Retrieval of Vertical Profiles of HCHO and CHOCHO From MAX-DOAS Data Measured During the CINDI-3 Campaign in Cabauw, The Netherlands, 2024

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Abstract: The focus of the third Cabauw Intercomparison campaign of UV-Vis DOAS measuring Instruments (CINDI-3), held in the Netherlands in 2024, was the measurement of various atmospheric species by different instruments. Among these species, formaldehyde (**HCHO**) and glyoxal (**CHOCHO**) are particularly interesting as they are released from biogenic, anthropogenic, and pyrogenic sources and can be measured almost all over the planet. However, the amounts of emitted HCHO and CHOCHO are usually small, often close to the detection limit of MAX-DOAS instruments, making the DOAS-Fit and therefore the retrieval of vertical profiles challenging.

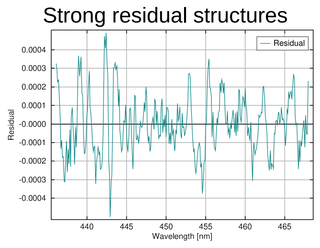
On this poster, we present HCHO and CHOCHO vertical profiles retrieved from MAX-DOAS data measured during the CINDI-3 campaign. A selection of different a priori profiles is presented and the retrieved profiles are discussed. Additionally, as the discussion about the best fit settings for CHOCHO is still ongoing, the impact of different fit settings on the vertical profile is shown. Furthermore, the diurnal and vertical distribution of HCHO and CHOCHO is discussed and compared. Finally, a more general discussion of profile retrievals of species with small abundance in the troposphere is presented and suggestions on how to improve these retrievals are made.

Introduction

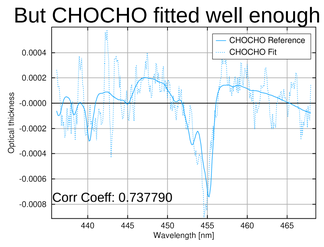
HCHO has an adequate abundance / signal to noise → DOAS-fit no problem
CHOCHO has smaller abundance / signal to noise → DOAS-fit problematic

CINDI3 CHOCHO fitting window: 436 – 468nm

Strong residual structures



But CHOCHO fitted well enough



Question: Are improvements on the fit possible and how does this propagate to vertical profiles?

How to find optimal fit settings for CHOCHO?

CINDI-3 CHOCHO Fit Settings:

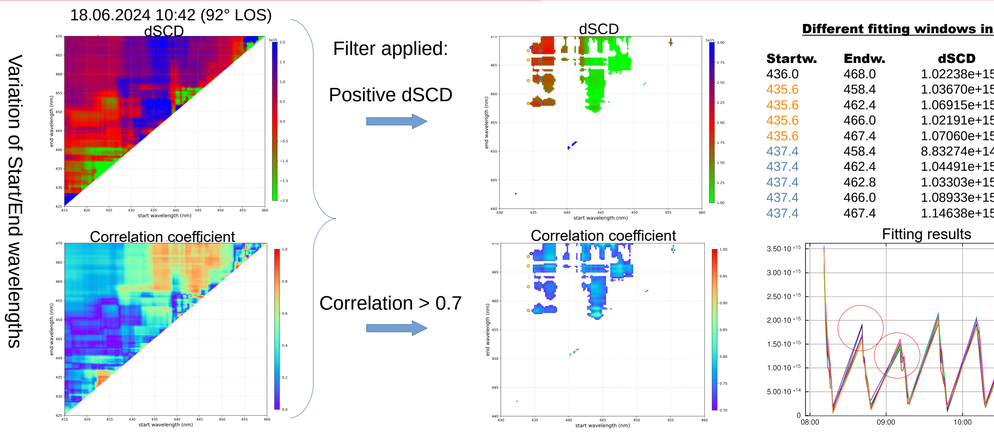
Fitting window:	436 – 468nm
Polynomial:	6th order
Reference spectrum:	Synchronized used here

Cross-Sections:

Ozone:	Serdyuchenko 2014 (223K)
NO_2:	Vandaele 1998 (294K)
NO_2 B:	Vandaele 1998 (220K)
O_4:	Finkenzeller/Volkamer 2022 (293K)
CHOCHO:	Volkamer 2005 (296K)
H_2O:	HITRAN2012, Rothman 2013 (293K)
Ring:	QDOAS, SAO2010, van Roozendael

Parameters which can be altered:
- Does not have a strong impact
- Does have an impact

Variation of Start/End wavelengths

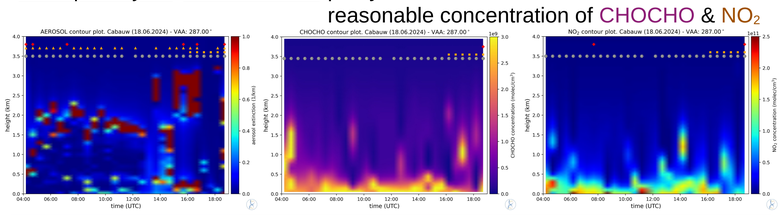


Different fitting windows in detail

Startw.	Endw.	dSCD	Corr.
436.0	468.0	1.02238e+15	0.737790
435.6	458.4	1.03670e+15	0.779923
435.6	462.4	1.06915e+15	0.735825
435.6	466.0	1.02191e+15	0.760696
435.6	467.4	1.07060e+15	0.751246
437.4	458.4	8.83274e+14	0.748573
437.4	462.4	1.04491e+15	0.753938
437.4	462.8	1.03303e+15	0.749792
437.4	466.0	1.08933e+15	0.797842
437.4	467.4	1.14638e+15	0.790340

Impact of fit settings

Example day 18th of June 2024: partly clouded
reasonable concentration of CHOCHO & NO_2

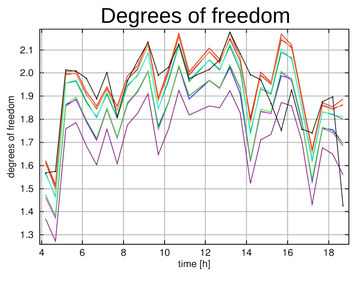


Profiling metrics for 10 different fitting windows

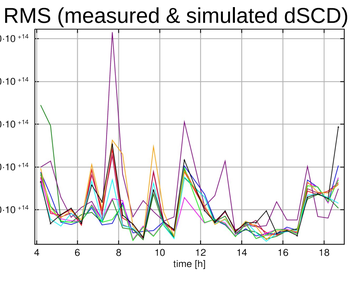
436.0 - 468.0	437.4 – 458.4
435.6 - 458.4	437.4 – 462.4
435.6 - 462.4	437.4 – 462.8
435.6 - 466.0	437.4 – 466.0
435.6 - 467.4	437.4 – 467.4

Large differences in almost every metric. Profiles might differ strongly even though the dSCDs vary only slightly.

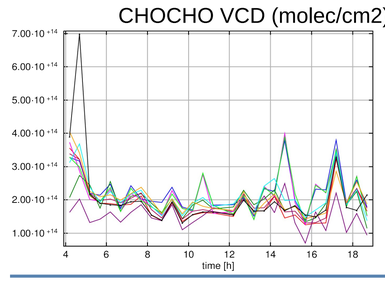
Degrees of freedom



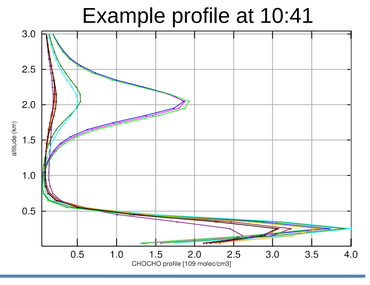
RMS (measured & simulated dSCD)



CHOCHO VCD (molec/cm2)

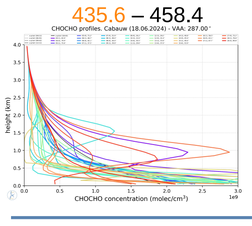


Example profile at 10:41

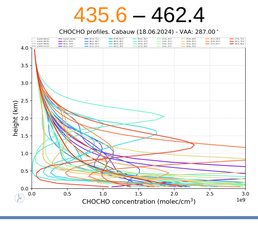


Example profiles for 3 different fitting windows

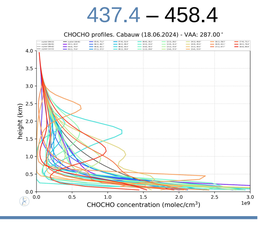
435.6 – 458.4



435.6 – 462.4



437.4 – 458.4



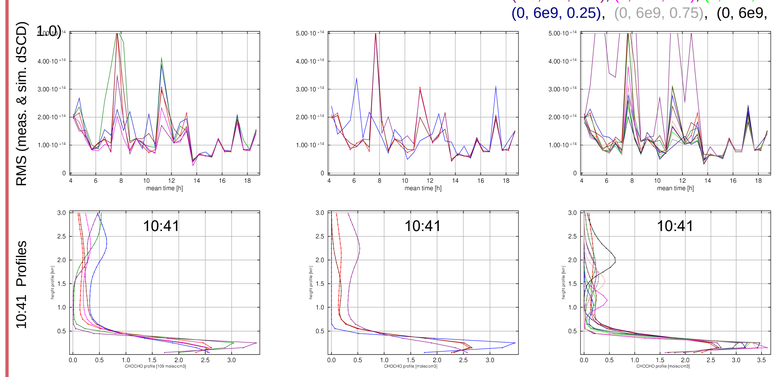
Retrieval settings:

	CHOCHO	Aerosol
A priori profile:	Exp., 2e9 molec/cm2 at surface SH of 1km	Exp., 0.183 1/km at surface SH of 1.25km
A priori variance:	100%	100%
A priori FWHM:	0.2km	AERONET phase fct and SSA

Impact of a priori

Example day 18th of June 2024, Fitting window 437.4 – 458.4nm:

Linear	Boltzmann	Gaussian
Varying surface conc.: 0.5e8, 1e9, 2e9, 4e9, 6e9, (Exp)	Varying fct param.: 0.2, 0.4, 1.0, 2.0, (Exp)	Varying Altitude, width, max: (0, 0.5, 2e9), (0, 1.0, 2e9), (0.5, 0.5, 2e9) (1.0, 0.5, 2e9), (0, 4e9, 0.5), (0, 6e9, 0.5) (0, 6e9, 0.25), (0, 6e9, 0.75), (0, 6e9,



Typical profile shapes are exponential. Depending on the true atmosphere, other functions lead to better results and give insight into the real conditions.

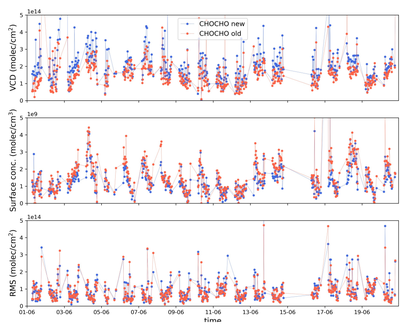
Elevated layer in the evening means high RMS if a priori profile forces high concentrations close to the surface.

Applied settings

Comparison between results from CINDI-3 fit and new settings

CINDI-3:	436.0 – 468.0
New:	435.6 – 466.0

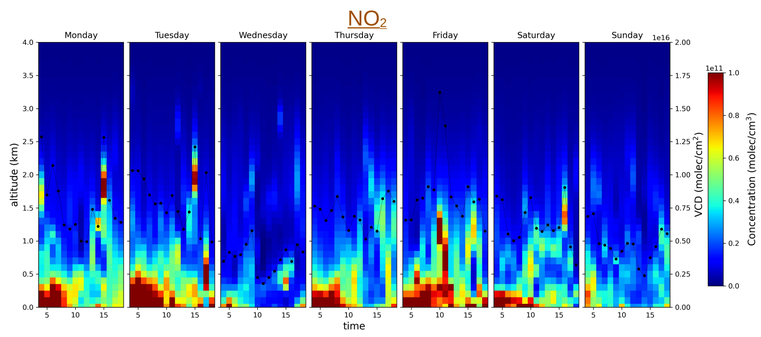
- VCD much higher
- Surface conc. slightly lower
- RMS on a similar level



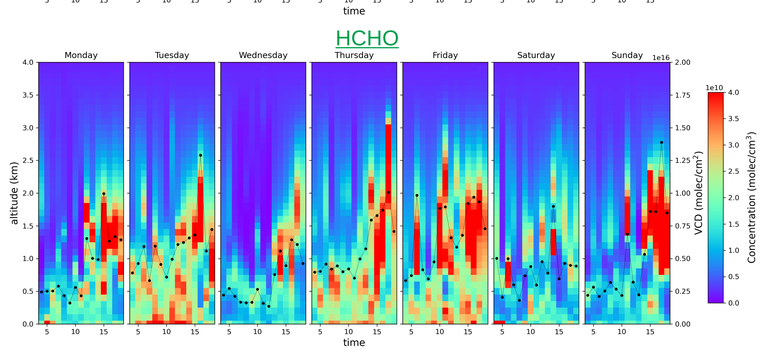
Discussion of profiles

Average hourly weekday profiles:

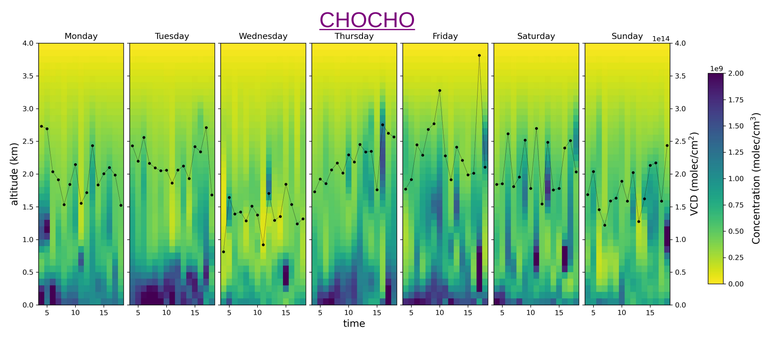
NO_2



HCHO



CHOCHO



- NO_2 is mostly located close to the ground and has lower values on the weekend → anthropogenic emission
- HCHO is more pronounced in higher altitudes → a background level due to methane oxidation, but concentrations close to the surface indicate anthropogenic emissions (to a smaller fraction) or possibly VOC emissions
- CHOCHO can be found close to the surface and does not show changes due to the day of the week → Indication for emission by oxidation of VOCs and anthropogenic emissions (to a smaller fraction)

Conclusions

- CHOCHO fitting and profile retrievals:
- Fitting of CHOCHO is difficult due to its small amount in the atmosphere
- Many different fitting windows lead to stable and similar dSCD values
- → This supports the fact that CHOCHO was really measured
- Even though dSCD-values look similar, small changes have a big impact on resulting profiles
  - Total concentrations change as well as VCD
  - The vertical distribution is 'usually' not as much affected
- Use of different a priori profiles can support the finding of CHOCHO in different altitudes. e.g. concentrations in higher altitudes in the evening

General discussion:

- Short measurement period makes conclusions regarding emissions difficult but not impossible
- NO_2 has predominantly anthropogenic sources
- HCHO is formed predominantly by the oxidation of methane and some none methane hydrocarbons (NMHC)
- CHOCHO is formed mainly by the oxidation of VOC and some anthropogenic NMHC as supported by its vertical distribution

Outlook

- Instruments with higher signal-to-noise ratio are needed to improve the retrieval of weaker absorbers (e.g. CHOCHO)
- More effort (e.g. fit window, a priori settings) is needed to retrieve reliable profiles from small absorbers
- Longer time series are needed to decrease uncertainties in retrieval results

Acknowledgement:
We gratefully thank ESA for their financial support for the FRM4DOAS 2-0 project as well as the University of Bremen for its additional financial support.

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