Supplement

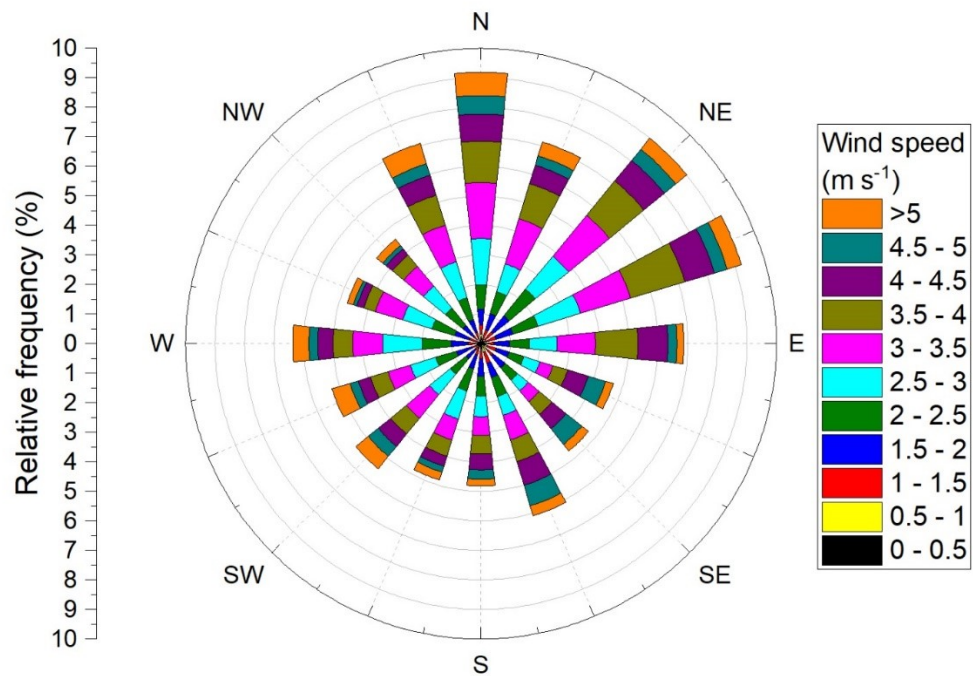**S1 Wind rose**

5   **Figure S1: Wind rose coloured according to wind speed as measured during the ACROSS campaign.**

S2 NO₃ reactivity measurements above and below the canopy

Figure S2 shows the time-series of k^{VOC} measured at 5.5 m (every odd hour) and at 40 m (every even hour) between July 18 and July 23. Note that the data coverage of k^{VOC}(5.5 m) is reduced due to missing NO measurements. During the daytime period of July 21, k_{day}^{VOC} is about (0.05 ± 0.03) s⁻¹ at both heights. From ca. 17:00 UTC on, k^{VOC}(5.5 m) and k^{VOC}(40 m) diverge with an increase in both the magnitude and variability of the former and a continuous decrease in the latter to the instrument LOD of 0.006 s⁻¹ at ~22:30 UTC. On this night, there was a moderate temperature inversion (ΔT = -2.9 K, Fig. 2) and the inlet at 40 m (ca. 20 m above canopy level) was thus effectively decoupled from any sources of biogenic emissions, explaining the low reactivity at this height. Furthermore, contrary to the daytime when the variability in k^{VOC} was similar at both heights, at night k^{VOC} (40 m) is less affected by short-term fluctuations, presumably a result of enhanced mixing above canopy. It is also observed that k^{VOC}(5.5 m) and k^{VOC}(40 m) show a similar diel profile on July 19-20. However, k_{day}^{VOC} between the two heights differ by a factor of 2 and a weaker nocturnal gradient in k_{night}^{VOC} (only a factor of 4) occurs. The latter presumably results from a weaker, less stable temperature inversion ($\Delta T \approx$ -0.5 K, Fig. 2) during that night.
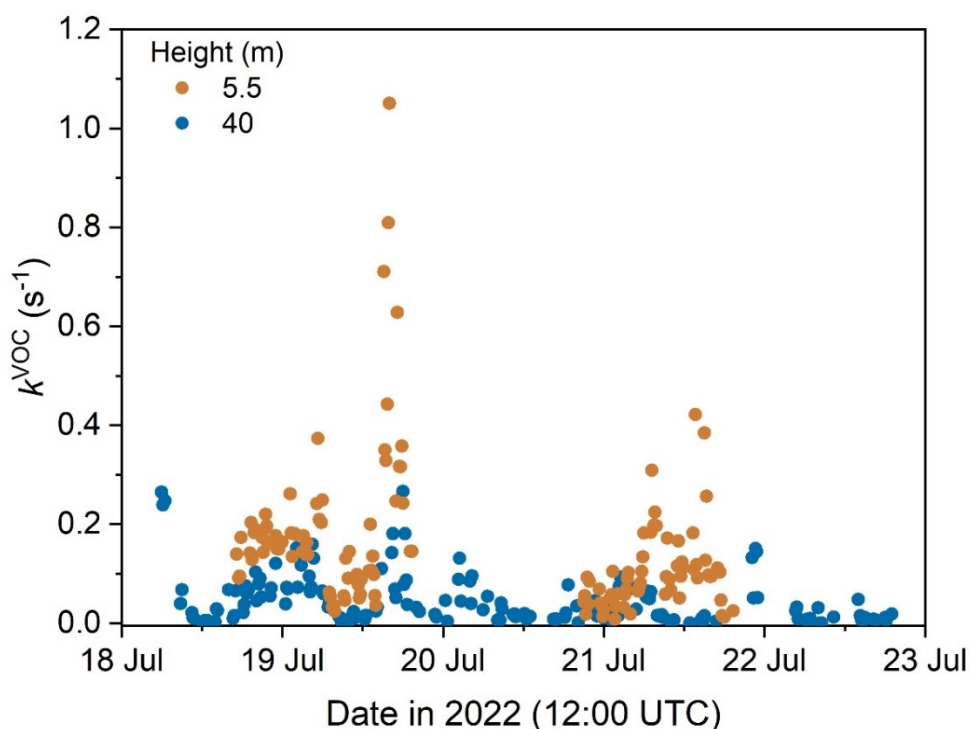
Figure S2: Time series of k^{VOC} (10 min averages) at 5.5 m (dark orange dots) and 40 m (blue dots) between July 18 and July 23 during the ACROSS campaign. Major and minor ticks on the x-axis represent 12:00 and 00:00 UTC, respectively.

S3 Impact of OH, XO₂ and heterogeneous reactions of N₂O₅ on NO₃ loss

A chemical ionization mass spectrometer (CIMS) measured the sum of peroxy radicals ($XO_2 = RO_2 + HO_2$) as well as OH radicals ca. 3 m above ground level via their conversion to sulphuric acid (H_2SO_4) by sulphur dioxide (SO_2). Nitrate ions (NO_3^-) serve as ionization agent. The associated measurement uncertainty of XO_2 is ca. 30 % (2σ) with an LOD of 2×10^6 molecule cm⁻³ (4 min). A detailed description of the instrument can be found in Kukui et al. (2008). IUPAC-recommended rate coefficients (IUPAC, 2024) were used to derive pseudo first-order NO₃ loss rates. In case of XO_2, the rate coefficient of RO_2 was set to the value of HO_2 (4×10^{-12} cm³ molecule⁻¹ s⁻¹), since isoprene-derived RO_2 are suspected to be a factor of two more reactive (4.6×10^{-12} cm³ molecule⁻¹ s⁻¹) towards NO₃ (Dewald et al., 2020) than for instance ethyl peroxy radicals. Losses of NO₃ via its reaction with OH, HO₂ and RO₂ (Fig. S3) were, with a campaign-averaged mean contribution of 0.003 s⁻¹, found to be insignificant compared to photolysis and VOC-induced losses.
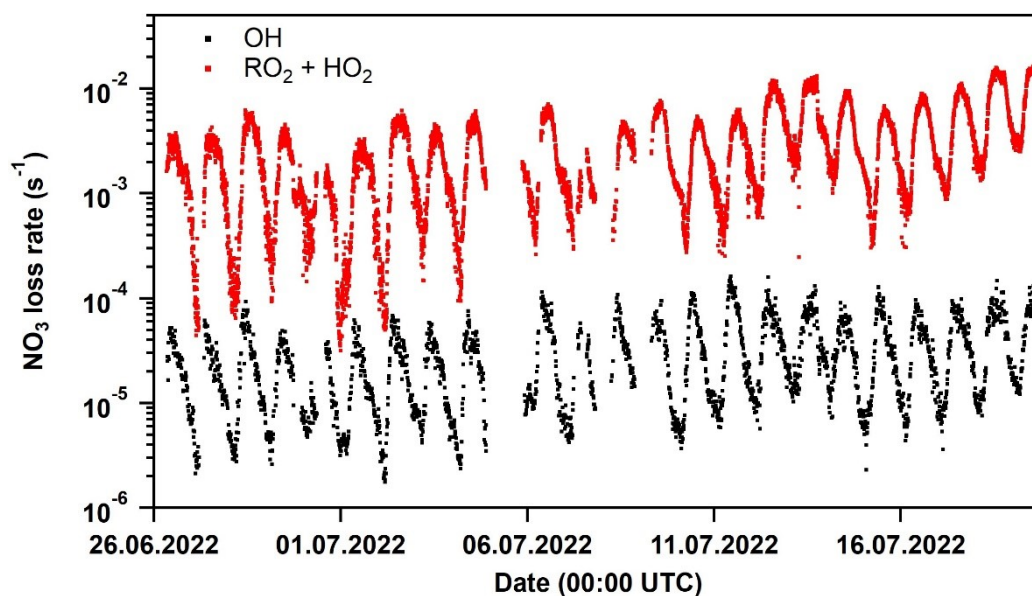

Figure S3: Time series of pseudo first-order NO₃ loss rates from OH (black) and RO₂ + HO₂ (red).

In addition, neither direct nor indirect heterogeneous losses (via N₂O₅) of NO₃ are expected to contribute significantly to the NO₃ loss term. Assuming a large uptake coefficient γ of 0.03 for N₂O₅ (featuring a mean molecular velocity c of 26233 cm s⁻¹ at 298 K) and a surface area (A_S) of 1.5×10^{-6} cm² cm⁻³ in a semi-rural environment (Phillips et al., 2016) together with the equilibrium constant (K_{eq}) for reactions R3 and R4 of 2.8×10^{-11} cm³ molecule⁻¹ at 298 K (IUPAC, 2024) would result in a k_{het} $= 0.25\gamma c A_s K_{eq}[NO_2] = 4 \times 10^{-4}$ s⁻¹ in case of 2 ppbv NO₂ at noon (see Fig. 1). Heterogeneous uptake is thus only of very minor importance below the canopy.

S4 NO₃ loss rates (sum, NO, photolysis) above and below the canopy between July 18 and July 23
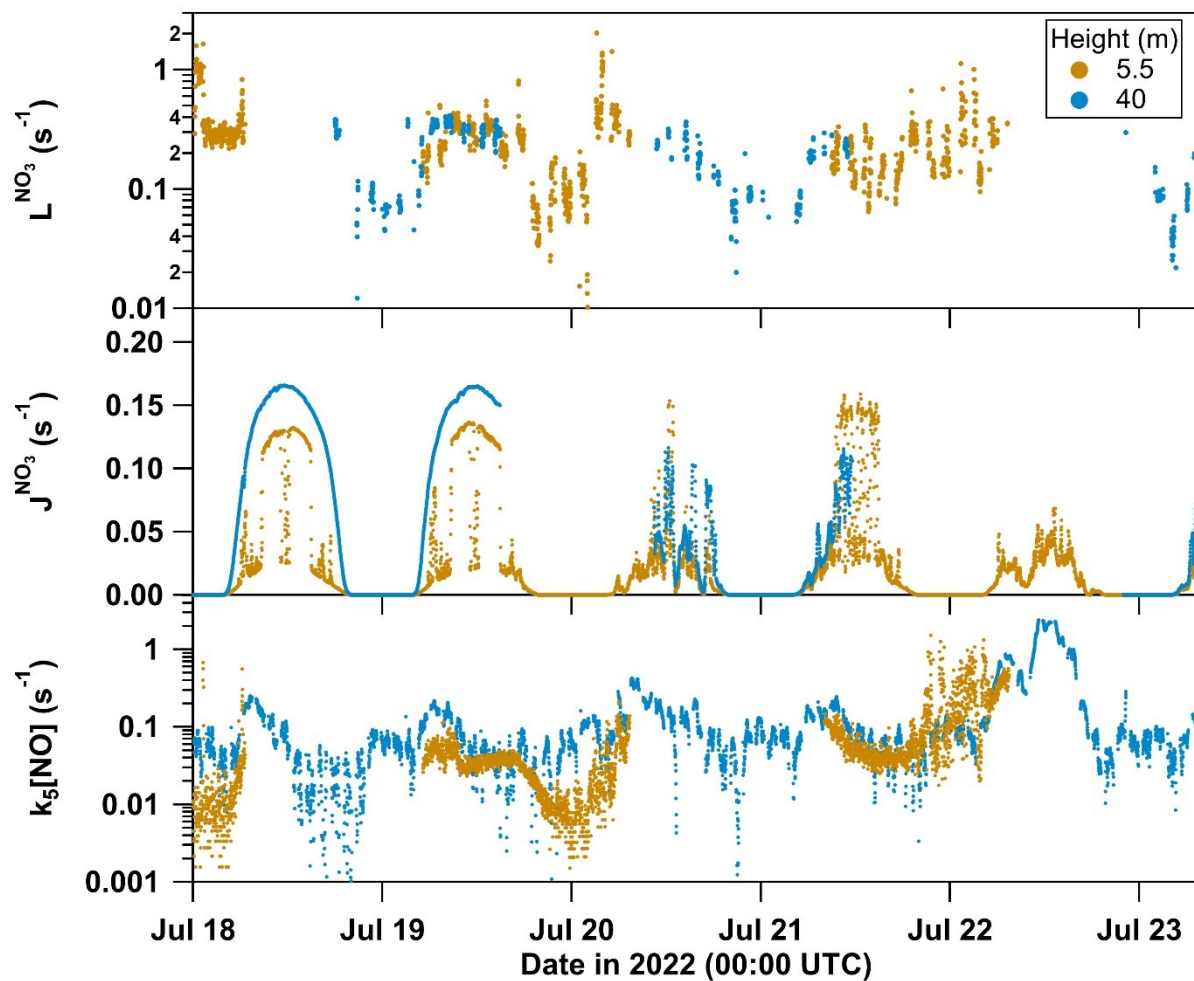

Figure S4: Time series of $k_5[NO]$, J^{NO_3} as well L^{NO_3} at 5.5 m (dark orange dots) and 40 m (blue dots) between July 18 and July 23 during the ACROSS campaign. Major and minor ticks on the x-axis represent 00:00 UTC.

S5 NO₃ photolysis rates above and below the canopy
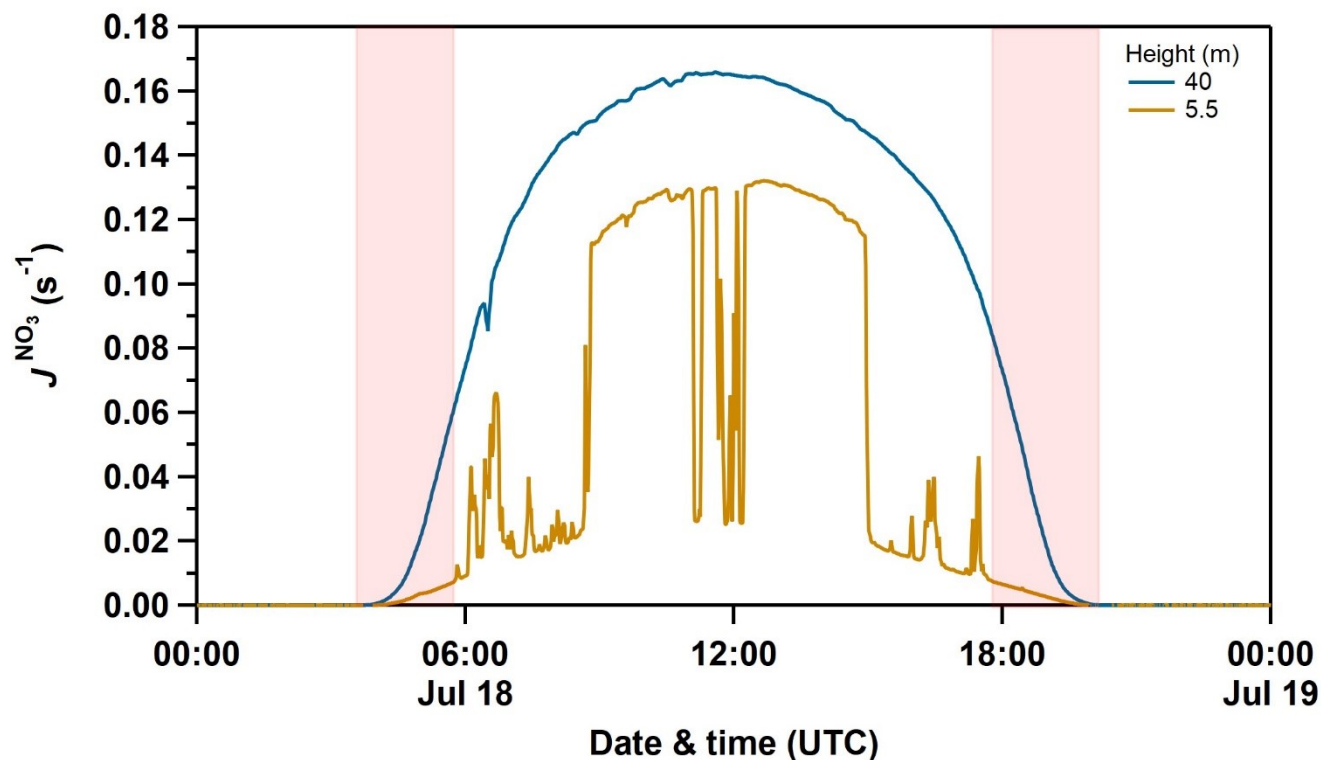
Figure S5: Exemplary diel profile of NO₃ photolysis rates (J^{NO_3}) measured in the clearing below the canopy (orange line, 5.5 m) versus those measured on top of the tower above the canopy (blue line, 40 m) during the ACROSS campaign on a clear day. The red shades mark periods in the early morning and the late afternoon when only diffuse sunlight reached the spectral radiometer below the canopy. As a consequence, J^{NO_3} (5.5 m) was on average a factor of 12.5 lower than J^{NO_3} (40 m) during these periods.

S6 Fractional contributions of OH, O$_3$ and NO$_3$ to oxidation of other monoterpenes
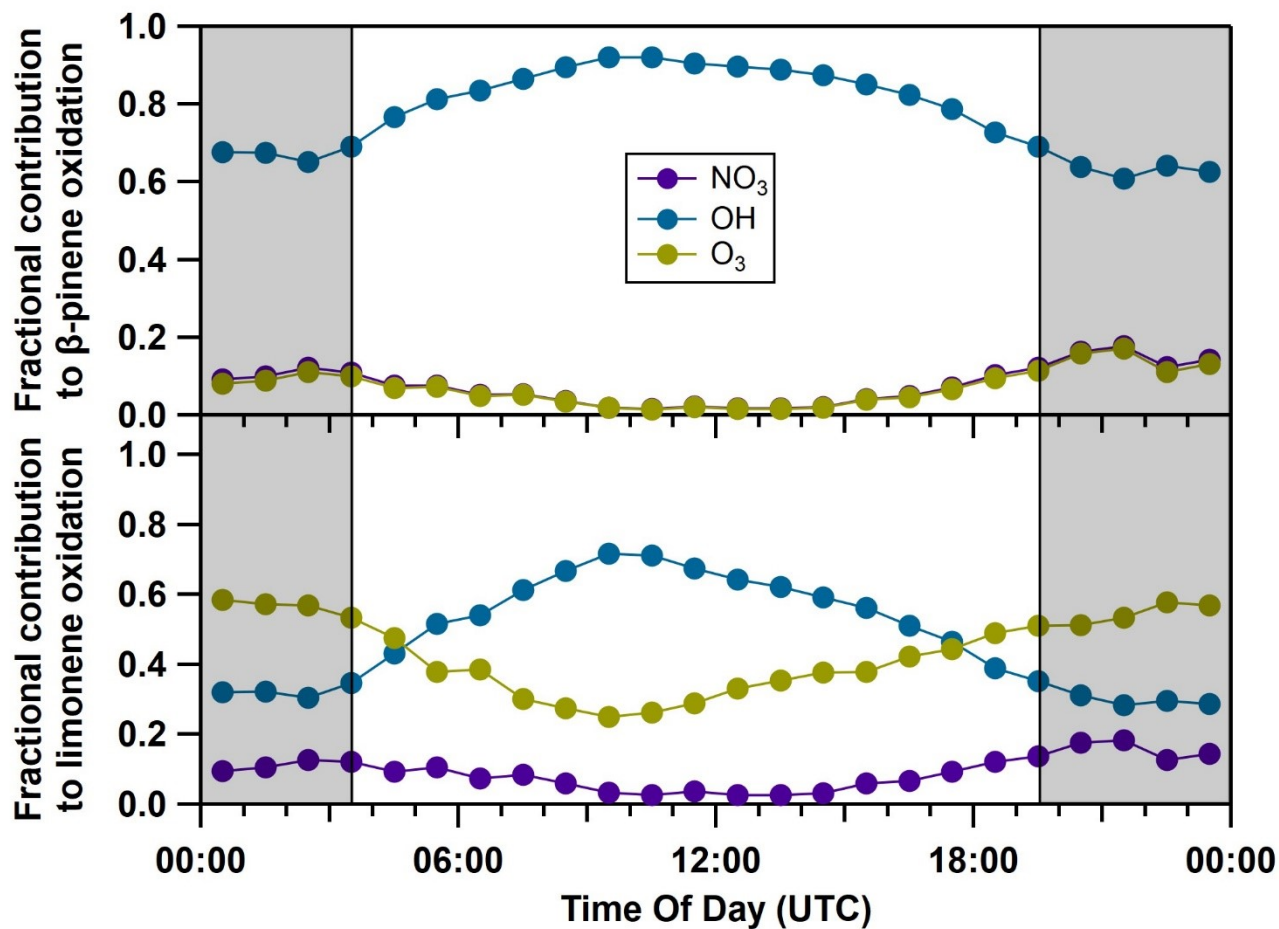
Figure S6: Median diel cycles (1h, circles) of fractional contributions of NO$_3$ (violet), OH (green) and O$_3$ (dark yellow) to the oxidation of β-pinene (upper panel) and limonene (lower panel) during the ACROSS campaign. The nighttime period is grey-shaded.

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