

Atmospheric impact of sesquiterpenes in the Amazon rainforest

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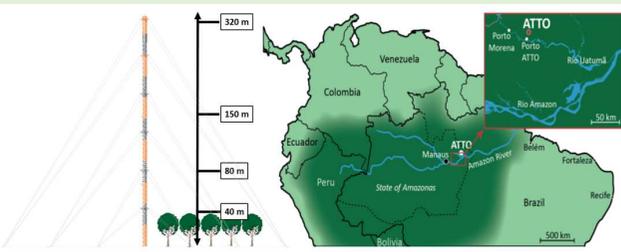


1. RESEARCH GOAL

Sesquiterpenes (C₁₅H₂₄) are highly reactive biogenic volatile organic compounds playing an important role in atmospheric chemistry. Once emitted from the Earth's surface, primarily by vegetation, they are rapidly oxidized to semivolatile oxygenated organic species that can lead to secondary organic aerosols (SOA) that influence climate. In the pristine Amazon rainforest, oxidation of sesquiterpenes is initiated by the hydroxyl radical (OH) and ozone (O₃). We measured sesquiterpenes in March 2018 (wet season) and November 2018 (dry season) from central Amazonia, at the remote field site ATTO (Amazonian Tall Tower Observatory), Brazil.

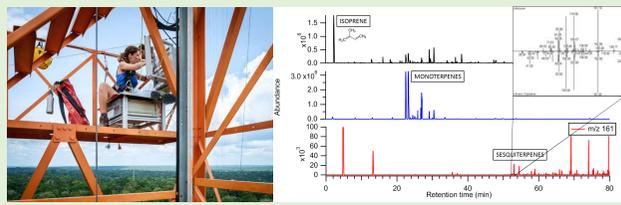
2. FIELD SITE

The Amazonian Tall Tower Observatory (ATTO, 02°08.752'S, 59°00.335' W) is located 150 km NE of the closest large city, Manaus (Brazil). The dominant wind direction at the site (NE), therefore the anthropogenic influence of Manaus is negligible and the site reflects close to pristine tropical forest conditions all year round [1].



3. METHODS

Samples were collected on adsorbent filled tubes equipped with ozone scrubbers at different heights above the forest canopy. Sampling occurred every three hours for two weeks at 80m and 150m (wet season) and every hour for three days at 80m, 150m and 320m (dry season). Samples were then analysed in the laboratory with a TD-GC-TOF-MS (Thermodesorption-Gas Chromatographer-Time Of Flight-Mass Spectrometer, Markes International). Simultaneous measurements of O₃ and meteorological parameters were made at the nearby 80m walk-up tower. Identification of the chromatographic peaks was achieved by injection of standard molecules and by matching literature mass spectra. Quantification of the chemical compounds was achieved by injection of a standard mixture containing terpenes.

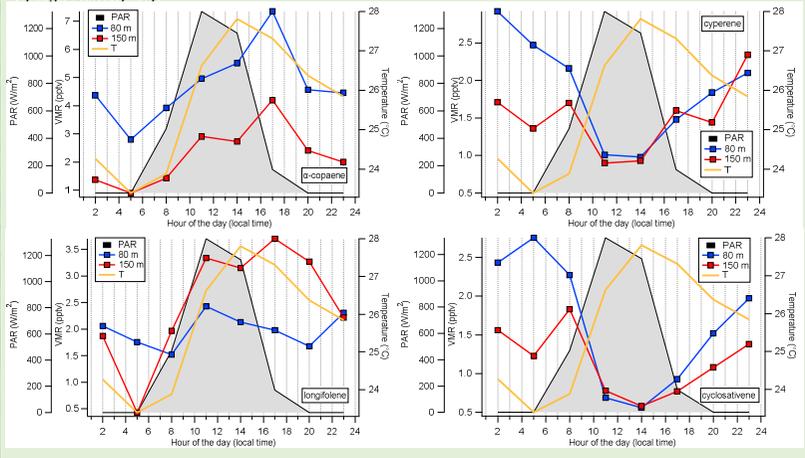


Installation of sampling tubes in the automatic sampler at 150 m on the ATTO tower. Sampling is performed directly at the tower height to reduce losses

Extracted ion chromatograms from one sample taken at 80m during daytime in the dry season. The top figure shows the MS fragmentation at -70eV and the fragments comparison with the NIST library for alpha-copaene.

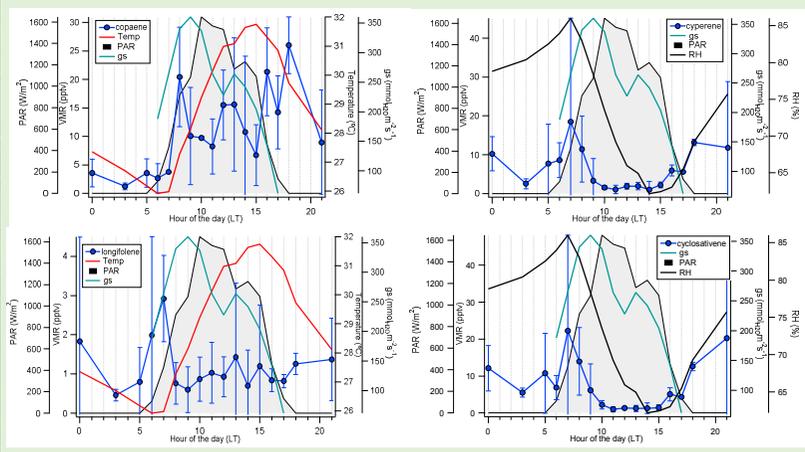
4.1 RESULTS: WET SEASON 2018

The most abundant sesquiterpene measured at ATTO is (-)-alpha-copaene. Its diel profile varies with photosynthetically active radiation (PAR) and temperature, suggesting the canopy to be the main emission source. Other identified sesquiterpenes show a consistent mirrored cycle, with their concentration being higher by night than by day.



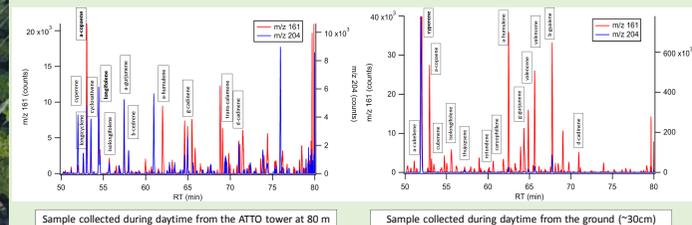
4.2 DRY SEASON 2018

The diel patterns observed during the wet season are confirmed for the dry season samples. Copaene and longifolene volume mixing ratio (VMR) varies with PAR, stomatal conductance (gs) and temperature, while cyperene and cyclosativene VMR varies with RH. Ambient VMR are larger in the dry season than during the wet season.



4.3 FINGERPRINTING THE SOURCE OF EMISSION

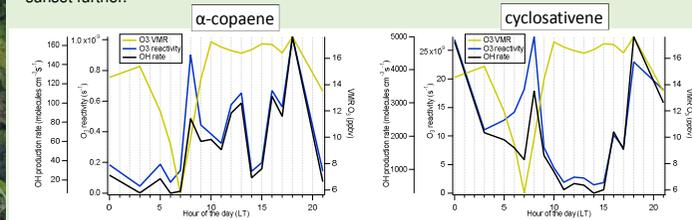
Air samples taken at the ground are qualitatively and quantitatively different to those collected at different altitudes from the tower, suggesting multiple emission sources, specifically soil and canopy.



4.4 O₃ REACTIVITY and OH PRODUCTION RATE

$$\frac{d[OH]}{dt} = (yield)k[sesquiterpene][O_3]$$

Sesquiterpenes show common maximum VMR at sunrise (~6:00 local time, UTC-4h) and sunset (~18:00 local time, UTC-4h). The peak at sunrise is coincident with a strong decrease in ozone concentration (>50% decrease on average during the dry season). The strongest effect is registered during the dry season, when sesquiterpenes and ozone concentrations are highest. Maximum production rates of hydroxyl radical (OH) from SQTP ozonolysis are found when O₃ reactivity and VMR are highest impacting atmospheric photochemistry at sunrise and sunset further.



5. SUMMARY

- First preliminary results of speciated sesquiterpenes from the ATTO tower
- (-)-alpha-copaene has the highest VMR, its diel pattern varies with PAR, stomatal conductance and temperature
- Samples taken at different heights are qualitatively and quantitatively different: pointing at different sources of emissions
- Largest atmospheric impact occurs in the dry season, at sunrise and sunset (~6:00, ~18:00, local time)

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