

Impact of HOMs on ambient monoterpene SOA formation in a German forest

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Introduction

Secondary organic aerosols (SOA) are formed by the reaction of volatile organic compounds (VOCs) from either anthropogenic or biogenic sources. The mechanism of SOA formation is a complex system involving a large number of reactions and chemical species. The complexity of SOA formation leads to large uncertainties in modelling predictions and potential climate impacts. In recent years, the importance of highly oxygenated organic molecules (HOMs) in SOA formation has been demonstrated. In order to better assess this issue, an intensive field campaign took place in July 2014 at the Forest Research Station of the University of Bayreuth (Germany) where two sites were equipped (Brüggemann et al., 2017, Fig. 1).

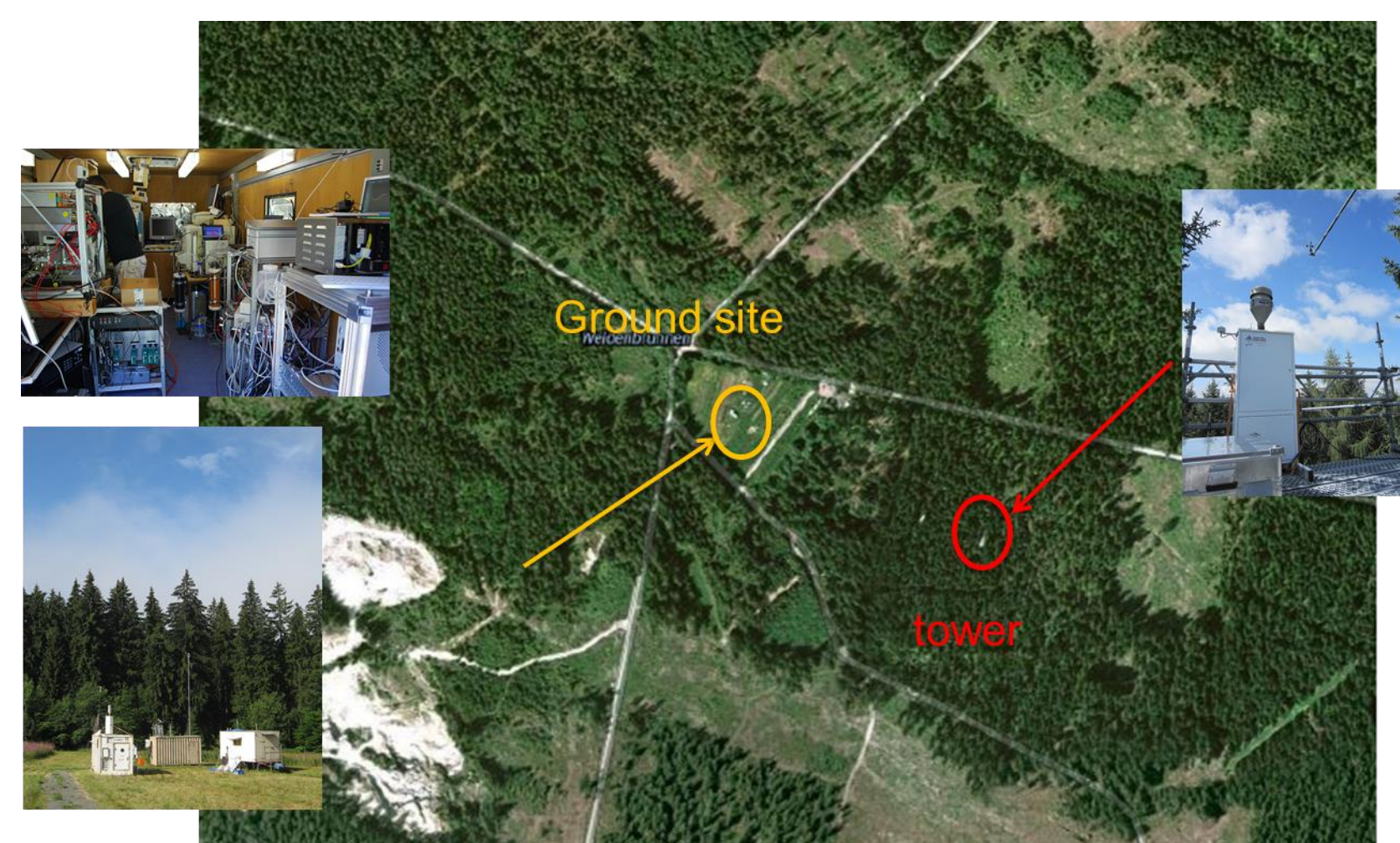


Fig. 1: Localization of the two sampling sites (tower and ground) used for the campaign. The two sites were approximately 250 meters from each other.

A complementary suite of real-time mass spectrometers including a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS), a Chemical Ionization Atmospheric-Pressure interface Time-of-Flight Mass Spectrometer (CI-APIToF-MS) and an Aerosol Flowing Atmospheric-Pressure Afterglow Mass spectrometer (AeroFAPA-MS), were deployed at the ground site (Fig. 1). In addition, offline chemical analysis based on a day-night regime of high-volume quartz filter samples, was performed focused on Biogenic SOA tracers, as well as particulate HOMs tracers. A total of 3 high volume Digital samplers were used: a PM₁ was deployed at the ground site, while two PM₁₀ were installed at the tower at 12 and 21 m height.

Experimental conditions

Overview aerosol composition and sizing

The aerosol particles were mostly made of organic and sulfate (Fig. 2) with a very low contribution of black carbon supporting the low contribution of anthropogenic sources. Moreover, the frequent new particle formation support the local SOA formation from biogenic sources (Fig. 2).

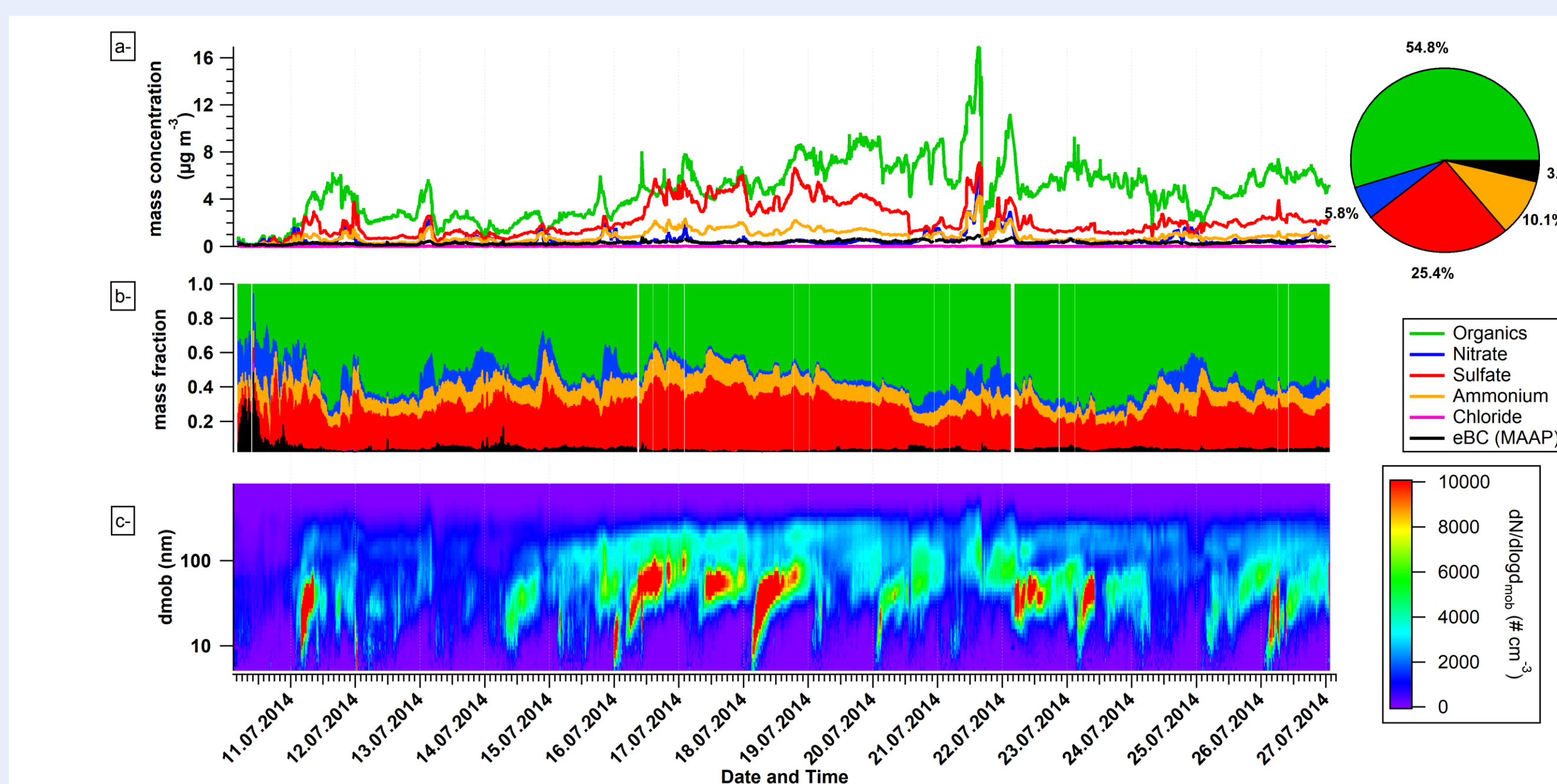


Fig. 2: overview of the aerosol chemical mass concentration (a) and mass fraction (b) as measured by the AMS and MAAP. The pie chart on the upper right corner corresponds to the averaging values over the entire sampling period. Particle number size distribution measured by the T-SMPS is plotted in (c).

Gas and particulate HOMs identification

HOMs were measured in both gas and particle phases. For the gas phase, an online Chemical Ionization Atmospheric-Pressure interface Time-of-Flight Mass Spectrometer (CI-API-ToF-MS; Jokinen et al., 2012) using nitric acid as ionization agent was used, while for the particulate monoterpenes related HOMs were identified by LC-MS from the two PM₁₀ filters according to Mutzel et al. (2015). Although a good relationship between the two phases can be found during day time (Fig. 3), this correlation disappears during night emphasizing the decrease of gas phase HOMs formation during night while particulate HOMs can still be detected.

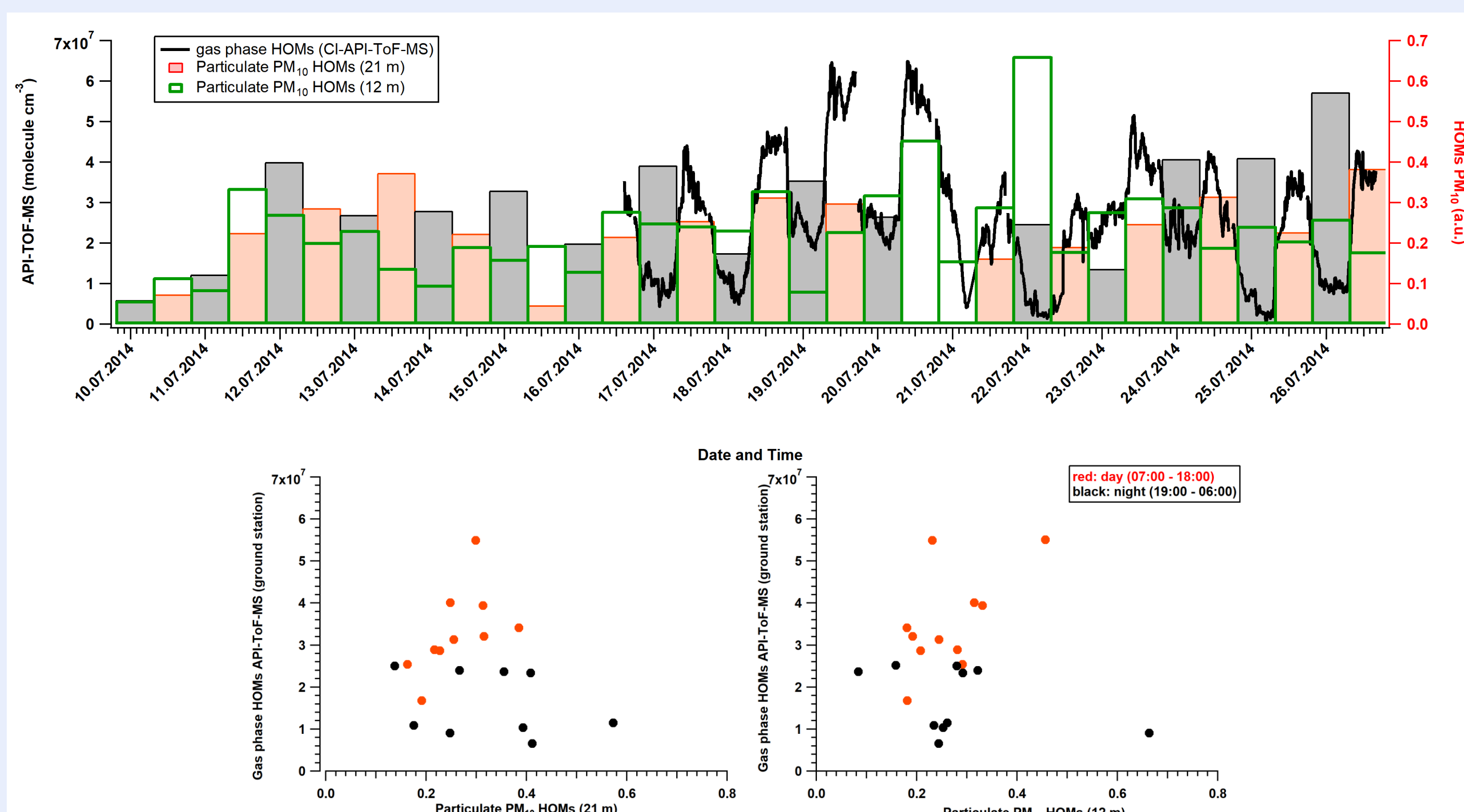


Fig. 3: Comparison between gas phase HOMs detected by CI-API-ToF-MS at the ground site and PM₁₀ particulate HOMs identified on filter samples at the two levels of the tower.

Monoterpenes SOA contribution

Identification

The organic and inorganic mass spectra measured by the AMS were combined to perform source apportionment of the full aerosol particle chemical composition, and factor identification was determined using available offline measurements. From the 8 factors identified, one was specifically associated with the monoterpene SOA tracer consequently named monoterpenes-SOA factor (MT-SOA) (20 % of total PM₁, Fig. 4).

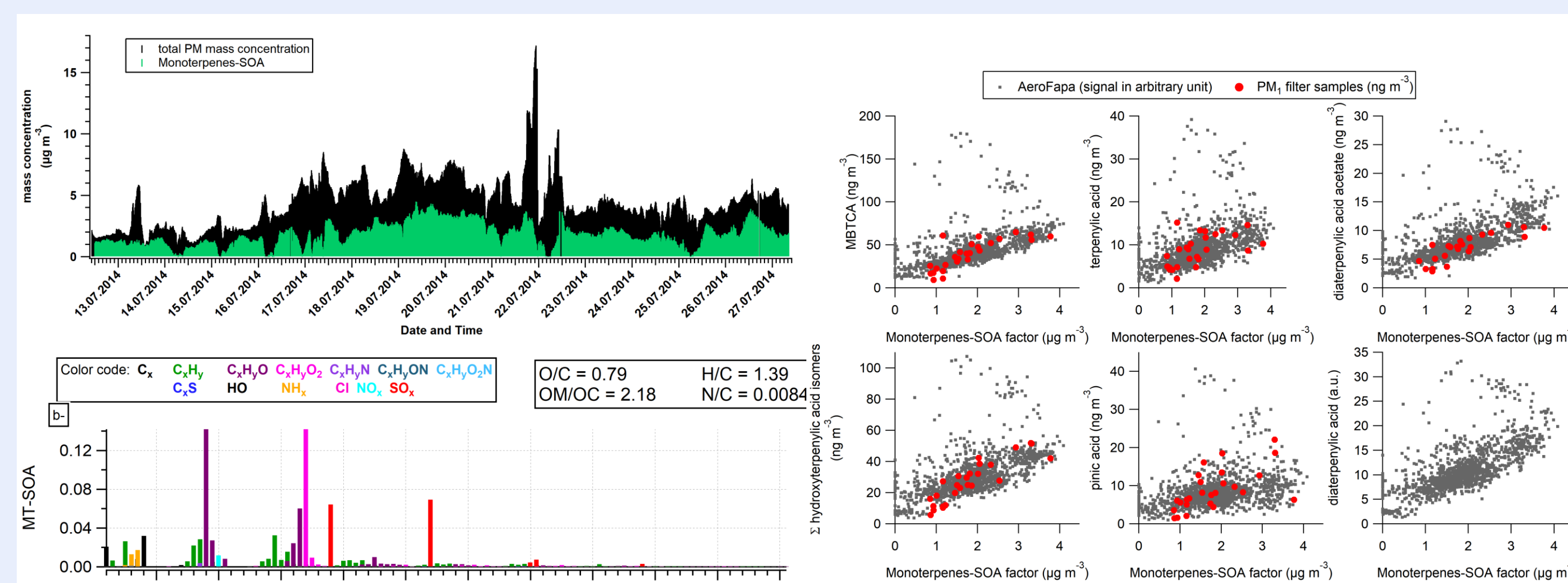


Fig. 4: Identification of the monoterpenes-SOA factor with its time series, mass spectrum, and correlation with specific tracers from PM₁ filter samples as well as the AERO-FAPA.

Connecting HOMs and Monoterpenes-SOA formation

The linear relationship between HOMs and the MT-SOA revealed the direct role played by HOMs on particulate biogenic SOA formation in-situ (Fig. 5).

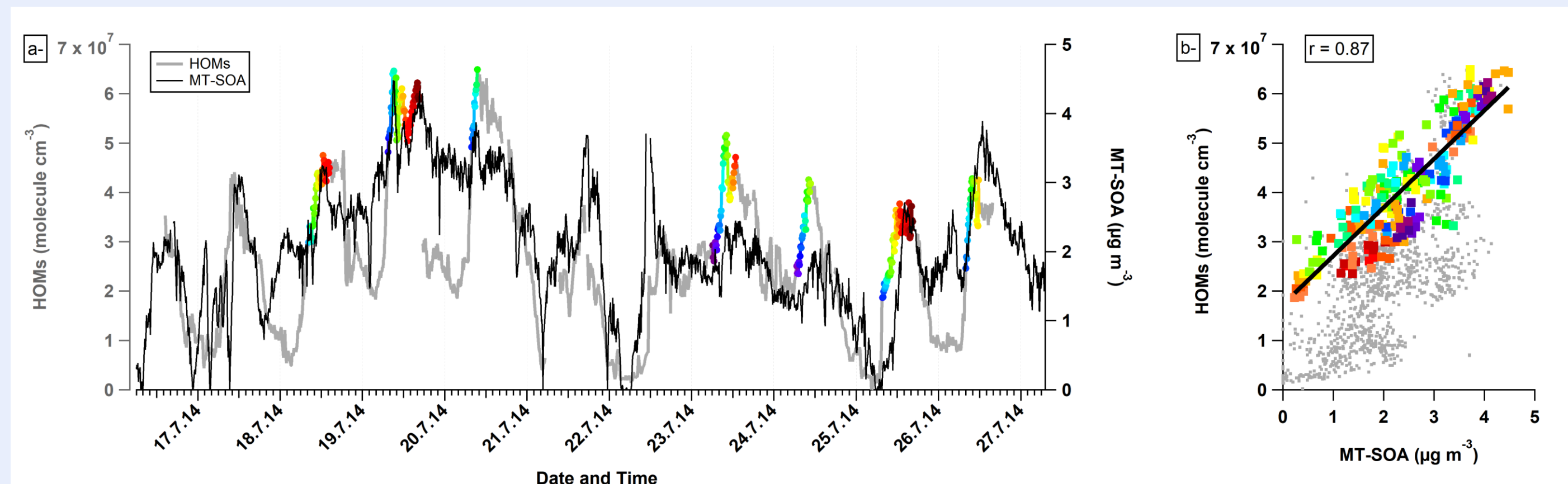


Fig. 5: Evidence of the HOMs contribution to the monoterpenes-SOA formation during days with new particles formation.

Conclusion

The unique combination of online and offline measurements used in this work enables an accurate identification and quantification of monoterpene SOA as well as the relationship between HOMs in the gas phase and in the particle phase. Furthermore, the strong linear correlation between HOMs and monoterpene SOA emphasizes the key contribution of the identified HOMs to the formation of monoterpene SOA. Our results will significantly contribute to improve our understanding of bio-SOA formation and improve the modelling of bio-SOA at local and global scales.

References

Jokinen, T. et al., Atmos. Chem. Phys., 12, 4117-4125, 2012. Mutzel, A. et al., Environ. Sci. Technol., 49, 7754-7761, 2015. Brüggemann, M. et al., Atmos. Chem. Phys., 17, 1453-1469, 2017.