# Investigating vertical gradients of trace gases and aerosol at the Amazon Tall Tower Observatory (ATTO) using MAX-DOAS measurements

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## A. MEASUREMENT SITE AND STRATEGY

The Amazon Tall Tower Observatory (ATTO) is located in a pristine rain forest in the central Amazon Basin, about 150 km northeast of Manaus/Brazil. During the wet season probed air masses are clean originating from NE directions, while in the dry season E to SE winds bring more polluted air from more urbanised and deforestation regions to the site (Andreae et al., 2015).

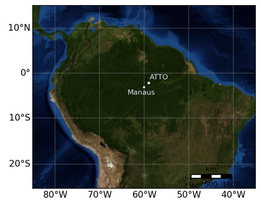


**Fig. 1:** Location of the ATTO site.

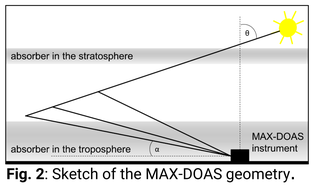


**Fig. 2**: Sketch of the MAX-DOAS geometry.

In October 2017, a MAX-DOAS instrument was installed at ATTO followed by a second one in March 2019. The instruments are placed at 80 m and 298 m altitude on the ATTO tower, corresponding to ca. 40 m and 260 m above the canopy. This setup leads to long slant light paths (up to 20 km) in the lowest atmospheric layers and thus to high sensitivities to the different trace gases.

Multi AXis-Differential Optical Absorption Spectroscopy (MAX-DOAS) uses trace gas absorptions in spectra of scattered sunlight recorded at different elevations and allows to retrieve vertical profiles of trace gas concentrations (e.g. $NO_2$, HCHO and CHOCHO) and aerosol extinction below about 4 km (on clear days). In addition, directly comparing the VCDs and concentrations (at instrument altitude) measured by both instruments allows to identify (small scale) vertical gradients of trace gas and aerosol abundances providing important insights into the chemical processing of the different species.

**Fig. 3:** MAX-DOAS instrument mounted on the ATTO tower.

## B. TRACE GAS TIME SERIES

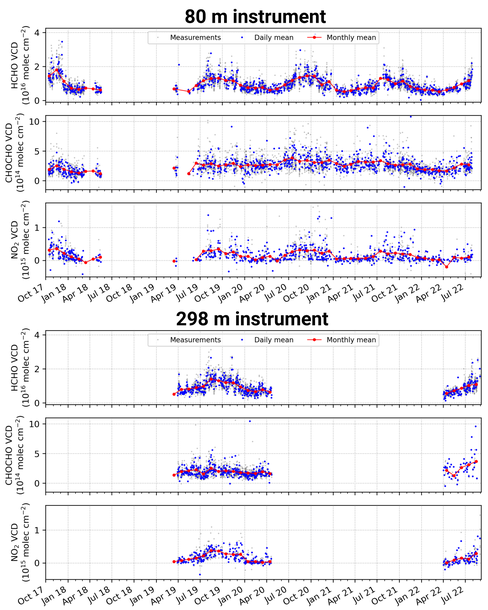


**Fig. 4**: Time series of HCHO, glyoxal and $NO_2$ VCDs for both instruments.

## C. TRACE GAS CORRELATIONS

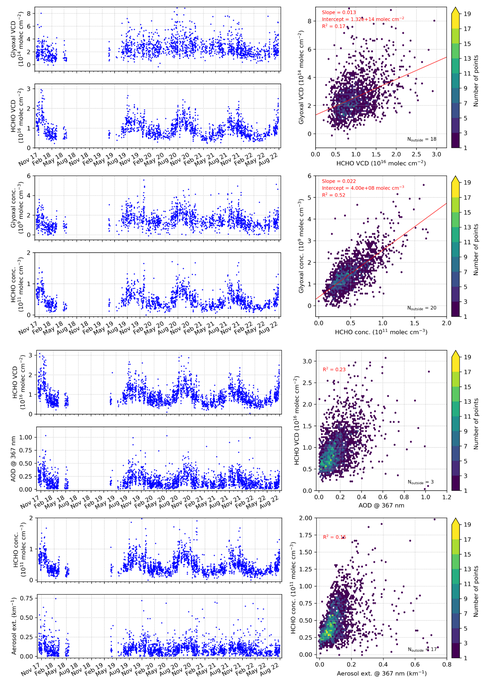


**Fig. 5**: Time series and correlations of hourly mean HCHO and glyoxal VCDs and concentrations at instrument altitude as well as AODs and aerosol extinctions (367 nm) for the 80 m instrument.

"In boxes C, D and F, the term "concentrations" refers to the mean concentration in the 400 m above instrument height.

- HCHO and glyoxal concentrations* correlate well, while the correlation is weaker for the VCDs
- Slopes of the linear regressions are 2.2 % and 1.3 % for concentrations and VCDs, respectively
- Similar results are obtained for the 298 m instrument but slightly worse correlations (not shown)

➔ Close relation between both species indicates similar/common sources but different atmospheric processing

➔ Different vertical distributions of both species with glyoxal located closer to the ground, while HCHO profiles reach higher

➔ Seasonal investigations: glyoxal is less reduced during the wet season indicating different chemical regimes in both seasons (compare $R_{GF}$ in box D)

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- HCHO and aerosol abundances are reasonably correlated, whereby the correlation is higher for the column quantities of both species
- Similar results for the 298 m instrument (not shown)
- Seasonal investigations: worse correlations in the wet season and best correlation in the dry season (not shown)

➔ Potential effect of biomass burning events

➔ Formation of secondary organic aerosol

➔ Further studies needed here

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- Correlations involving $NO_2$ show more complex patterns (not shown)

➔ $NO_2$ is often below the detection limit (compare Fig. 4)

➔ $NO_2$ abundances are affected by pollution from more densely populated regions and biomass burning fires

## D. RATIO GLYOXAL TO HCHO ($R_{GF}$)

- Systematic seasonal variations of $R_{GF}$ obtained from VCDs and concentrations
  - Higher $R_{GF}$ in the wet season (3.1 % / 3.3 %)
  - Lower $R_{GF}$ in the dry season (2.1 % / 2.7 %)

➔ Stronger relative increase of HCHO in the dry season

➔ Different processing of both species and different chemical regimes (e.g. VOC compositions) in the wet and dry season (supported by other studies e.g. Gomes Alves et al., 2023)

➔ Higher $R_{GF}$ eventually related to stronger contribution of monoterpenes vs. lower $R_{GF}$ when isoprene alone dominates (Kaiser et al., 2015: threshold under biogenic influence ~ 2.5 % to 3 %)

- Small differences in $R_{GF}$ from both quantities (profile shapes of both species differ, compare box E)
- Slight tendency in the dry season itself

➔ Effect of biomass burning?

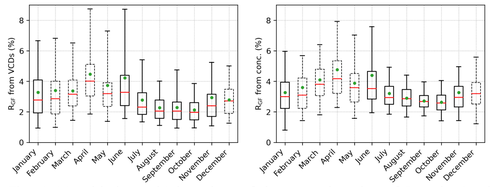


**Fig. 6**: Monthly box-whisker-plots of the annual cycles of $R_{GF}$ obtained from VCDs (left) and concentrations (right) for the 80 m instrument.

## E. PROFILES

- All profiles show an artefact in the lowermost layers (too low concentrations) which is related to the specific profile parametrisation used in MAPA (Beirle et al., 2019)
- HCHO profiles reach up to ca. 2 km with the bulk concentrated in a layer with a vertical extension of ca. 700 m
- Glyoxal profiles are shallower reaching up to ca. 1.75 km and the layer containing the bulk is vertically less extended
- $NO_2$ profiles are shallowest (direct emissions) reaching only to ca. 1.5 km
- Seasonal variations reflect differences in mixing and chemical processes

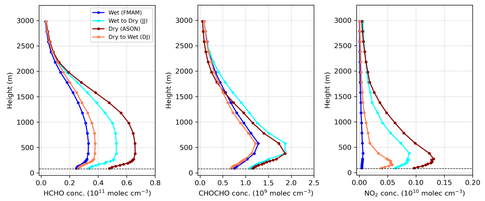


**Fig. 7**: Seasonal median profiles of HCHO, glyoxal and $NO_2$ concentrations.

## F. COMPARISON OF THE INSTRUMENTS

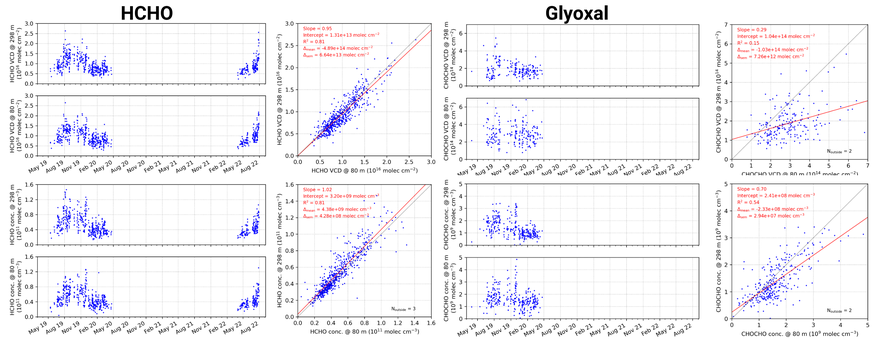


**Fig. 8**: Comparison of HCHO and glyoxal VCDs and concentrations obtained for both instruments.

- HCHO results of both instruments agree well
  - VCDs are higher at 80 m, while the concentrations are higher at 298 m
- Glyoxal results differ more between both instruments
  - VCDs are notably lower at 298 m, while better agreement is found for concentrations but still smaller values are found for the 298 m instrument

➔ HCHO concentrations increase within the lowest 200 m above the canopy, while glyoxal concentrations decrease significantly within this altitude range

## G. CONCLUSION AND OUTLOOK

- HCHO, glyoxal, $NO_2$ and aerosol extinction were successfully retrieved
- Glyoxal profiles are notably shallower than HCHO profiles
- Direct comparison of both instruments ➔ small scale vertical gradients (~ 200 m) ➔ insights into different production and degradation mechanisms of HCHO and glyoxal ➔ HCHO is net formed within the lowest 200 m above the canopy, while glyoxal is net degraded
- $R_{GF}$ suggests different VOC compositions in the dry and wet season
- Measurements are also influenced by biomass burning events
- Outlook:
  - Extend time series and more detailed analyses including additional data sets, e.g. measurements of isoprene or monoterpenes

**Contact in case of questions and comments**:
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*Link to abstract and digital version of the poster*

**REFERENCES**: *Andreae et al., 2015. The Amazon Tall Tower Observatory (ATTO): overview of pilot measurements on ecosystem ecology, meteorology, trace gases, and aerosols. ACP 15, 10723-10776.*
*Kaiser et al., 2015. Reassessing the ratio of glyoxal to formaldehyde as an indicator of hydrocarbon precursor speciation. ACP 15, 7571-7583.*
*Beirle et al., 2019. The Mainz profile algorithm (MAPA). AMT, 12. 1785 – 1806.*
*Gomes Alves et al. 2023. Intra- and interannual changes in isoprene emission from central Amazonia. ACP 23, 8149-8168.*

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