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Short-lived organic nitrates in a suburban temperate forest: an indication of efficient assimilation of reactive nitrogen by the biosphere?

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Table S1: Average midday values used to calculate production rates and uncertainties in table S3.

	Midday average	
	Phase 1	Phase 2
NO_2 (pptv)	446	713
NO (pptv)	45	36
O_3 (ppbv)	35	56
J_{NO3} (s^{-1})	0.09	0.11
k^{BVOC} (s^{-1})	0.08	0.12
OH (molecule cm^{-3})	2.1×10^6	3.5×10^6
β	0.282	0.316
$[NO_3]ss$ (pptv)	0.076	0.168
ANs (pptv)	81	161
α-pinene (pptv)	342[a], 254[b], 210[c]	493[a], 365[b], 303[c]
β-pinene (pptv)	20[a], 59[b], 35[c]	29[a], 85[b], 51[c]
Limonene (pptv)	40[a], 78[b], 105[c]	59[a], 114[b], 153[c]
Isoprene (pptv)	913	2264
RH (%)	43	28

[a]Using the mixture with 10% limonene, 5% β-pinene, and 85% α-pinene.
[b]Using the mixture with 20% limonene, 15% β-pinene, and 65% α-pinene.
[c]Using the mixture with 30% limonene, 10% β-pinene, and 60% α-pinene.

Table S2: Uncertainties associated with measurements, rate coefficients and steady-state calculations used in Table S3.

	Uncertainty
OH calibration	25%
β (extremes)	30%
α^{NO_3}, α^{RO_2+NO}, α^{O_3}	20%
k^{BVOC} (Campaign average)[a]	30%
J_{NO3}	5%
O_3	2%
NO_2 (1 min averages)	7% + 9.7 pptv + (20 pptv * RH/100)
NO	10%
ANs (10 min averages)	28% + 8.6 pptv
PANs (10 min averages)	21% + 6.3 pptv
$k(NO_2+O_3)$[b]	15%
$k(NO+NO_3)$[b]	26%
$[NO_3]ss$	Around 40%

Table S3: Average production rates of alkyl nitrates from NO_3-, O_3-, and OH-initiated oxidation of BVOCs at midday for three different potential mixtures of monoterpenes calculated using the average midday values in table S1 and the associated uncertainties are calculated using the uncertainties described in table S2 and table 1. The percentages represent the relative uncertainty.

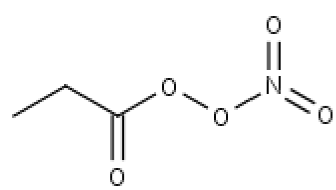
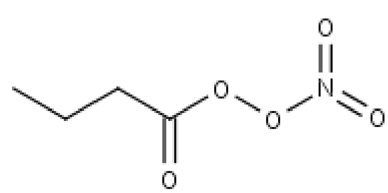
Phase 1	**30% limonene, 10% β-pinene, and 60% α-pinene**	**20% limonene, 15% β-pinene, and 65% α-pinene**	**10% limonene, 5% β-pinene, and 85% α-pinene**
$\sum P_{ANs}^{NO3}$ (pptv h^{-1})	9.2 ± 3.2 (±34%)	8.6 ± 2.8 (±32%)	7.4 ± 2.5 (±34%)
$\sum P_{ANs}^{O3}$ (pptv h^{-1})	6.6 ± 2.4 (±36%)	6.4 ± 2.5 (±38%)	6.6 ± 3.0 (±46%)
$\sum P_{ANs}^{OH}$ (pptv h^{-1})	41 ± 13 (±31%)	40 ± 13 (±31%)	38 ± 13 (±33%)
$\sum P_{ANs}$ (pptv h^{-1})	56 ± 13 (±24%)	55 ± 13 (±24%)	52 ± 13 (±25%)
ANs lifetime (h)	0.7 ± 0.3 (±45%)	0.7 ± 0.3 (±45%)	0.6 ± 0.3 (±46%)
Phase 2			
$\sum P_{ANs}^{NO3}$ (pptv h^{-1})	37 ± 14 (±37%)	35 ± 13 (±36%)	31 ± 12 (±39%)
$\sum P_{ANs}^{O3}$ (pptv h^{-1})	18 ± 6.1 (±35%)	17 ± 6.4 (±37%)	18 ± 7.8 (±44%)
$\sum P_{ANs}^{OH}$ (pptv h^{-1})	159 ± 56 (±35%)	158 ± 56 (±35%)	151 ± 56 (±37%)
$\sum P_{ANs}$ (pptv h^{-1})	213 ± 58 (±27%)	210 ± 57 (±27%)	200 ± 57 (±28%)
ANs lifetime (h)	1.3 ± 0.6 (±43%)	1.3 ± 0.6 (±43%)	1.2 ± 0.5 (±44%)

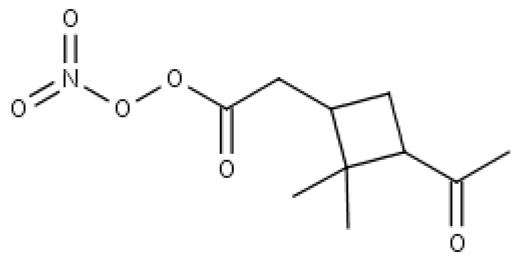
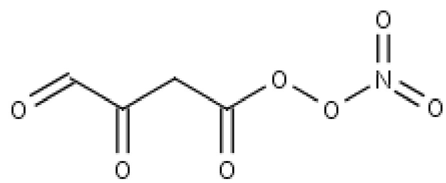
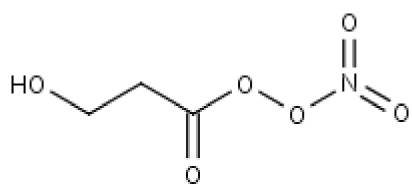
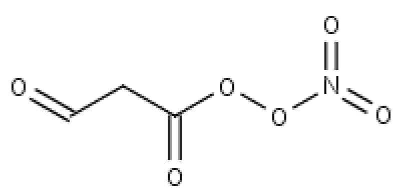
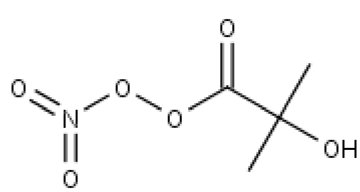
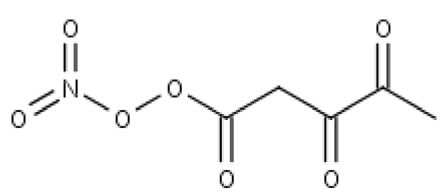
Box model results:

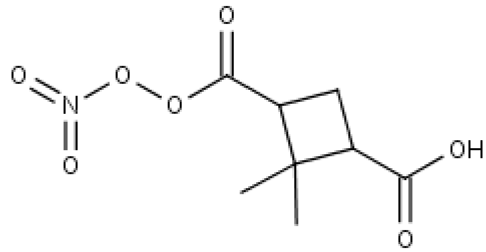
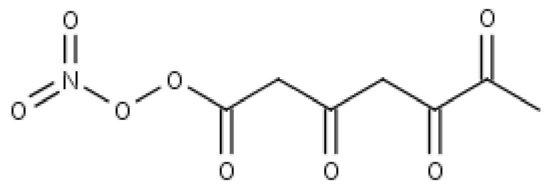
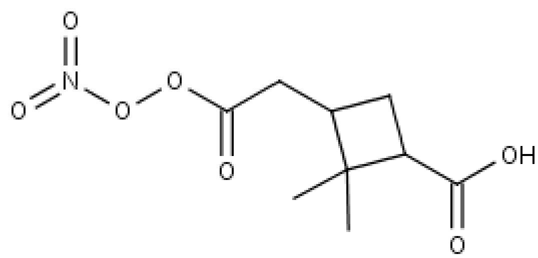
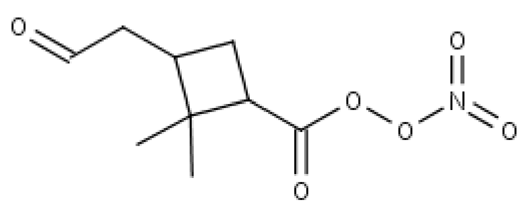
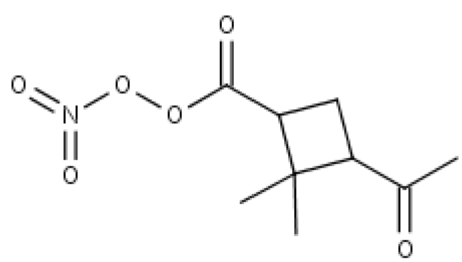
According to the model, at daytime (06:00-18:00 UTC, 08:00-20:00 LT), PAN contributes 61-78 % and 58-72 % of ∑PANs for the low and high precursor day, respectively. The nighttime PAN contribution to the ∑PANs is lower at 48-70 % and 48-60 %, respectively. The lower contribution of PAN to ΣPANs at nighttime is related to the high nighttime mixing ratios of monoterpenes (caused by the vegetation emitting BVOCs into a shallow boundary layer), which degrade to form larger PANs (see Table S4) compared to PAN. During the BEARPEX-2007 campaign in the Sierra Nevada Mountains, PAN was determined at local noon time to contribute 70-90 % of ∑PANs (Wolfe et al., 2011), which is in reasonable agreement with our daytime results. MPAN contributes with around 2 % at nighttime and up to 4 % at daytime according to the model, which should both be seen as upper estimates since isomerization is not taken into account. PPN formation accounts for less than 0.1 % of the modelled PANs. A list of all the modelled PANs is given in Table S4.

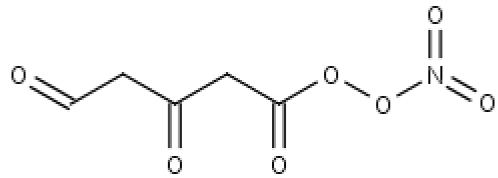
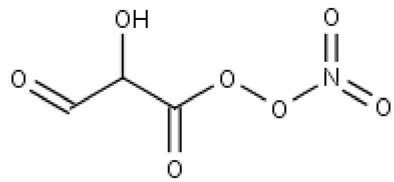
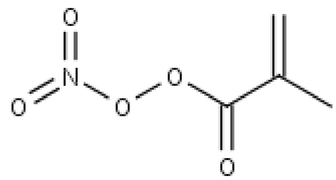
The model generated high amounts of HPAN ($HOCH_2C(O)O_2NO_2$) from glycolaldehyde, despite HPAN having a very short thermal lifetime (Zheng et al., 2011) and never having been detected in ambient air samples. In order to reduce the modelled contribution of HPAN to ΣPANs, an arbitrary loss term (10 times that of the other PANs) was included in the model.

Table S4: List of PANs included in Figure 8 under "Other PANs" from the MCM coming from the degradation of acetaldehyde, isoprene, propane, n-butane, isobutane, α-pinene, β-pinene, and limonene.

MCM Name	Structure
PPN	
PBN	

C10PAN2	
C312COPAN	
C3PAN1	
C3PAN2	
C4PAN5	
C5PAN9	

C721PAN	
C7PAN3	
C811PAN	
C89PAN	
C9PAN2	

CHOC3COPAN	
HCOCOHPAN	
MPAN	

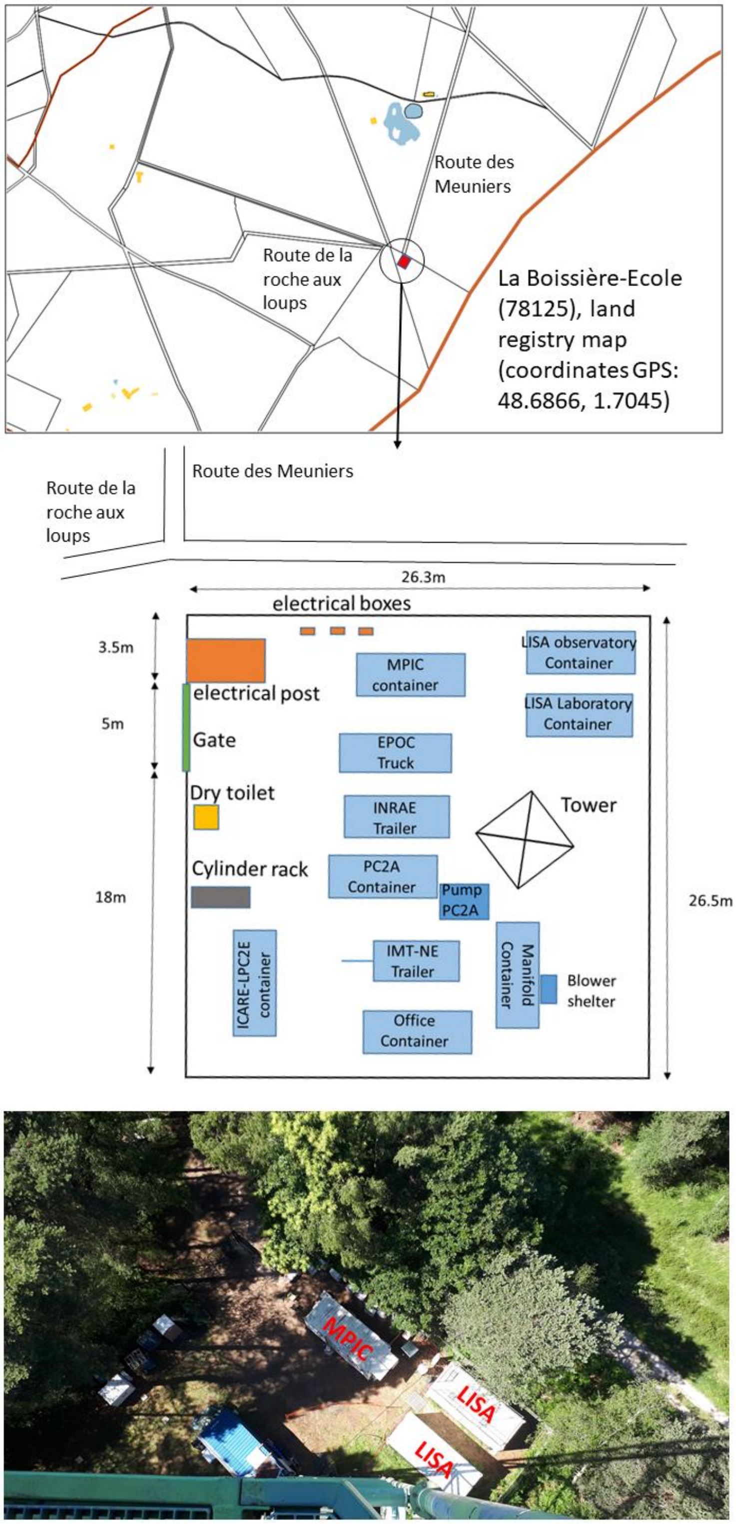


Figure S1a: Top panel shows a land registry map with the Rambouillet forest site shown as the red box. The middle panel shows an overview of the location of the tower and containers in the clearing. The bottom panel shows a picture from the tower looking down onto the MPIC and LISA containers at 16:45 LT (14:45 UTC).

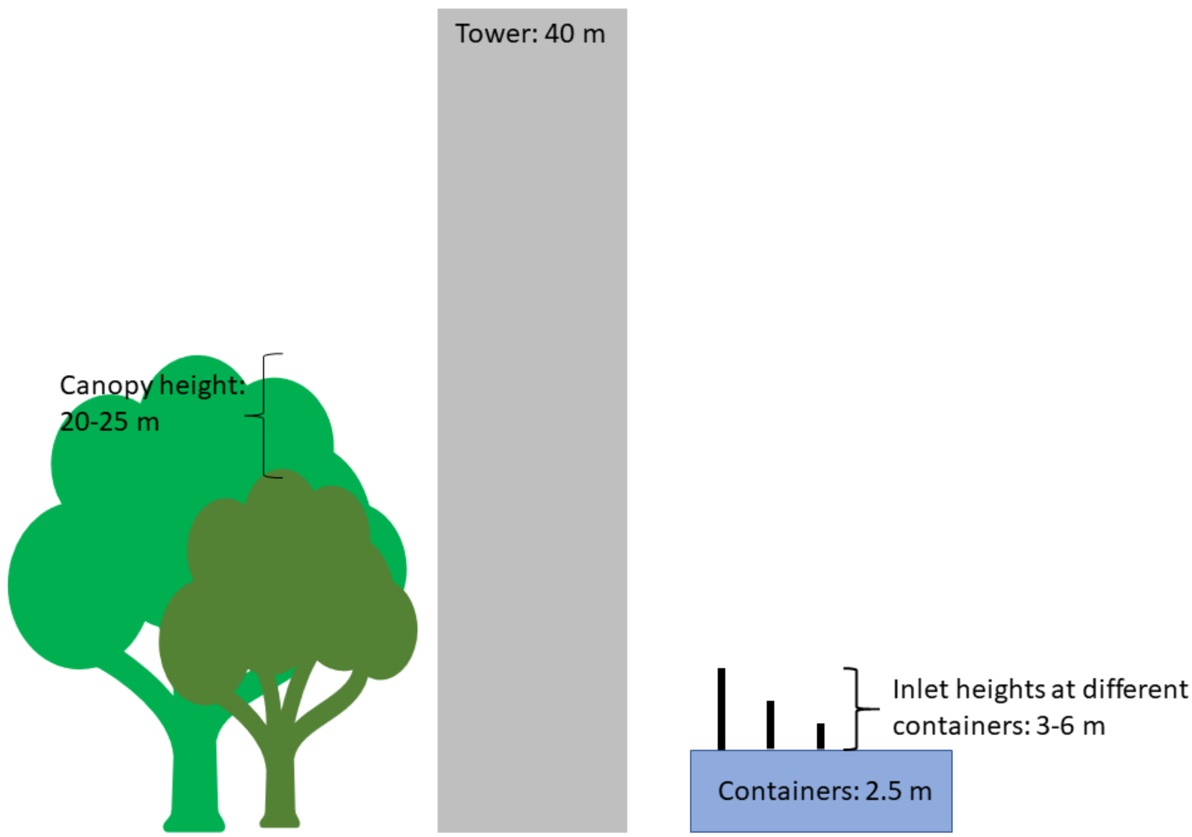


Figure S1b: Side-view of the canopy height, tower height, and inlet heights. Note that the figure is not made to scale.

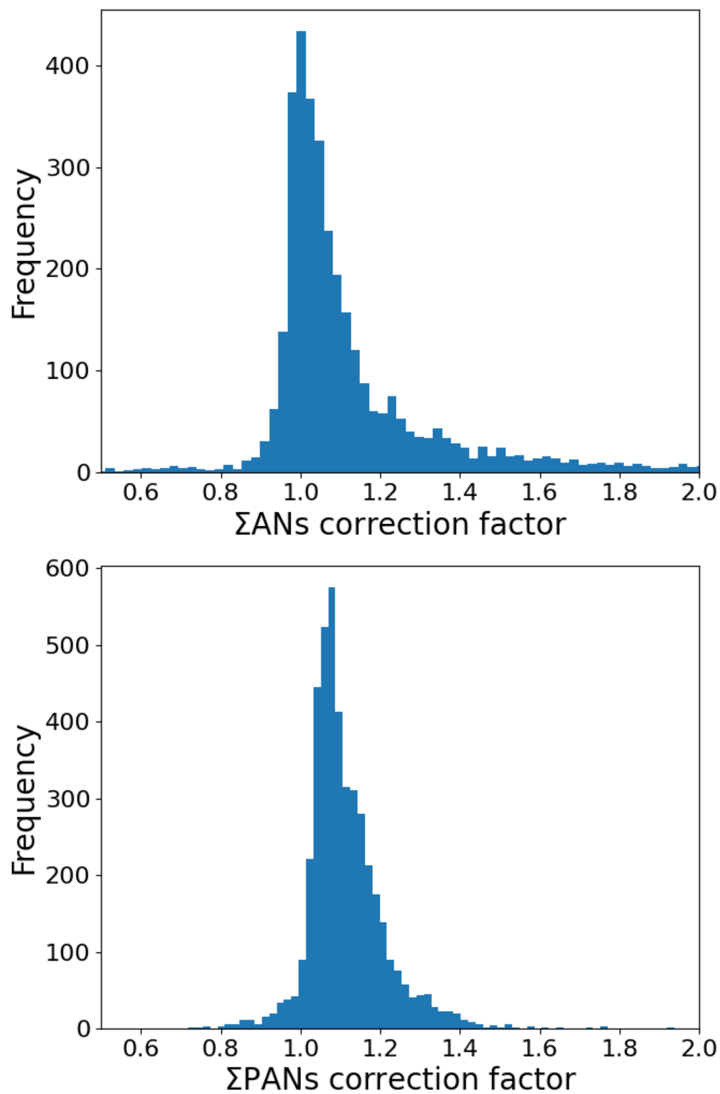


Figure S2: Distribution of correction factors for the ΣANs (top) and ΣPANs (bottom) measurements.

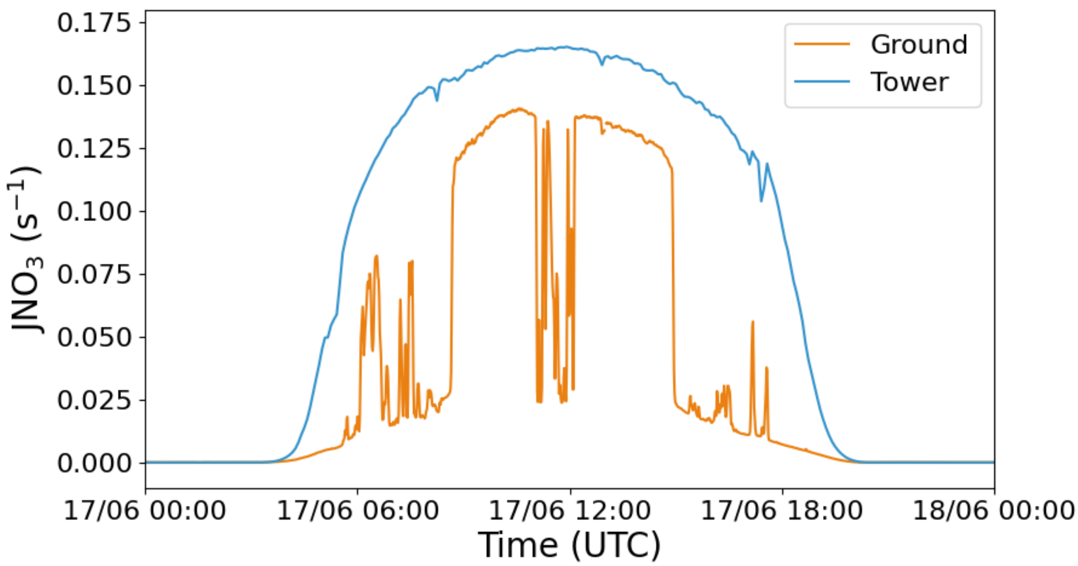


Figure S3: Comparison of JNO_3 measured on top of the MPIC container (ground) and on top of the tower during ACROSS.

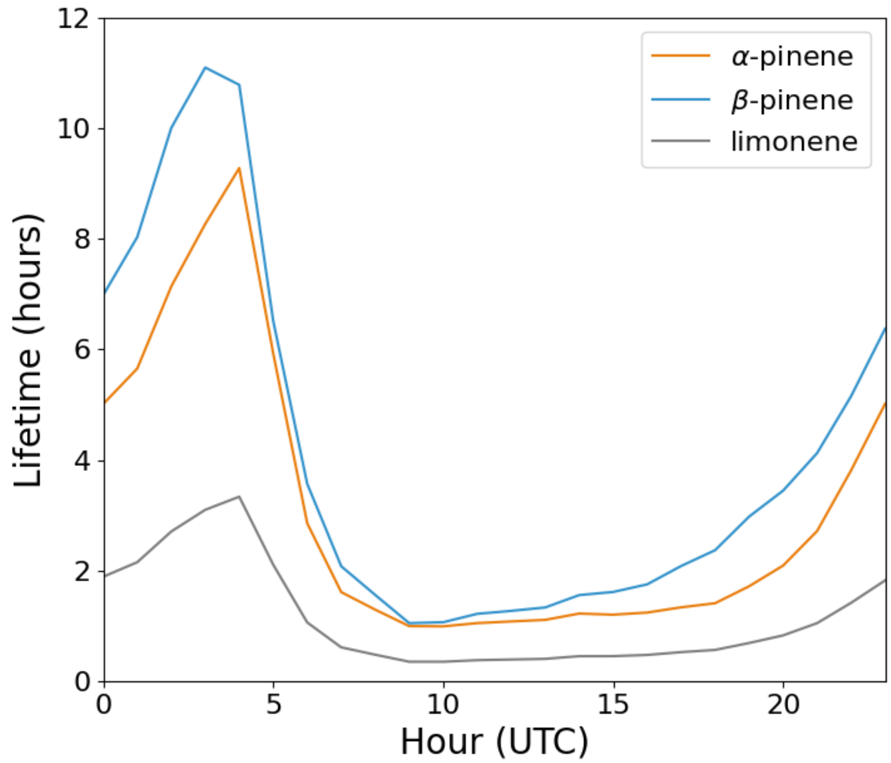


Figure S4: The derived diel profile of the lifetime of α-pinene, β-pinene, and limonene during the ACROSS campaign when taking reactions with OH, O_3, and NO_3 into account using the rate coefficients in Table 1.

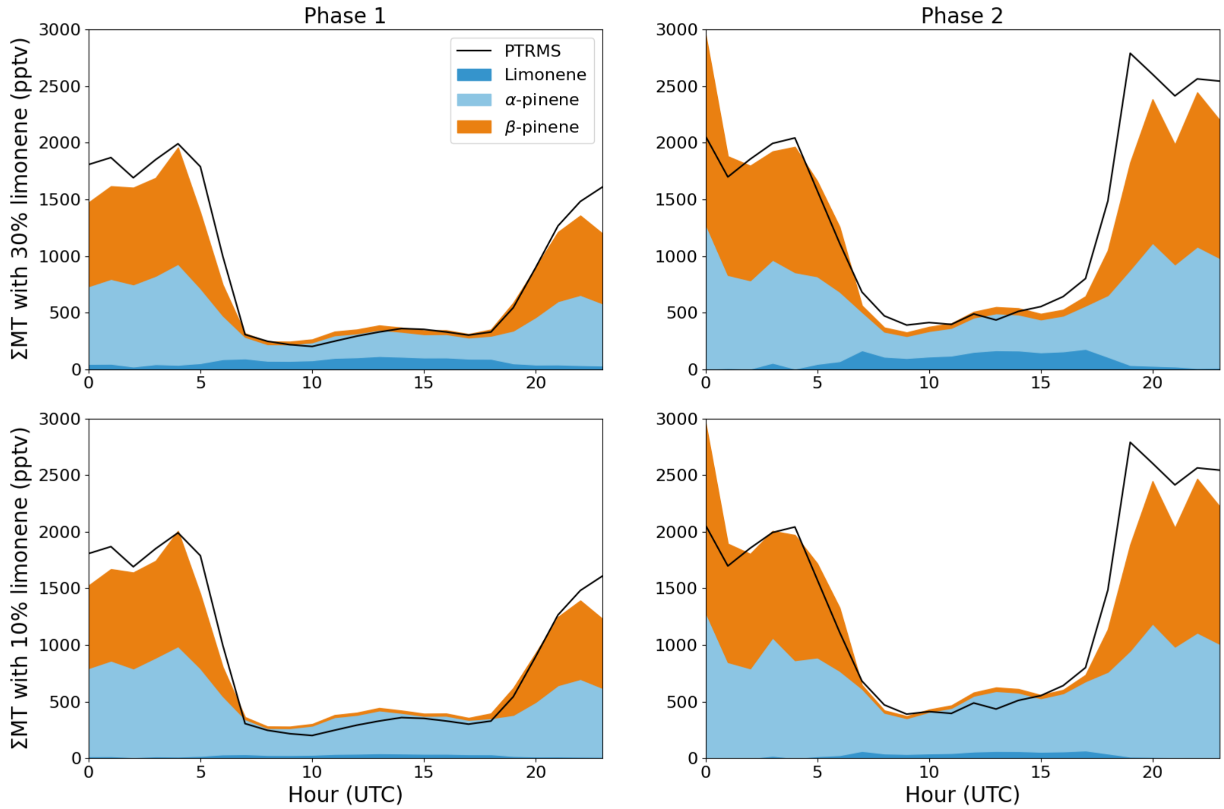


Figure S5: Average diel profiles for the measured total monoterpenes by PTRMS for phase 1 (left) and 2 (right) together with the derived monoterpene mixtures of 10% β-pinene, 60% α-pinene, and 30% limonene (top) and 5% β-pinene, 85% α-pinene, and 10% limonene (bottom) using 57% β-pinene and 43% α-pinene when temperature inversions higher than 1°C is observed.

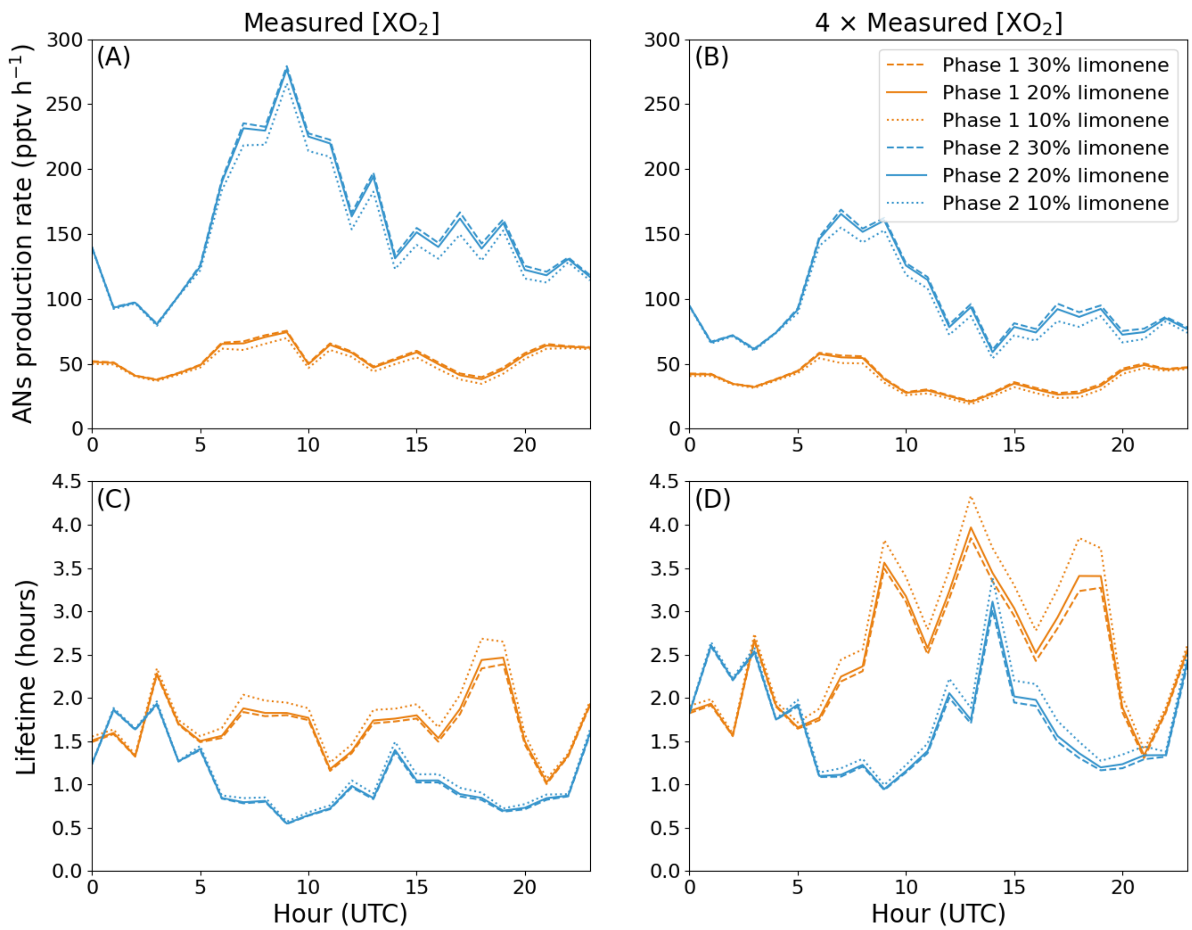


Figure S6: Average diel profiles of the total ANs production rate (top) and lifetime (bottom) for phase 1 (orange) and 2 (blue) for the three different monoterpene mixtures including limonene (dotted, solid, and dashed lines) using the measured $[XO_2]$ (left) and 4 × $[XO_2]$ (right).

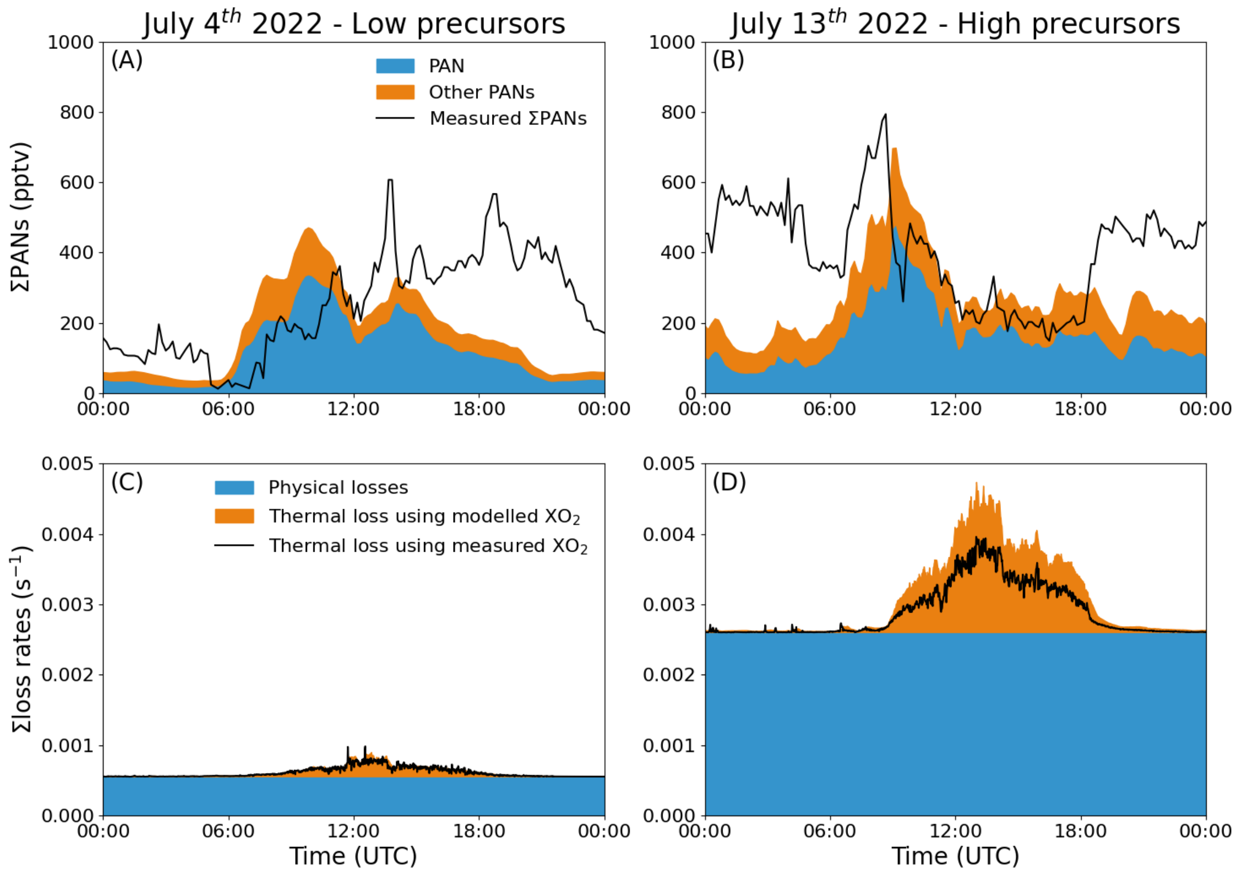


Figure S7: The measured and modelled when optimizing for daytime agreement ∑PANs is plotted for two individual days; one with low precursors (A) and one with high precursors (B). The optimised physical loss for each day is shown in panel C and D together with the thermal decomposition when taking recombination into account using both the measured and modelled mixing ratio of XO_2.

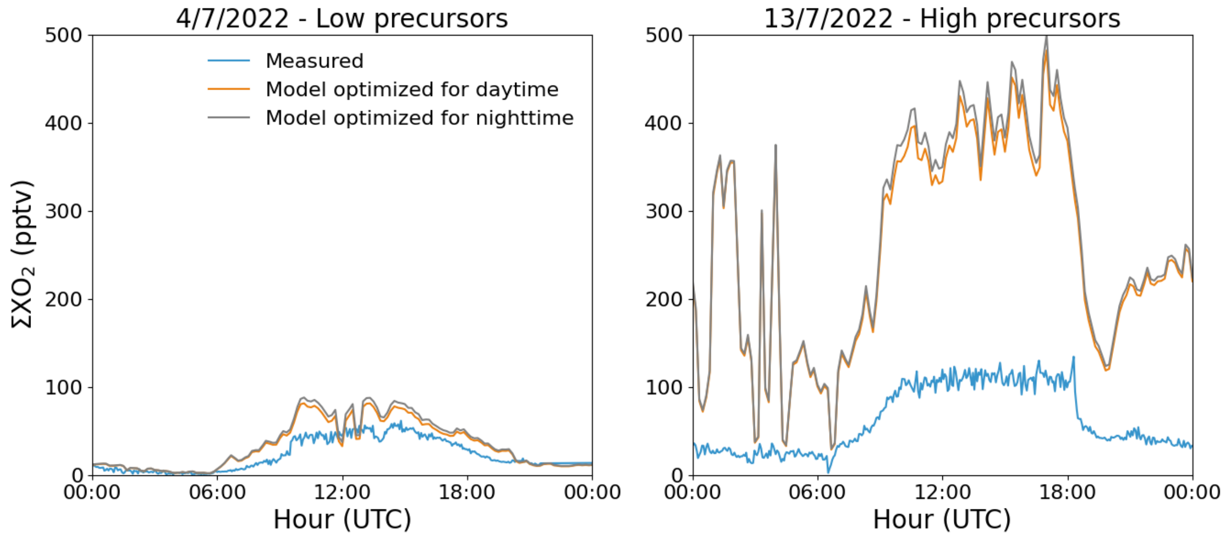


Figure S8: Measured and modelled XO_2 for a low and high precursor (of PANs) day.

References:

Wolfe, G. M., Thornton, J. A., Bouvier-Brown, N. C., Goldstein, A. H., Park, J. H., McKay, M., Matross, D. M., Mao, J., Brune, W. H., LaFranchi, B. W., Browne, E. C., Min, K. E., Wooldridge, P. J., Cohen, R. C., Crounse, J. D., Faloona, I. C., Gilman, J. B., Kuster, W. C., de Gouw, J. A., Huisman, A., and Keutsch, F. N.: The Chemistry of Atmosphere-Forest Exchange (CAFE) Model – Part 2: Application to BEARPEX-2007 observations, Atmos. Chem. Phys., 11, 1269-1294, 10.5194/acp-11-1269-2011, 2011.

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