# Supplement of

# Isothermal evaporation of $\alpha$ -pinene secondary organic aerosol particles formed under low-NO<sub>x</sub> and high-NO<sub>x</sub> conditions

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#### S1.1 T<sub>max</sub> – C\* calibration

We calibrated the relationship between the desorption temperature with the maximum signal (T<sub>max</sub>) and saturation vapor concentration (C\*) by measuring a homologous series of polyethylene glycols (PEGs, PEG 4 - 8) with well characterized saturation vapor pressure (psat) (Krieger et al., 2018; Ylisirniö et al., 2021). For the FIGAERO-CIMS setup used in this study, the  $p_{sat}$  value of an observed molecule can be calculated from the  $T_{max}$  value with the maximum signal as follows:

$$\ln(p_{sat}) = -0.21 \times T_{max} - 0.62 \tag{S1}$$

As non-nitrated organics dominated in all  $\alpha$ -pinene SOA particle samples (Figure S2 and Figure S3), we performed

#### S1.2 Selection of the optimal PMF solution

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independent PMF analysis on the non-nitrated organics and organic nitrates data sets. Such approach enables us to not only better resolve organic nitrates into factors but also explore the compositional similarities between the low-NO<sub>x</sub> and high-NO<sub>x</sub> conditions in terms of the non-nitrated organic compounds. We investigated PMF solutions with up to 15 factors for the data set of non-nitrated organics and up to 10 factors for the data set of organic nitrates, with fpeak values of -0.5, 0, and 0.5. After a thorough inspection of all PMF solutions, the 12-factor solution at fpeak = 0 was chosen for non-nitrated organics data set. 15 For the organic nitrates data set, the eight-factor solution at fpeak = -0.5 was selected. These two selected PMF solutions yielded the most interpretable results. The PMF results and corresponding factor mass spectra for non-nitrated organics are shown in Figure S4 and Figure S5, and those for organic nitrates are presented in Figure S6 and Figure S7.

The quality of PMF solutions was indicated with the goodness-of-fit parameter (Q/Qexp) as a function of number of factors in Figure S8. The unscaled residuals, relative residuals, and scaled residuals of the 10 - 12 factor solutions for the non-nitrated

- 20 organics are depicted in Figure S9, and those of the five - eight factor solutions for the organic nitrates are shown in Figure S10. With a 10-factor PMF solution for the non-nitrated organics data set or a five-factor solution for organic nitrates data set, we already observed relative residuals of less than 5 % for the majority of data and very subtle changes in the  $Q/Q_{exp}$ . However, increasing from 10 to 12 factors for the non-nitrated organics improved the reconstruction of peak shapes for many ions and also identified one more meaningful sample factor improving the interpretability of the aqueous phase processes. In the same
- 25 way, increasing from five to eight factors for the organic nitrates resulted in a better reconstruction of peak shapes for many ions and also finding two more meaningful sample factors which captured different types of organic nitrates in the samples. Further increasing the number of factors for non-nitrated organics and organic nitrates resulted in either over-splitting an existing sample factor into two or introducing more background factors. Thus, 12 factors were chosen for the non-nitrated organics data set, and eight factors for the organic nitrates one.

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	Low-NO <sub>x</sub>	High-NO <sub>x</sub>	
[VOC] <sub>OFR</sub> (ppb) <sup>a</sup>	$254\pm11$	11 296 ± 14	
$[N_2O]_{OFR}(\%)$	N/A	$1.82\pm0.10$	
[O <sub>3</sub> ] <sub>OFR</sub> (ppm) <sup>b</sup>	$9.76\pm0.31$	$6.85\pm0.36$	
T <sub>OFR</sub> (°C)	$24.6\pm0.9$	$28.14\pm0.91$	
RH <sub>OFR</sub> (%)	$44.4 \pm 2.3$	$38.74\pm2.63$	
Nominal residence time (s)	160	160	
effective OH exposure (10 <sup>11</sup> molec cm <sup>-3</sup> ) <sup>c</sup>	$2.6\pm0.3$	$1.72 \pm 0.07$	
$\frac{[RO_2] + [NO]}{[RO_2] + [HO_2]}$	N/A	$1.30\pm0.18$	
oxygen-to-carbon (O:C) <sup>d</sup>	$0.77\pm0.03$	$0.74\pm0.01$	
oxidation state $(OS_c)^d$	$0.05\pm0.04$	$0.02\pm0.02$	

Table S1. Summary of experimental conditions and results of α-pinene SOA generation

<sup>a</sup> Mixing ratio of  $\alpha$ -pinene was corrected with the dilution of O<sub>3</sub>-contained flow but without the loss due to pure ozonolysis at the inlet. <sup>b</sup> O<sub>3</sub> was measured at the OFR outlet after 254-nm UV lamps were switched on but without the addition of  $\alpha$ -pinene and N<sub>2</sub>O. <sup>c</sup> OH exposure was calculated with the OFR model (Peng et al., 2015; Peng et al., 2016) by taking the external OH reactivity into account. <sup>d</sup> The values of the oxygen to carbon ratio (O:C) and the oxidation state (OS<sub>c</sub>) were derived from the HR-ToF-AMS measurement data of monodisperse SOA particles which represents the initial particle population used for isothermal evaporation measurements.

Table S2. Ranges of parameters for scaling the normalized sum thermograms of RTC stages

SOA System	Fresh Condition	RTC	VFR <sub>avg,RTC</sub>	a	ß
		Condition	$VFR_{avg, fresh}$	u <sub>Mw</sub>	Pρorg
Low-NO <sub>x</sub>	Dry, fresh	Dry, RTC	[0.85, 0.91]	[0.98, 1.02]	[1, 1]
	High RH, fresh	High RH, RTC	[0.57, 0.73]	[1.02, 1.04]	[1.01, 1.01]
High-NO <sub>x</sub>	Dry, fresh	Dry, RTC	[0.89, 0.93]	[0.99, 1]	[1, 1]
	High RH, fresh	High RH, RTC	[0.67, 0.82]	[0.97, 1.09]	[0.99, 0.99]

Table S3. Ranges of parameters for calculating the net change ratio (NCR) for each PMF sample factor

SOA System	Ref. Condition	Condition j	VFR <sub>avg,j</sub> VFR <sub>avg,ref</sub>	$\alpha_{Mw}$	$\beta_{\rho_{org}}$
Low-NO <sub>x</sub>		Dry, RTC	[0.85, 0.91]	[0.98, 1.02]	[1, 1]
	Dry, fresh	High RH, fresh	[0.77, 1.05]	[1.01, 1.10]	[0.99, 0.99]
		High RH, RTC	[0.56, 0.60]	[1.03, 1.13]	[1, 1]
High-NO <sub>x</sub>		Dry, RTC	[0.89, 0.93]	[0.99, 1]	[1, 1]
	Dry, fresh	High RH, fresh	[0.74, 0.95]	[0.97, 0.99]	[0.99, 0.99]
		High RH, RTC	[0.61, 0.64]	[0.96, 1.06]	[0.98, 0.99]



**Figure S1**. Sum thermograms (STG) (a – d) and median desorption temperature ( $T_{50}$ , diamonds) (e) for the low-NO<sub>x</sub> case under dry (RH < 7 %) and high RH (80 % RH) conditions. Non-nitrated organics and organic nitrates are indicated by  $C_xH_yO_z$ and  $C_xH_yN_{1,2}O_z$ , respectively. On the panels (a – d), the solid black lines indicate the total signals of STGs with the green and yellow areas marking the contributions of  $C_xH_yO_z$  and  $C_xH_yN_{1,2}O_z$  to the STGs, respectively. The gray-striped areas represent the differences in STGs between fresh and RTC stages. The color bands on the abscissa indicate volatility classes. Note that we presented the STGs of RTC stages after accounting for changes in the average VFR (VFR<sub>avg</sub>) between fresh and RTC stages during the FIGAERO sample time. As the signals of the organic nitrates were too low to derive reliable  $T_{50}$  values, we only show the values for the total signal in panel (e).

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Figure S2. Integrated mass spectra for  $\alpha$ -pinene SOA particles formed under low-NO<sub>x</sub> conditions. Non-nitrated organics and organic nitrates are colored with green and yellow, respectively.



5 **Figure S3**. Integrated mass spectra for α-pinene SOA particles formed under high-NO<sub>x</sub> conditions. Non-nitrated organics and organic nitrates are colored with green and yellow, respectively.



**Figure S4**. Sample (solid lines) and back (dashed lines) factors from a 12-factor solution of non-nitrated organics in  $\alpha$ -pinene SOA particles under low-NO<sub>x</sub> and high-NO<sub>x</sub> conditions. In both columns, the desorption temperature ranges of different volatility classes are shown with color bands on the abscissa.



Figure S5. Normalized factor mass spectrums from a 12-factor solution of non-nitrated organics in α-pinene SOA particles.



**Figure S6**. Sample (solid lines) and back (dashed lines) factors from an eight-factor solution of organic nitrates in  $\alpha$ -pinene SOA particles under low-NO<sub>x</sub> and high-NO<sub>x</sub> conditions. In both columns, the ranges of desorption temperatures of different volatility classes are shown with color bands on the abscissa.



Figure S7. Normalized factor mass spectrums from an eight-factor solution of organic nitrates in α-pinene SOA particles.



**Figure S8**.  $Q/Q_{exp}$  values for PMF solutions for non-nitrated organics (red) and organic nitrates (gray) in  $\alpha$ -pinene SOA particle data sets. Solutions chosen in the analysis are highlighted with orange circles.



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**Figure S9**. Residuals, relative residuals, and scaled residuals for the 10 - 12 factor solutions for the non-nitrated organics in  $\alpha$ -pinene SOA particles. In the panel for the low-NO<sub>x</sub> condition (gray background), the order is: dry, fresh (0 – 200); dry, RTC (200 – 400); high RH, fresh (400 – 600); high RH, RTC (600 – 800); DMA blank 1 (800 – 1000); snap blank 25 (1000 – 1200). In the panel for the high-NO<sub>x</sub> condition (yellow background), the order is: dry, fresh (1200 – 1400); dry, RTC (1400 – 1600); high RH, fresh (1600 – 1800); high RH, RTC (1800 – 2000); DMA blank 2 (2000 – 2200); snap blank 37 (2200 – 2400); snap blank 40 (2400 – 2600).



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**Figure S10**. Residuals, relative residuals, and scaled residuals for the five – eight factor solutions for the organic nitrates in  $\alpha$ -pinene SOA particles. In the panel for the low-NO<sub>x</sub> condition (gray background), the order is: dry, fresh (0 – 200); dry, RTC (200 – 400); high RH, fresh (400 – 600); high RH, RTC (600 – 800); DMA blank 1 (800 – 1000); snap blank 25 (1000 – 1200). In the panel for the high-NO<sub>x</sub> condition (yellow background), the order is: dry, fresh (1200 – 1400); dry, RTC (1400 – 1600); high RH, fresh (1600 – 1800); high RH, RTC (1800 – 2000); DMA blank 2 (2000 – 2200); snap blank 37 (2200 – 2400); snap blank 40 (2400 – 2600).