

OH reactivity from NMVOCs at a mixed forest in Vielsalm (BE, July 2022)

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1. Introduction

i) Background

Non methane volatile organic compounds (NMVOCs) significantly contribute to OH reactivity. They affect both air quality and climate by being precursors of tropospheric O₃ and secondary organic aerosols. Moreover, their competition with CH₄ in terms of OH reactivity modulates the lifetime of this greenhouse gas.

Terrestrial ecosystems, and specifically forests, account for the majority of NMVOC emissions on a global scale. In order to reduce uncertainties in atmospheric chemistry and air quality modelling, it is important to understand both the (bi-directional) fluxes and reactivity of the emitted NMVOCs within, and above the forest canopy. Here, we compare the NMVOC OH reactivity based on online PTR-TOF-MS measurements with dedicated offline chromatography-based measurements performed in the framework of the intensive EMEP/ACTRIS campaign on O₃ and VOCs taking place in July 2022.

ii) Objectives

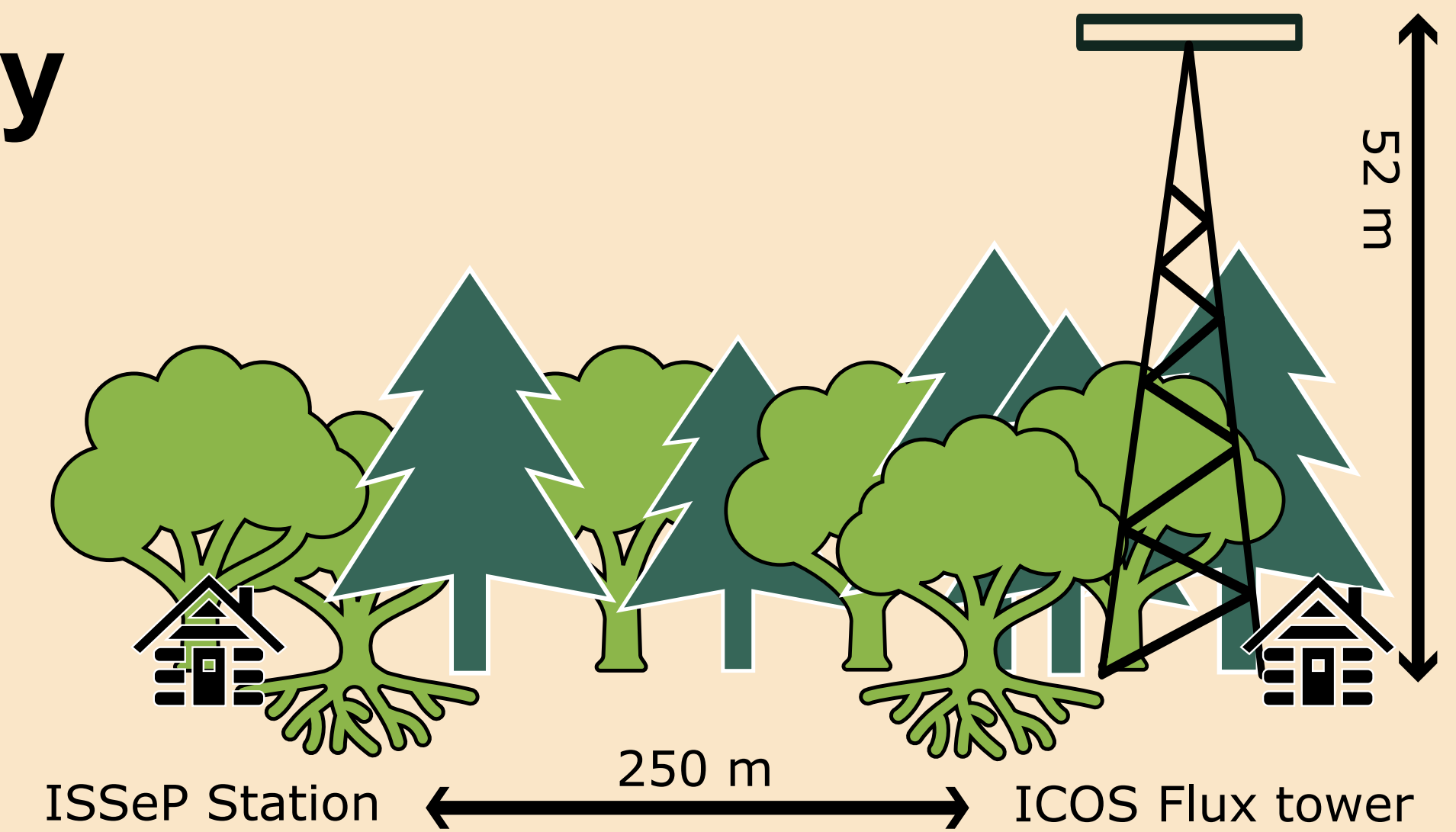
Support **PTR-TOF-MS spectrum analysis** to better identify the main isomers contributing to specific m/z values.

Compare **NMVOC OH reactivity** from long-term PTR-TOF-MS measurements with campaign based speciated chromatographic measurements.

2. Methodology

i) Site description

Mixed forest ecosystem in the Integrated Carbon Observation system (ICOS) network located in the Belgian Ardennes at about **450 m a.s.l.** and characterized by a **temperate maritime climate**.



Data presented for the **2022 EMEP Campaign** (Jul). **Fig 1:** Schematic representation of measurement sites in the Vielsalm forest.

ii) Instrumental setup

- Chromatographic analyses:** samples collected **once daily** at the ISSeP station during the EMEP campaign (**12-19 Jul 2022**) in canisters (12:00-13:00 UTC), on DNPH cartridges (12:00-16:00 UTC) and on TENAX sorbent tubes (12:00-14:00 UTC), and analysed by GC-MS, HPLC-MS, and GC-MS, respectively, by reference laboratories.
- PTR-TOF-MS** (PTR-TOF-4000, Ionicon Analytik GmbH): **Continuous** above-canopy measurements at the ICOS Flux tower (**12-31 Jul 2022**), interrupted by vertical profile measurements (21-31 Jul; 7 equidistant heights, once every 2.5 hours).

4. Results

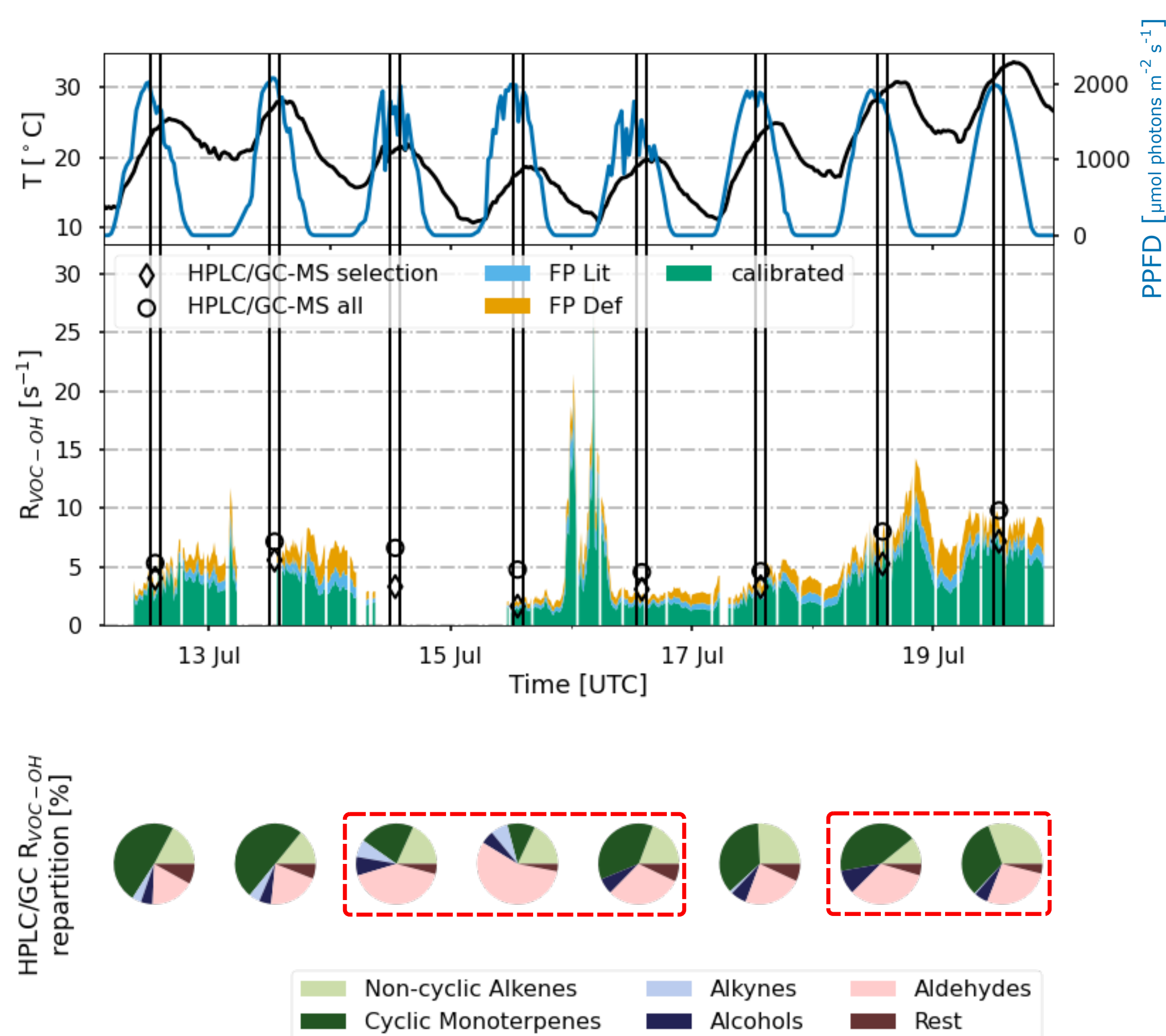


Fig 2: Temperature (T) and photosynthetic photon flux density (PPFD) at the top of the canopy (top). NMVOC-OH reactivity (R_{VOC-OH}) calculated from PTR-TOF-MS (15' mean; shaded area) and HPLC/GC-MS (markers) concentration measurements for the selection of compounds used to calibrate the PTR-TOF-MS, and all signals (middle). Chemical class contribution to total VOC-OH reactivity as determined from chromatographic analyses (bottom).

Periods of high R_{VOC-OH} :

- Peaks from 15-16 Jul (nighttime) related to monoterpene plumes from nearby **saw-mill**.
 - Peaks related to the **EU heatwave** with strong isoprene and monoterpene emissions.
- Total R_{VOC-OH} from PTR-TOF-MS is consistently **lower** compared to HPLC/GC-MS. This is partly due to inconsistencies related to aldehydes.
- Formaldehyde not quantified with PTR-TOF-MS (occurrence of back-reaction in drift tube).
 - High signal for pentanal** from GC-MS in disagreement with PTR-TOF-MS.

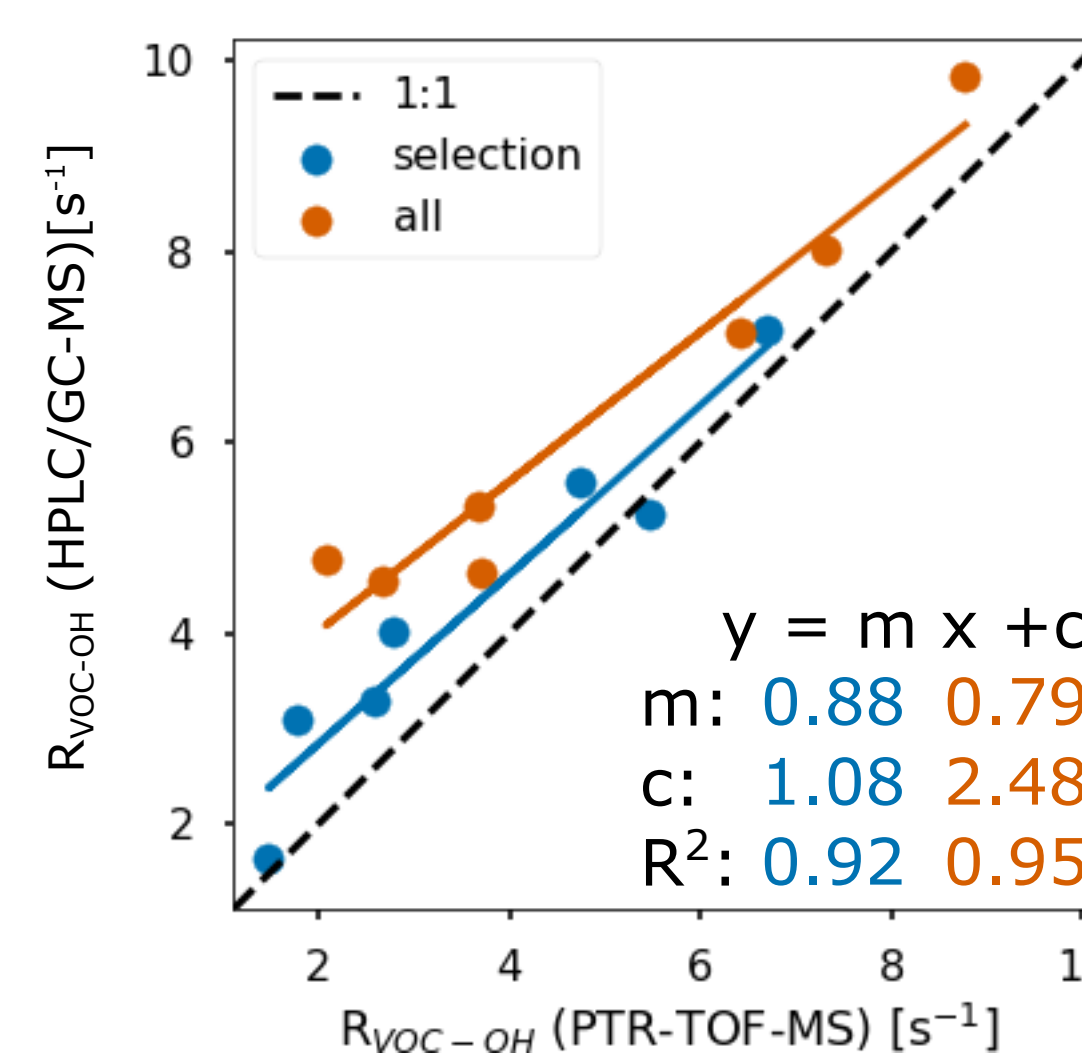


Fig 3: R_{VOC-OH} calculated from PTR-TOF-MS vs HPLC/GC-MS considering all compounds/ion signals, and the selection of compounds in the PTR-TOF-MS calibration standard.

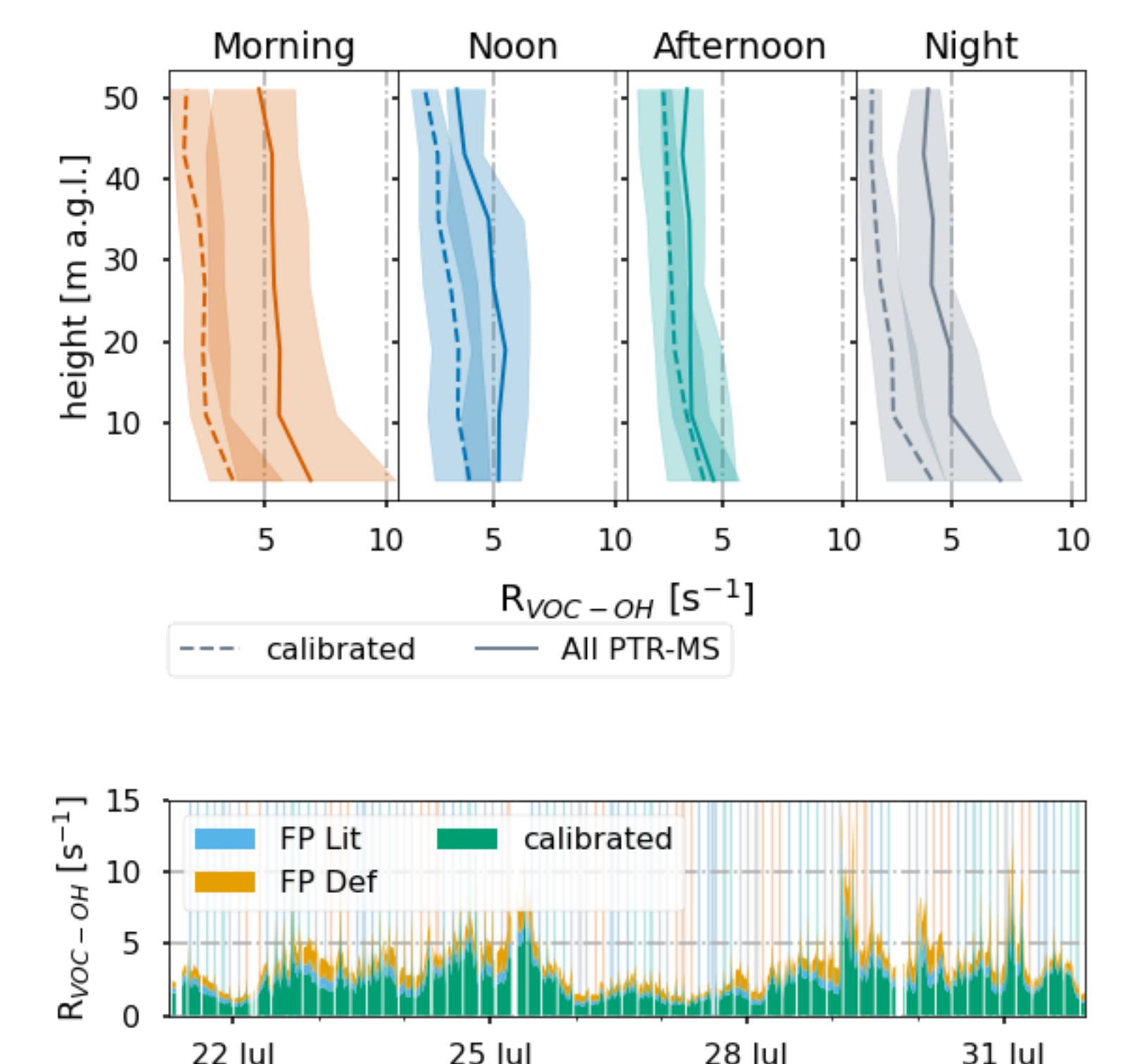


Fig 4: Vertical R_{VOC-OH} profiles calculated from PTR-TOF-MS measurements (21-31 Jul 2022) during Morning (3-9 UTC), Noon (9-15 UTC), Afternoon (15-21 UTC), and Night (21-3 UTC) and the associated continuous R_{VOC-OH} time-series.

Effects of non co-located measurements:

- Expect a **30/60%** (all/calibrated) difference between R_{VOC-OH} above the forest canopy and at the ground level around noon.
- Potential source of **offset** between PTR-TOF-MS and HPLC/GC-MS estimates

3. PTR-TOF-MS quantification

Twelve compounds are quantified directly using a PTR-TOF-MS calibration standard.

m/z value	Compound
33.0335	Methanol
42.0338	Acetonitrile
45.0335	Acetaldehyde
47.0492	Ethanol
59.0491	Acetone
69.0699	Isoprene
71.0491	MVK/MACR (50/50)
73.0684	MEK
93.0699	Toluene
107.0856	m-xylene
121.1012	1,2,4-trimethylbenzene
137.1325	Sabinene

A list of m/z values obtained in the Amazon rainforest by Pfannerstill et al. (2021) was used for ion signal attribution to biogenic VOCs.

Eleven additional compounds quantified from first principles using literature values for H₃O⁺/VOC reaction rate constants (e.g., Sekimoto et al. 2017) and product ion yields (**FP Lit**).

Additionally, 31 compounds were quantified using default ion/molecule reaction rate constants not taking into account any fragmentation. (**FP Def**)
 $k_{default} = 2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

5. Conclusions

The calibrated compounds account on average for 64% of the R_{VOC-OH} while compounds quantified using $k_{default}$ and no fragmentation account for 22%. Continuous online PTR-TOF-MS measurement provide more details on the evolution of R_{VOC-OH} during the heat wave compared to discrete daily samples of limited duration.

Although fair agreement is found between R_{VOC-OH} from PTR-TOF-MS and HPLC/GC-MS, local scale VOC concentration variability complicates direct comparison between above-canopy and surface level measurements.

References

Pfannerstill et al., Atmos. Chem. Phys. doi:10.5194/acp-21-6231-2021, 2021; Sekimoto et al., Int. J. Mass Spectrom. doi:10.1016/J.IJMS.2017.04.006, 2017.

Acknowledgements

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