Novel Aerosol Flow Reactor to Study Secondary Organic Aerosol

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Supplementary information

1. Instrument calibration

10   The SIFT-MS was calibrated daily using the manufacturer certified gas standard in accordance with the manufacturer instructions. The O_3 analyser was verified using a 49i-PS dual-cell photometer prior to use. This verification has been adopted by the National Institute of Standards and Technology as the principle technology for the international ozone standard. The 49i-PS photometer is annually calibrated using a certified source. The NO_x analyser was calibrated using a 1 ppm NO in N_2 standard diluted with zero air (PAG 003 Ecophysics, Switzerland) through a Multigas calibrator (Environics S6100, CT, USA).

15   The NO_2 conversion efficiency was calibrated *via* internal gas phase titration with ozone. The 1 ppm NO standard is provided by the National Physics Laboratory, the Global Atmospheric Watch (GAW) accredited Central Calibration Laboratory for NO_x and is referenced to the GAW global scale. The ELPI flow rate and particle size distribution were calibrated by the manufacturer prior to the start of the project. The ELPI electrometer was blank corrected before each experiment, as per manufacturer instructions.

Table S1 - Number of compounds identified in the ELPI SOA samples using UPLC-UHRMS

Exp. number[a]	Negative ionisation mode	Positive ionisation mode	Total number of compounds identified[b]
2	33	67	100
3	64	114	178
4	79	122	201
5	61	104	165
8	179	363	542
9	195	488	683
10	220	526	746
11	225	342	567
12	232	406	638
13	239	519	758
17	156	205	361
18	140	211	351
19	133	226	359
20	89	196	285
21	84	256	340
22	99	206	305
23	74	212	286
24	74	207	281
26	143	595	738
27	165	601	766
28	245	665	910
29	157	623	780
30	152	637	789
31	198	677	875
32	166	723	889
34	88	53	141
36	80	44	124
38	116	49	165

[a] = See Table 1 for experimental descriptions. [b] = The sum of the number of compounds identified in positive and negative ionisation mode.

Table S2 - Molecular formulae, retention and collection times of the standards used to quantify components in the α-pinene SOA samples generated from the experiments shown in Table 1.

Compound Number	Ionisation mode	UPLC-UHRMS t_R (mins)	MW (g mol^{-1})	Compound MF	DBE	MF error (ppm)	HPLC-ITMS t_R (mins)	Collection Time (mins)
1	+	1.27	204.14	$C_{10}H_{20}O_4$	1	-0.13	5.0	4.1 – 5.6
2	+	2.98	156.08	$C_8H_{12}O_3$	3	-0.42	11.9	10.9 – 12.5
3	+	6.42	170.09	$C_9H_{14}O_3$	3	0.13	27.3	26.7 – 27.8
4	-	7.41	216.10	$C_{10}H_{16}O_5$	3	0.67	32.3	31.3 – 33.0
5	-	6.37	186.20	$C_9H_{14}O_4$	3	0.62	29.9	29.1 – 30.4
6	+	9.72	230.15	$C_{12}H_{22}O_4$	2	-0.12	40.6	39.9 – 41.6
7	+	10.07	170.13	$C_{10}H_{18}O_2$	2	-0.001	45.1	44.6 – 45.6
8	+	11.56	186.12	$C_{10}H_{18}O_3$	2	-0.04	52.8	52.5 – 53.3
9	+	12.96	186.12	$C_{10}H_{18}O_3$	2	-0.03	59.0	58.7 – 59.7
10	+	16.55	308.23	$C_{19}H_{32}O_3$	3	-0.46	73.8	73.5 – 74.4
Terebic acid[*]	-	2.29	158.15	$C_7H_{10}O_4$	3	0.56	-	-
Terpenylic acid[*]	-	3.08	172.18	$C_8H_{12}O_4$	3	0.63	-	-
10-hydroxypinonic acid[*]	-	4.47	200.23	$C_{10}H_{16}O_4$	3	0.44	-	-
Norpinic acid[*]	-	4.99	172.18	$C_8H_{12}O_4$	3	0.46	-	-
Pinic acid[**]	-	6.37	186.20	$C_9H_{14}O_4$	3	0.47	-	-
Cis-pinonic acid[**]	+	8.40	184.23	$C_{10}H_{16}O_3$	3	0.07	-	-

[*] = Standard from Finessi et al. (2014). [**] = Authentic standard used.
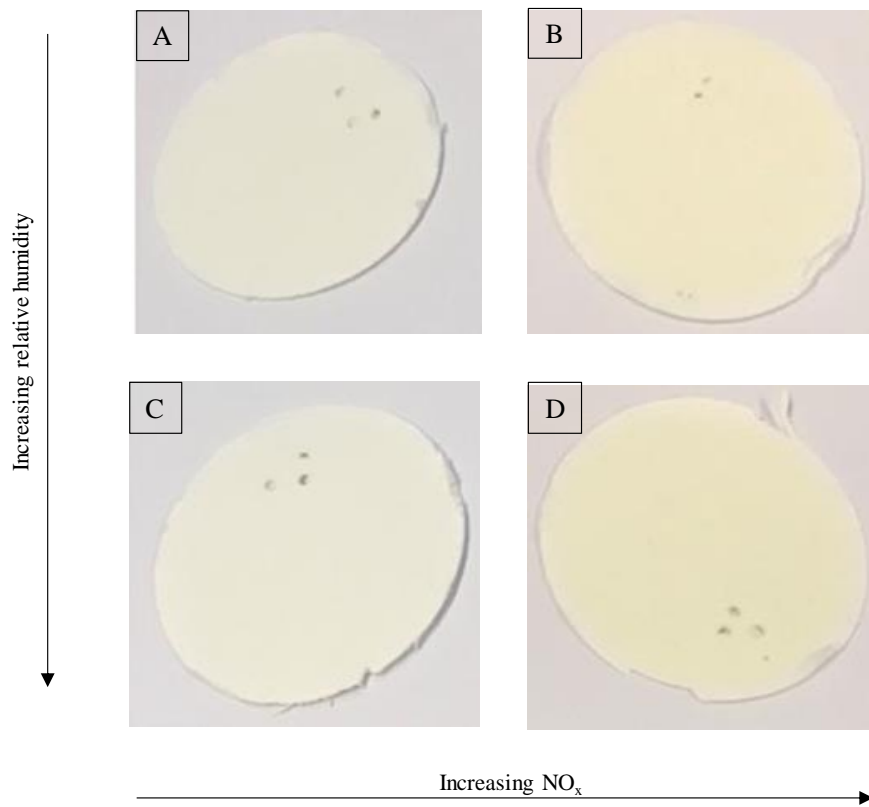
Figure S1 – SOA filters collected from the photo-oxidation of α-pinene at 20% (A and B) and 55% (C and D) relative humidity, displaying increasing light absorbing properties with increasing NO_x (shown as an example). A = no NO_x (exp. 3, see Table 1). B = VOC/NO_x ratio of 3 (exp. 13). C = no NO_x (exp. 5). D = VOC/NO_x ratio of 3 (exp. 10).
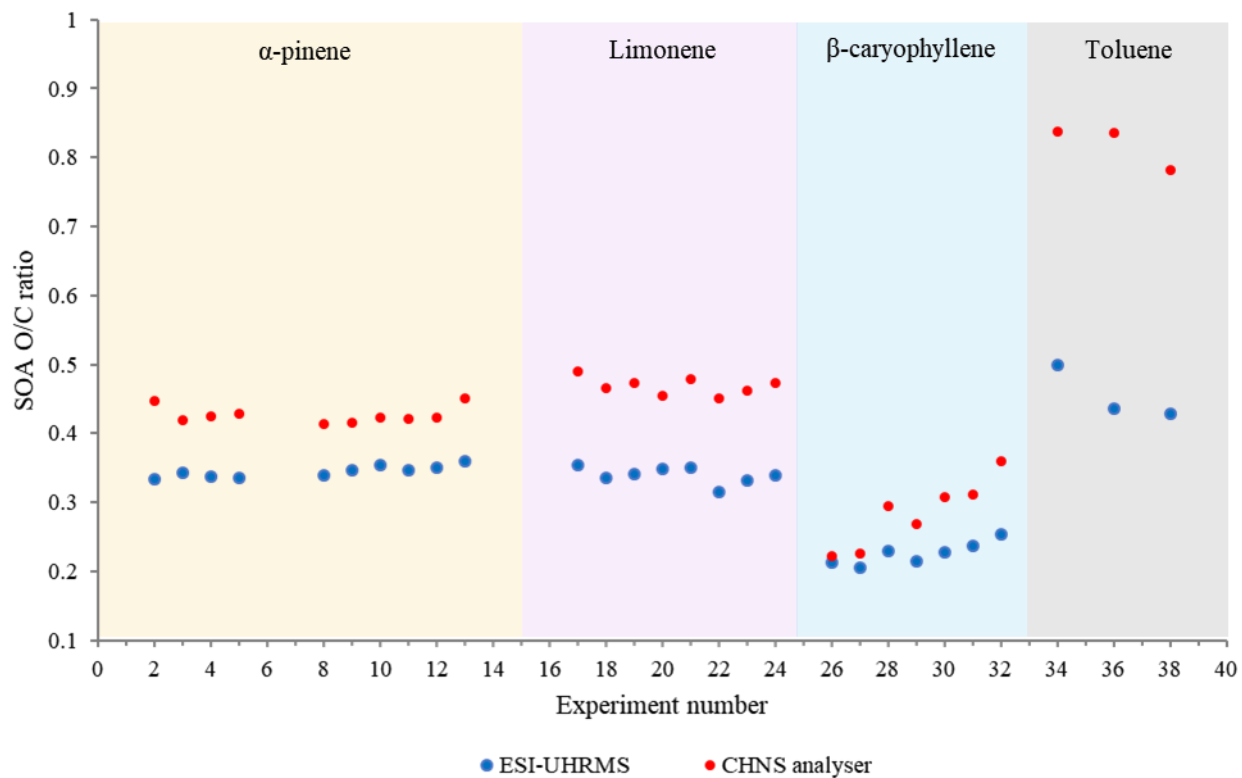
Figure S2 – Oxygen-to-carbon (O/C) ratio of the generated SOA samples determined from UHRMS and the CHNS elemental analyser. Shaded areas display the SOA samples formed from the photo-oxidation of α-pinene, limonene, β-caryophyllene and toluene. Experiment numbers correspond to Table 1.
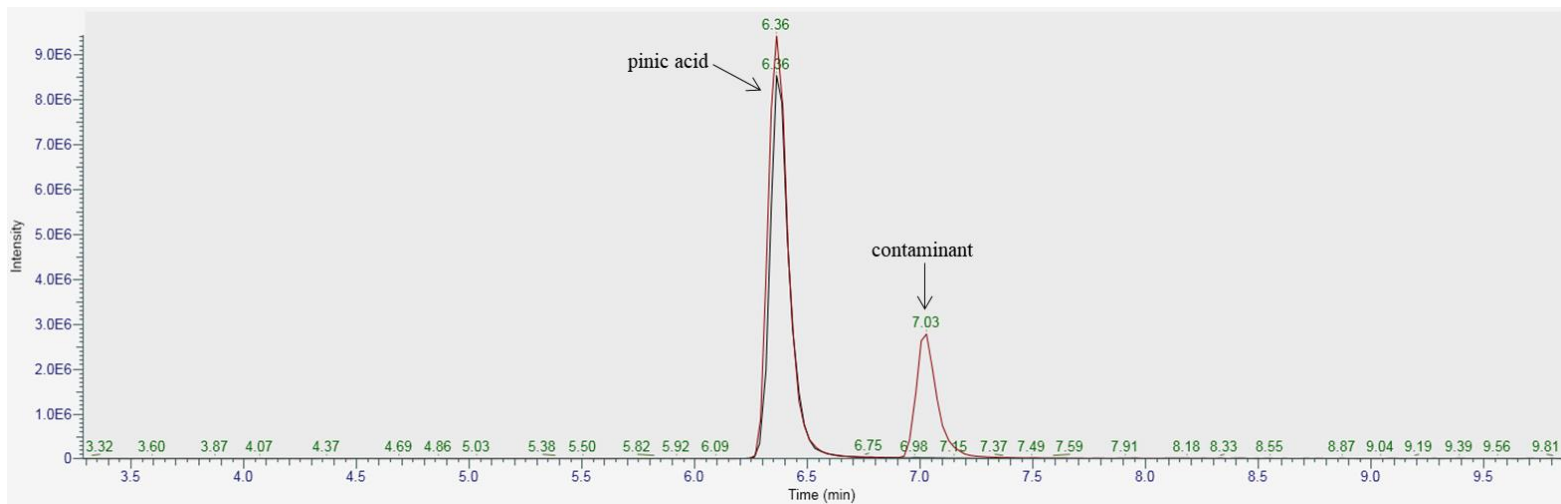
Figure S3 – A comparison of authentic (red) and generated (black, compound 5, see Table S1) standard of pinic acid at concentration of 1 ppm using UPLC-UHRMS.
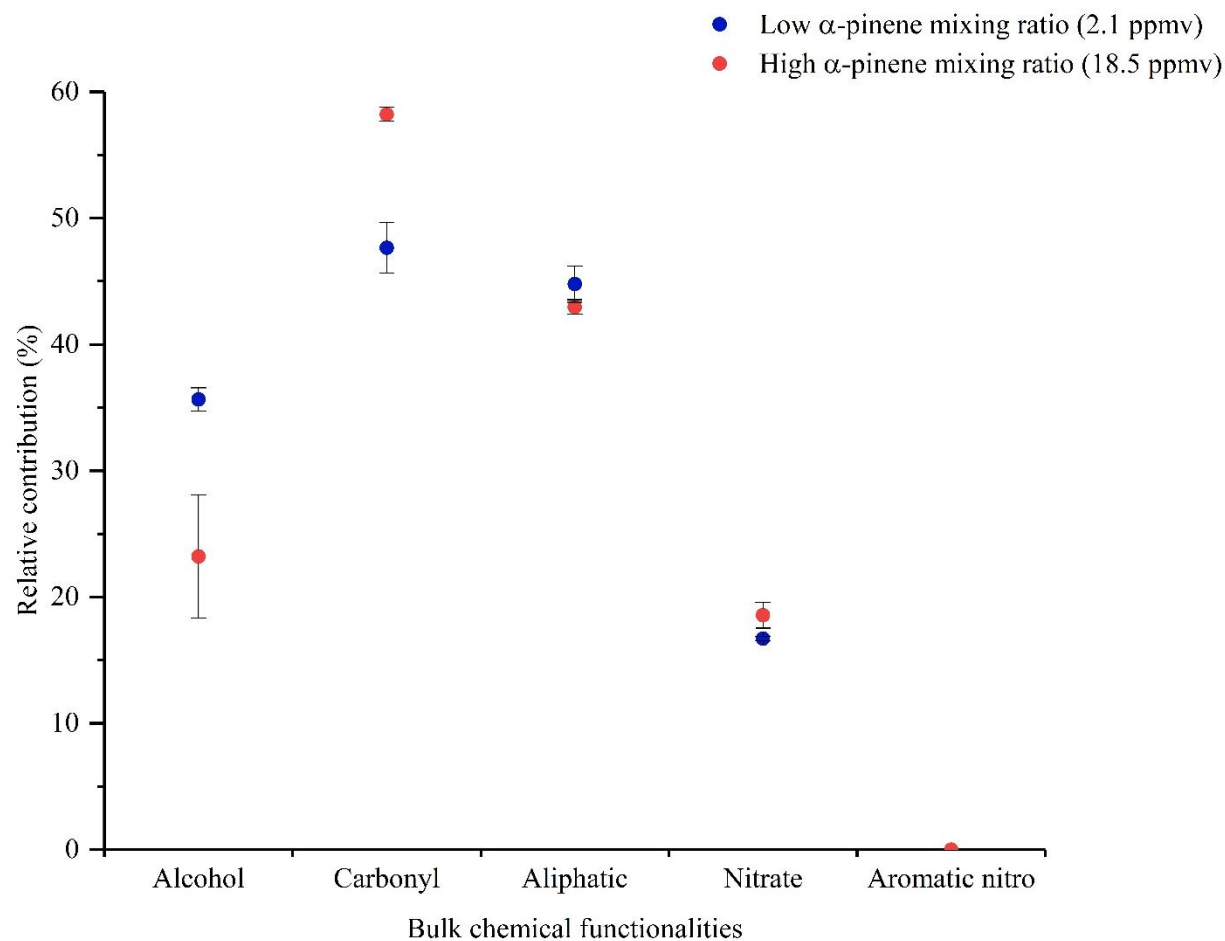
Figure S4 – A comparison of the bulk SOA chemical functionalities in two SOA samples formed from the photo-oxidation of α-pinene, with a VOC mixing ratio of 18.5 ppmv (exp. 10, see Table 1) and 2.1 ppmv (exp. 14). Both experiments were performed at a VOC/NO$_x$ ratio of 3 and a relative humidity of 55%. Data obtained from the ATR-FTIR spectrometer. The peak heights of each chemical functionality have been normalised to the total peak height of all integrated functionalities in each SOA sample, allowing direct comparison between samples.