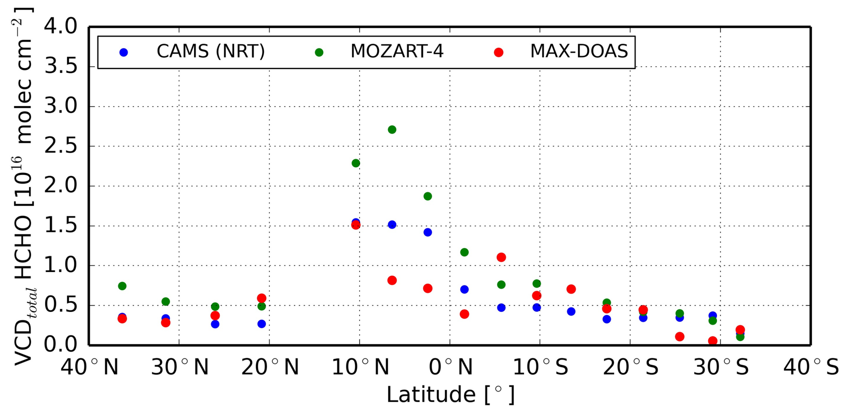

Figure 7: Comparison to model data
The latitudinal dependency of HCHO over the Atlantic Ocean is clearly visible in daily mean MAX-DOAS measurements as well as in model data. However, the model data show higher values in the area of western Africa, where continental outflow is expected. CAMS (NRT): 0.4°x0.4° (6h); Mozart-4:~1.9°x2.5° (6h).

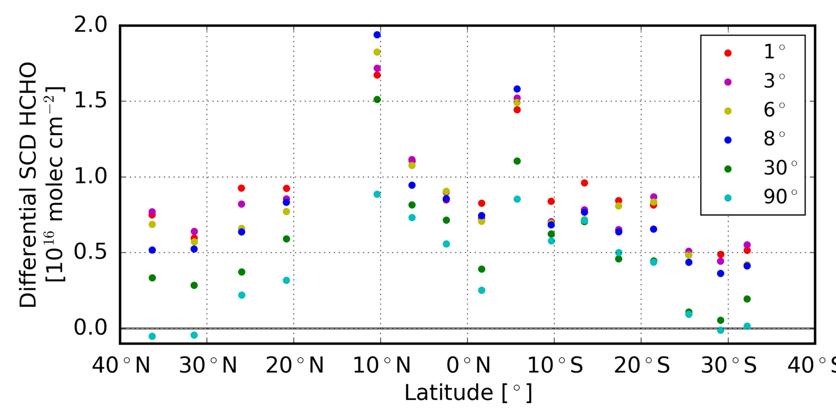

Figure 8: Elevation angle dependency of HCHO
The elevation angle with the highest differential SCDs depend on the latitude. This is expected from radiative transfer calculations, because the continental outflow is expected to be in the free troposphere.

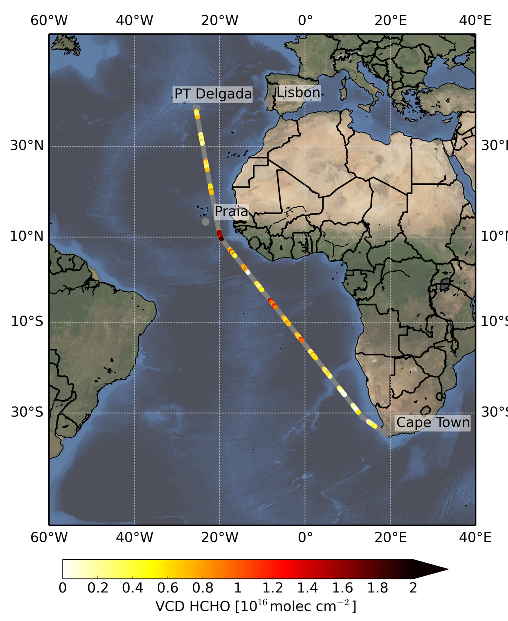

Figure 9: HCHO measurements
Individual measurements of HCHO along the cruise track. A similar behaviour is visible in Figure 7 and 8.

- a fixed reference spectrum (23.10.2016, noon) is used for this analysis
- for the calculation of HCHO VCDs, for simplicity we use the geometric approach: AMF = 1/sin(30°)
- daily means are calculated for SZA ≤ 70°
- box air mass factor (BAMF) calculations (not shown here) show a higher sensitivity for elevation angles between ~6° - ~30° for the free troposphere

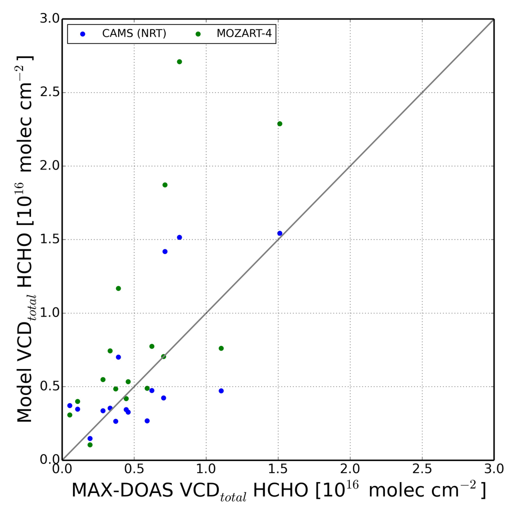

Figure 10: Correlation between model and MAX-DOAS measurements
The correlation coefficient between MAX-DOAS and CAMS is: 0.73; and the correlation between MAX-DOAS and MOZART-4 is: 0.74.

⇒ African continental outflow of HCHO can be detected

5 Summary & Outlook

Summary
- COPMAR was a measurement campaign in October 2016 in the Atlantic Ocean
- strat. NO_2 was successfully observed; latitudinal dependency and diurnal cycle are clearly visible
- outflow of HCHO from the African Continent can be observed
- we found high correlation for HCHO between MAX-DOAS measurements and model data
- SCIATRAN calculations show that the sensitivity in the free troposphere higher for elevation angles between ~6° - ~30°

Outlook
- investigation of stratospheric signals from O_3
- investigation of the outflow from Africa for additional species (NO_2 and CHOCHO) as well as the altitude for the outflow
- comparison with satellite data

References & Acknowledgements

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