High resolution mass spectrometric study of secondary organic aerosol particles from the Amazon rainforest

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Introduction

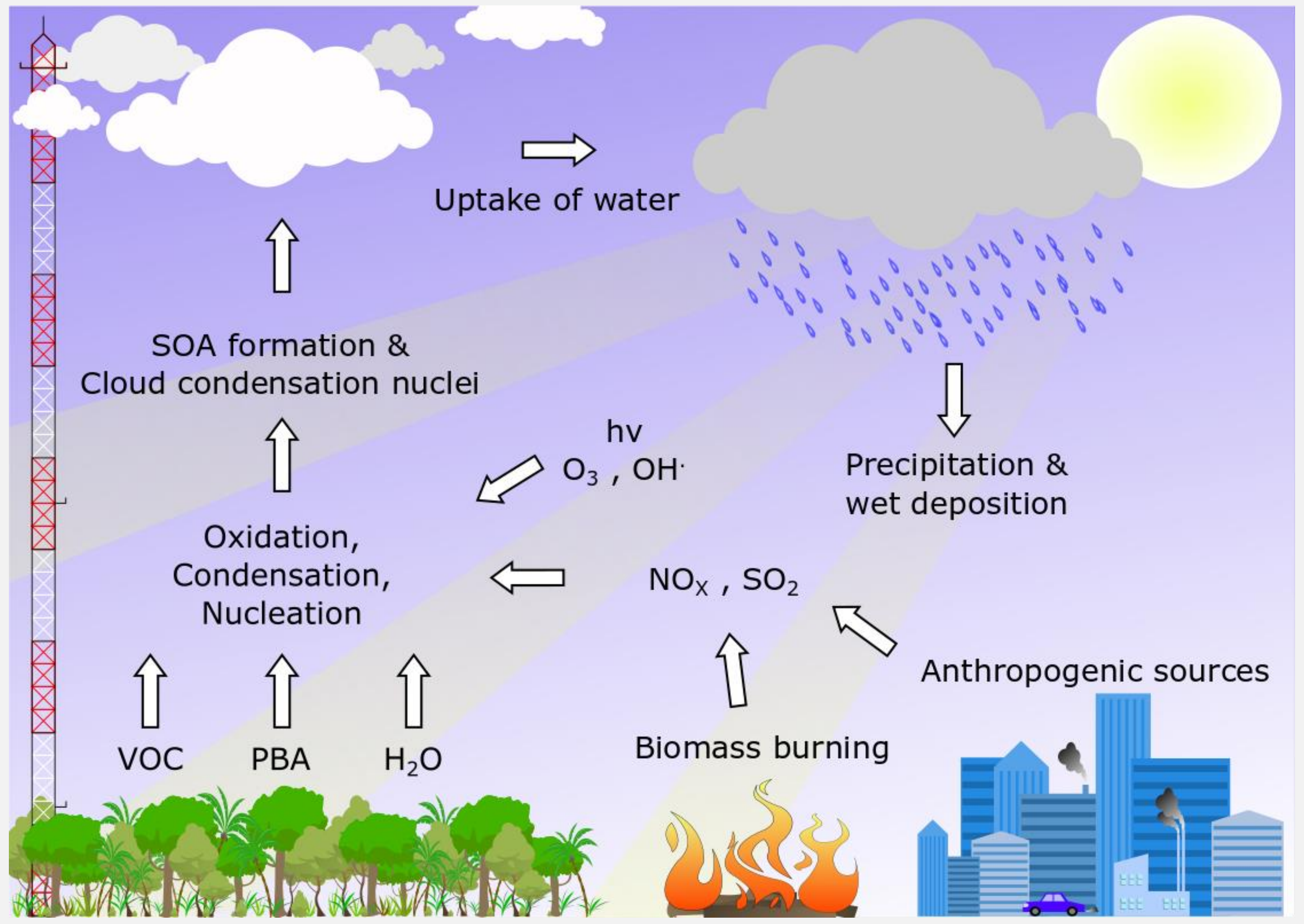


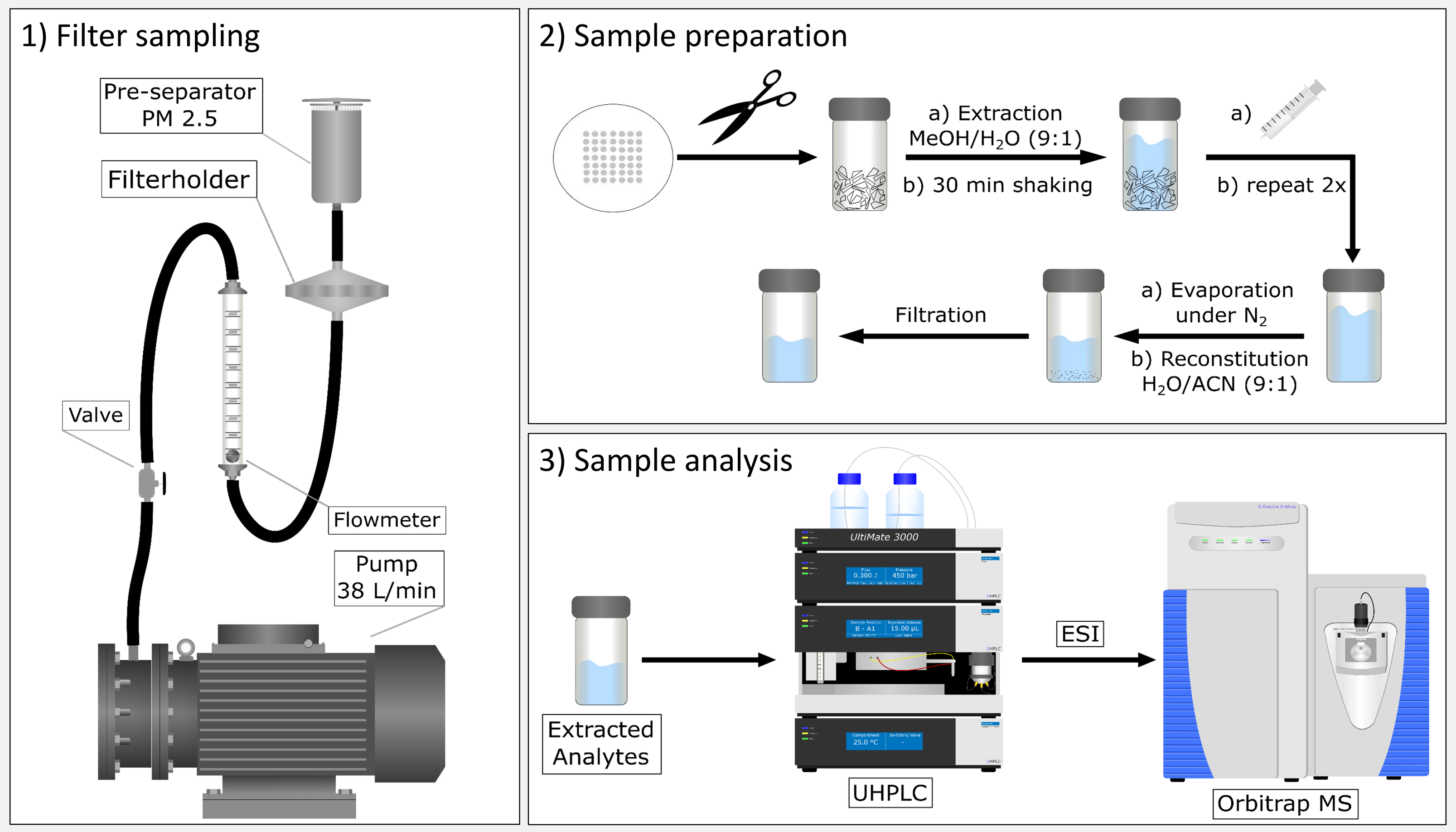
Fig.1: Principals of atmospheric particle formation. PBA = primary biogenic particles, VOC = volatile organic compound.

The Amazon rainforest is one of the most important pristine environments for atmospheric chemistry and biodiversity. This region allows the study of organic aerosol particles as well as their nucleation into clouds. However, the rainforest is subject to constant change due to human influences. Thus, it is essential to acquire actual climatic and atmospheric data over the next decades. The research site "Amazon Tall Tower Observatory" (ATTO) was established in the central Amazon Basin to perform long-term measurements under almost natural conditions. [1]

The chemical composition of atmospheric aerosols in the rainforest highly depends on the current season, since the Amazon basin exhibits huge variations of gaseous and particulate matter with clean air conditions during the wet season and polluted conditions during the dry season, due to biomass burning events [2]. For a comprehensive statement, it is necessary to perform field measurements under both conditions to study the isoprene and terpene secondary organic aerosol (SOA) contribution. For that reason, filter samples were collected at ATTO at different heights to analyze the aerosol composition emitted both from local and regional sources.

The application of high-resolution MS in combination with liquid chromatography allows the study of these complex mixtures of organic aerosols.

Experimental procedure



Chiral Separation of pinic acid

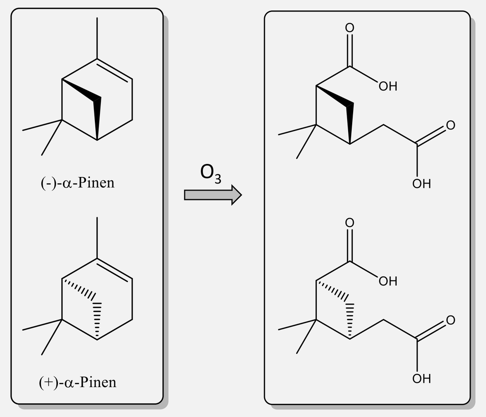


Fig.2: A HPLC method for chiral separation of pinic acid was developed using an Amylose based column.

The enantiomeric ratio of the volatile precursor compounds (+)- and (-)-α-pinene varied unexpectedly with tower height (Zannoni N. et al., 2019, submitted). The investigation of pinic acid in the particle phase could help to understand preferred reaction pathways.

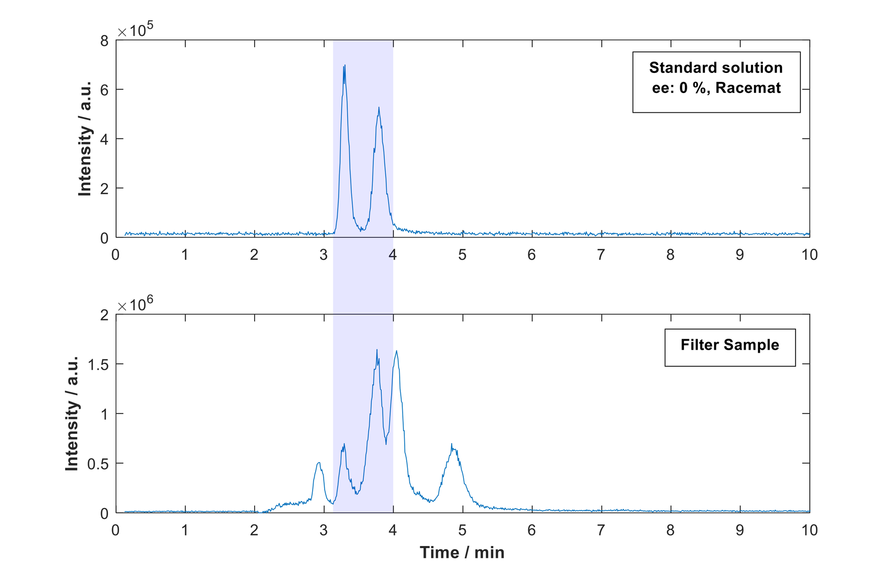


Fig.3: Top: Chromatogram of a 500 ng/mL pinic acid standard. The two enantiomers are baseline separated with equal signal areas. Bottom: The filter sample shows five distinct signals with the sum formula $C_9H_{14}O_4$.

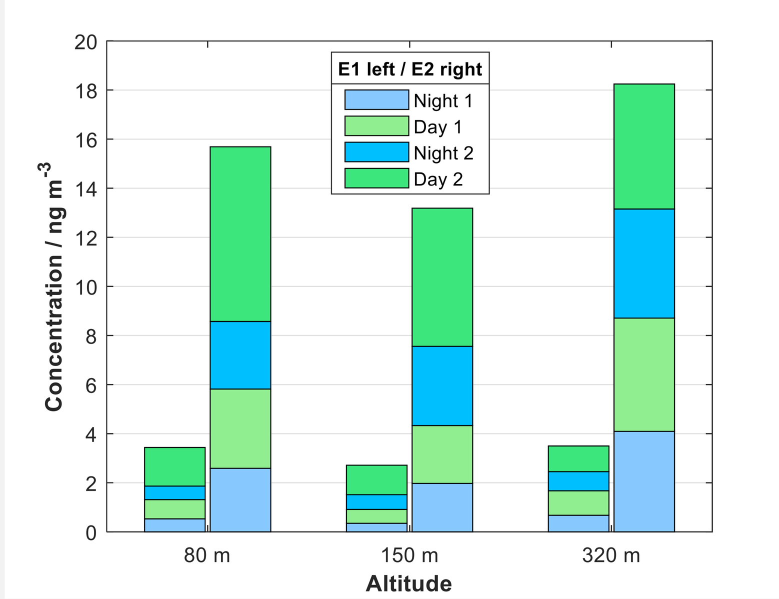


Fig.4: Absolute concentrations of the pinic acid enantiomers **E1** (left bar) and **E2** (right bar) in 12 filter samples during two days of March (wet season). The results show similar concentrations for all heights. However, the amount of **E1** was significantly lower in all samples.

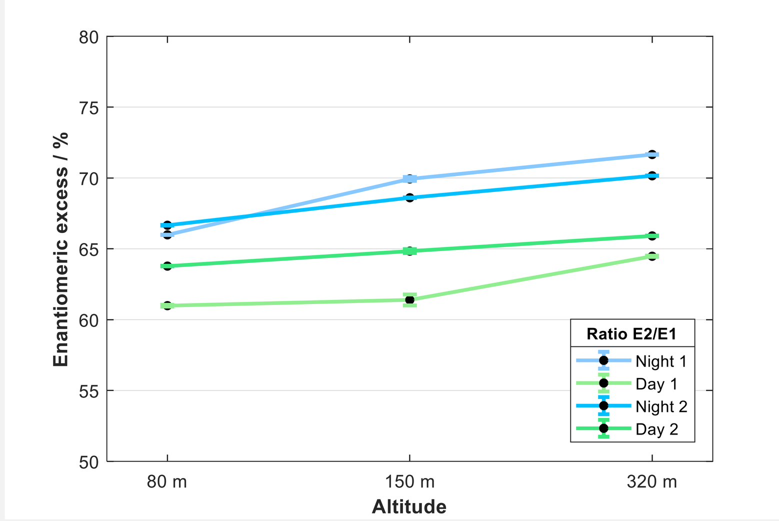


Fig.5: Surprising increase of the enantiomeric excess over the height of the tower (3% – 6%). Similar results were obtained for the dry season.

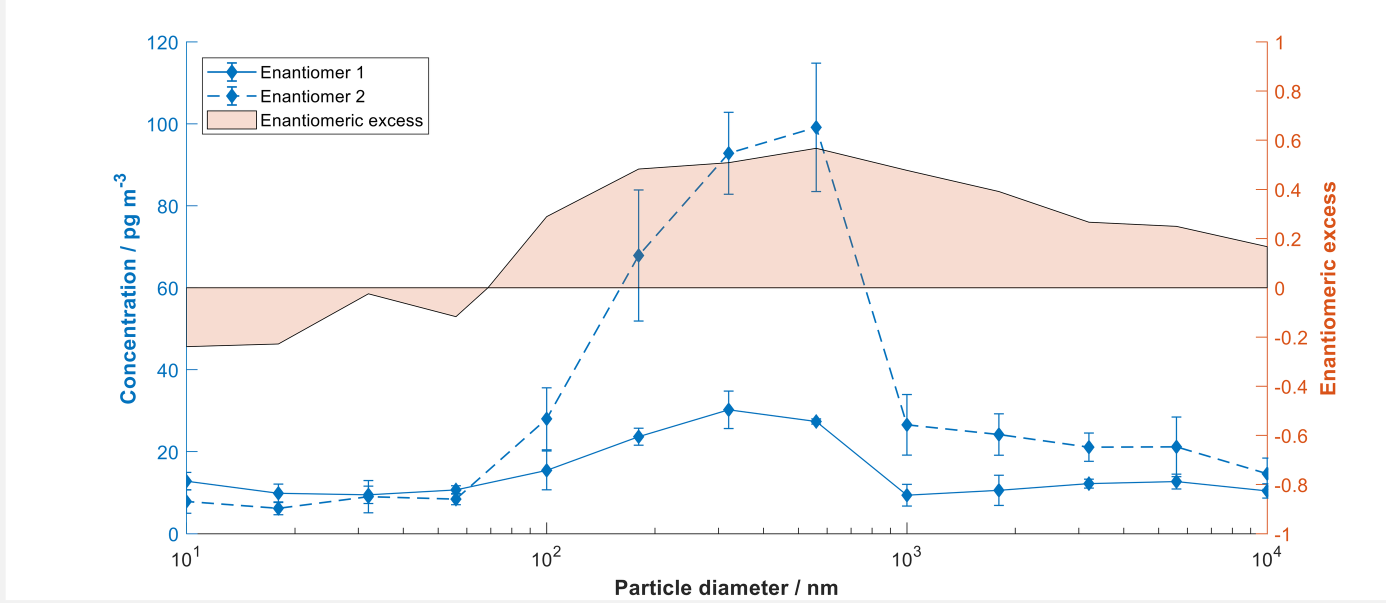


Fig.6: Evaluation of particle size resolved filter samples. For small diameters (< 60 nm) slightly higher concentrations of **E1** were detected. Up to 150 nm the concentration of **E2** strongly increases, leading to an enantiomeric excess of > 50 %. The measurements during both seasons show similar results.

- The surprising change of the enantiomeric ratio may indicate an unknown source or sink of pinic acid: a chiral oxidant or aerosol is needed to react with a specific enantiomer
- The uptake of pinic acid on particles between 100 – 1000 nm diameter seems to be preffered in contrast to smaller or bigger particles
- Chamber experiments of enantiopure standards may help to identify unknown signals and preffered reaction pathways

Investigation of aerosol chemical composition

Hierarchical Clustering [3]

- Algorithm to group similar samples and compounds into distinct clusters
- Dendrograms show similarity between variables
- Standardizised signal intensities: z-score with mean **μ** and standard deviation **σ**

$$z = \frac{(x - \mu)}{\sigma}$$

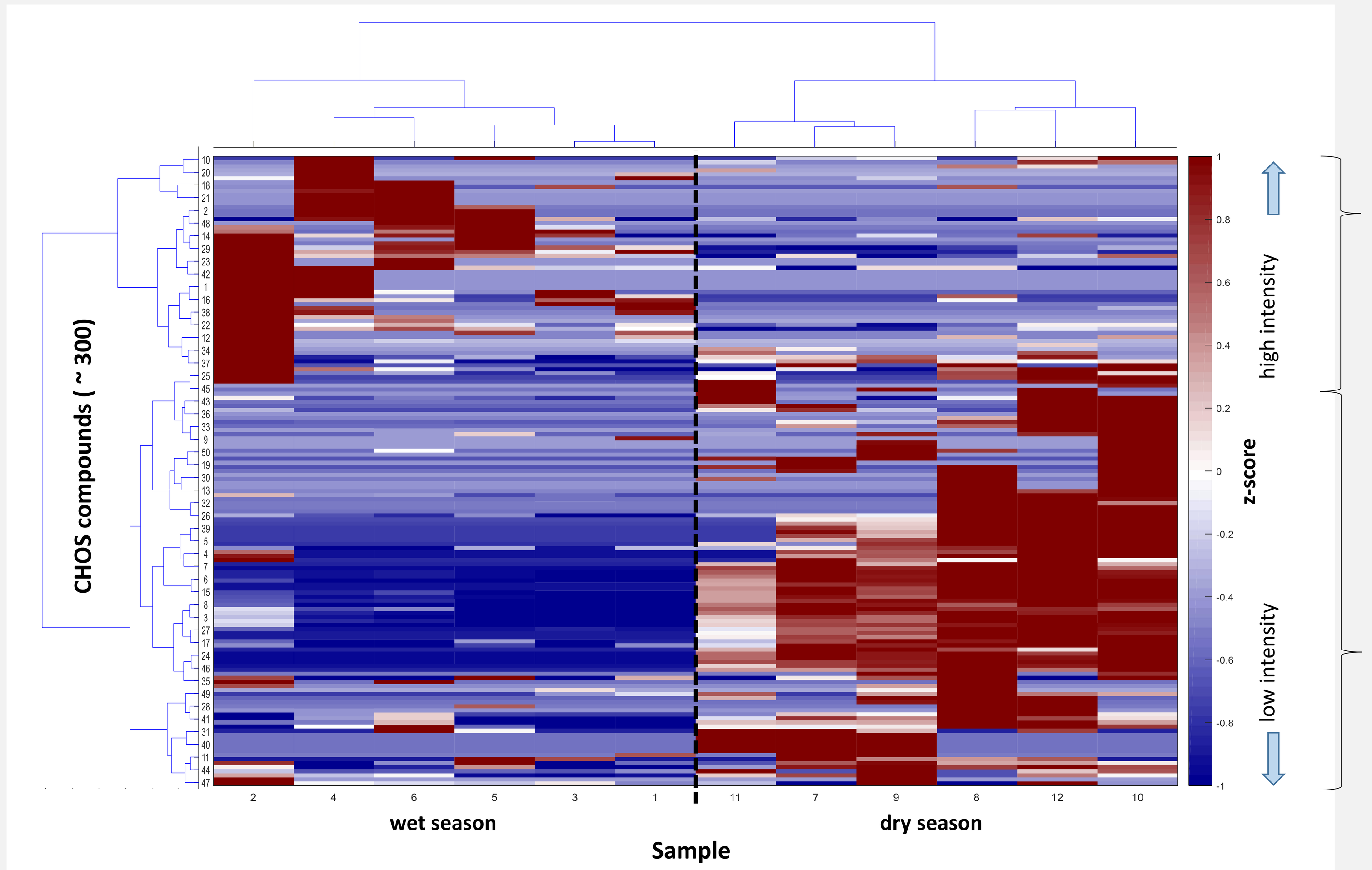
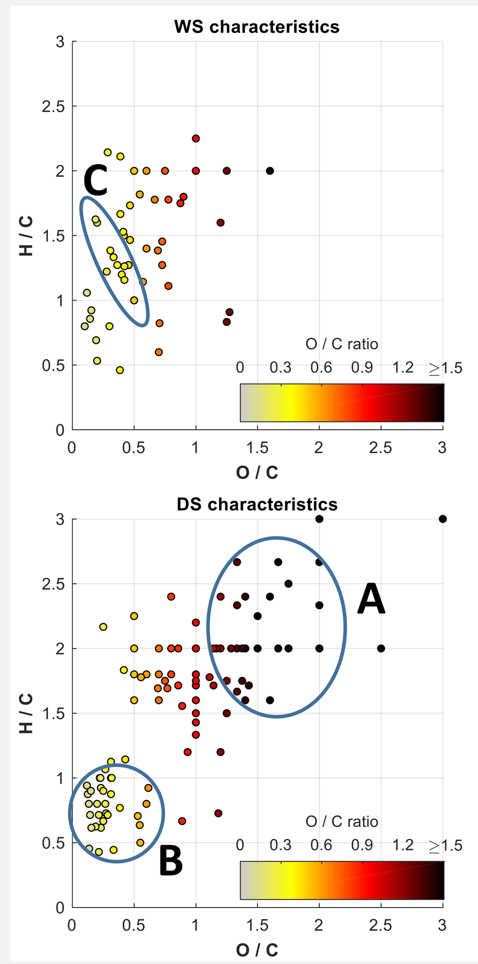


Fig.7: Cluster analysis of 12 samples over four days in total during both seasons 2019. Three different heights were sampled each day.



Van Krevelen plots: significant differences between the SOA chemical composition during wet season (top) and dry season (bottom)

Dry season is characterized by highly oxidized (region **A**) and unsaturated (region **B**) compounds, mainly due to biomass burning.

Wet season is characterized by more precipitation and therefore less aged SOA compounds

Homologous CHOS compounds (region **C**) were just detected during wet season → Source?

- Promising tool to link specific SOA compounds to certain climate conditions // comparison between different seasons possible
- Lab studies: molecular fingerprints of precursor oxidation will help to understand origin and contribution of VOCs in the Amazon region

References:

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