Supporting Information Section for "Photolytic processing of secondary organic aerosols dissolved in cloud droplets"

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Figure S1. Representative ESI (+) mass spectra of SOA collected via PILS extraction for the four initial precursor concentrations studied: (a) 0.05 ppm; (b) 0.10 ppm; (c) 0.5 ppm; (d) 1.0 ppm of limonene and O_3. Trimer and tetramer species were not visible in the 0.05 ppm spectrum, and tetramer species were not visible in the 0.1 ppm spectrum because these peaks fell below the signal-to-noise threshold used in the analysis.

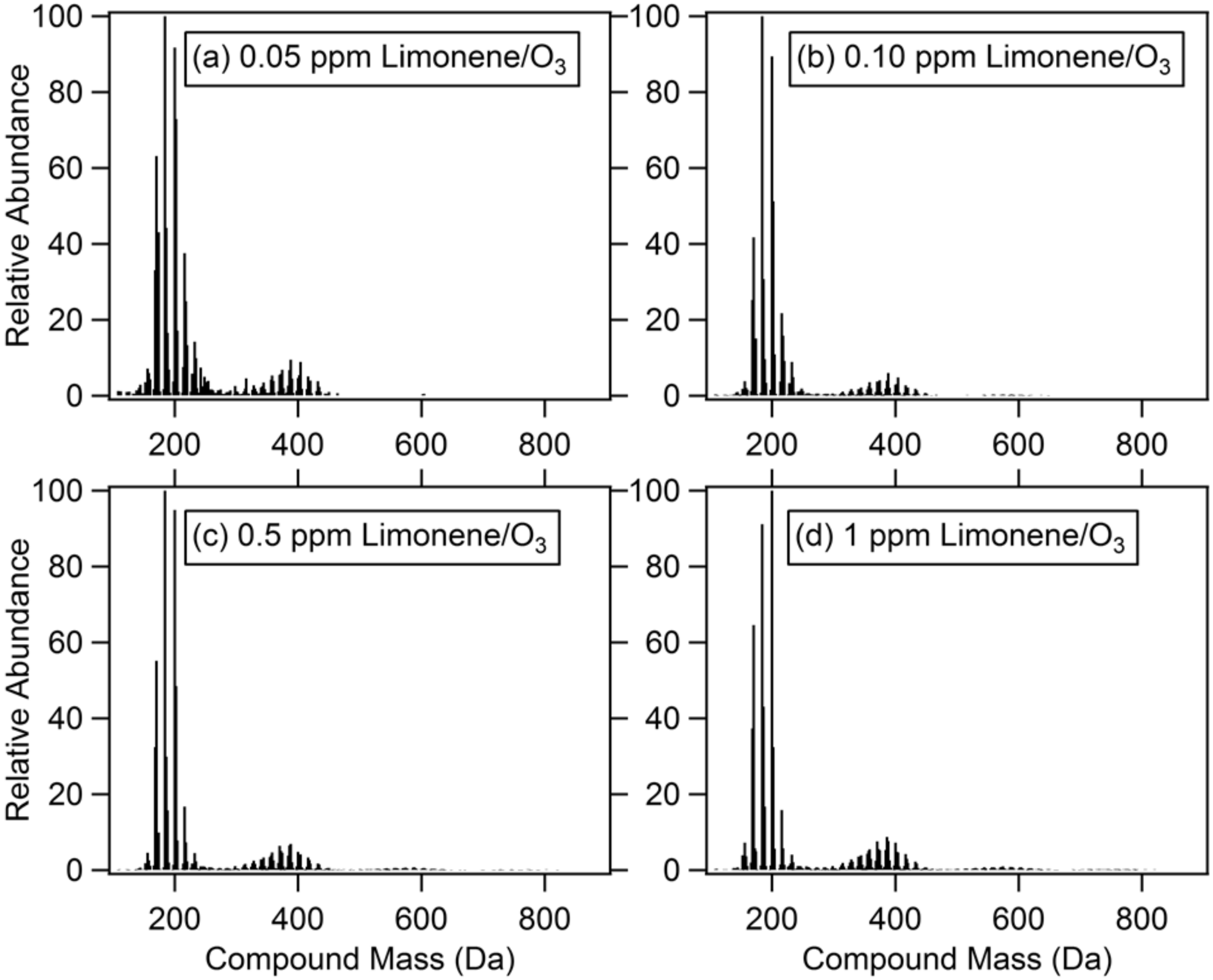

Figure S2. Representative ESI (-) mass spectra of SOA collected via PILS extraction for the four initial precursor concentrations studied: (a) 0.05 ppm; (b) 0.10 ppm; (c) 0.5 ppm; (d) 1.0 ppm of limonene and O_3. Tetramer species were not visible in the 0.05 and 0.10 ppm spectra because these peaks fell below the signal-to-noise threshold used in the analysis.

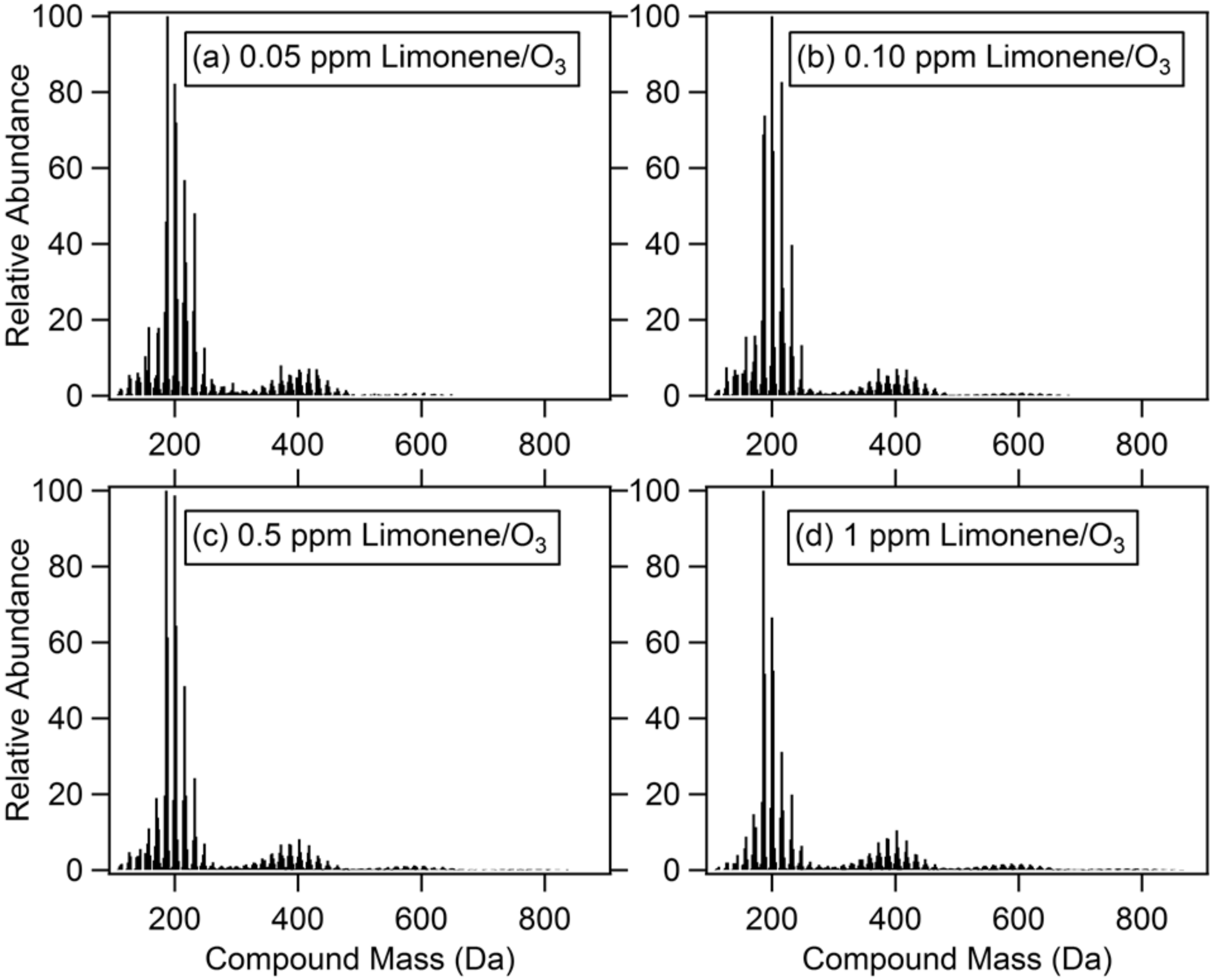

Figure S3. Representative ESI (+) mass spectra of 1 ppm limonene SOA collected via PILS: (a) before photolysis; (b) after 2 hours of photolysis; (c) after 24 hours of photolysis. All peaks are normalized to the most abundant peak in each mass spectrum. The observed m/z values have been converted to molecular weights of the neutral compounds. The corresponding ESI (-) mass spectra are shown in Fig. 2 of the manuscript.

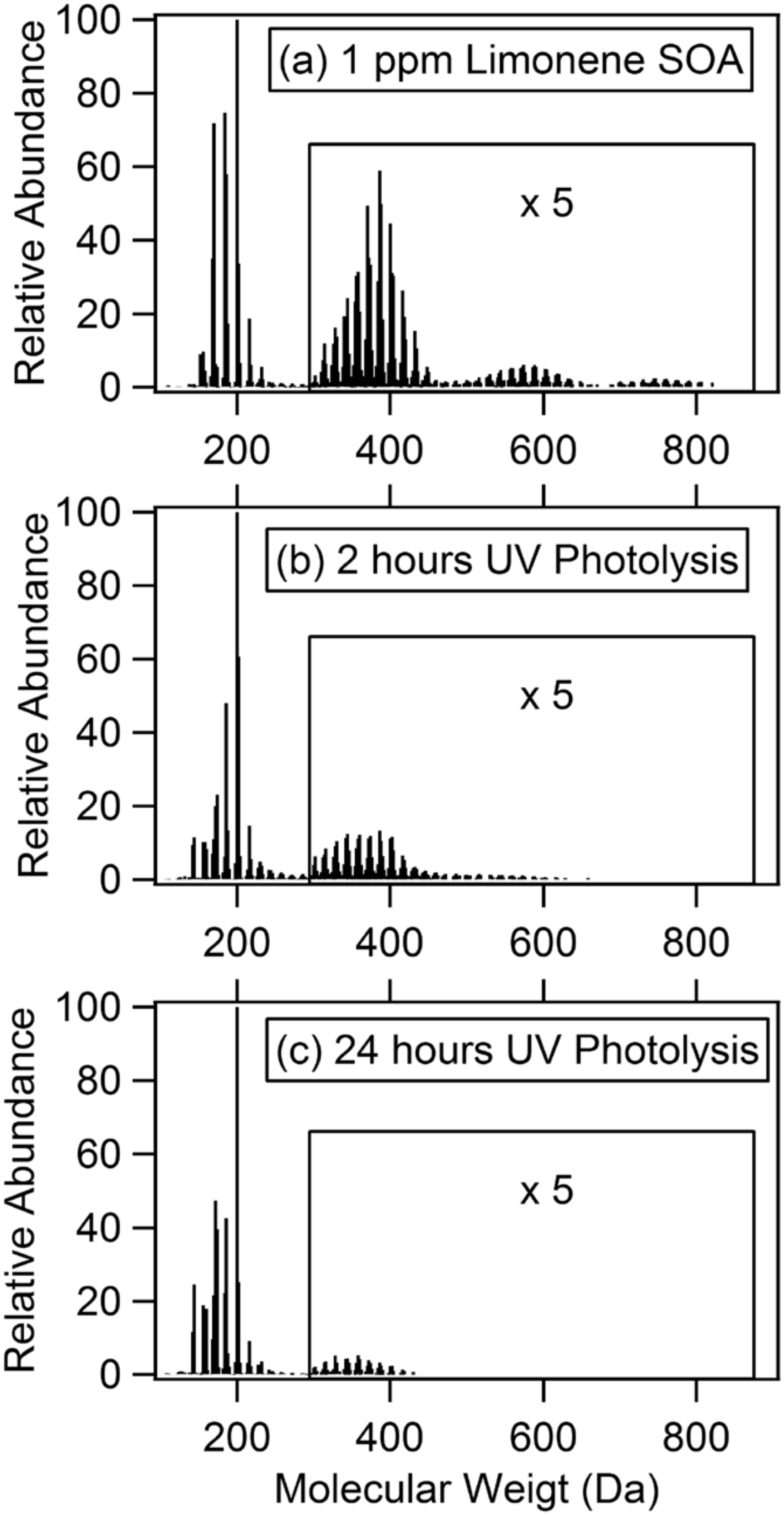

Table S1. Intensity weighted average values of O/C, H/C, DBE, OM:OC, and number of carbons per molecule calculated from mass spectra generated for each initial concentration of limonene and O_3 . The top and bottom sections of the table were calculated from ESI (-) and (+) mass spectra, respectively.

SOA Precursor Concentration (ppm)		0.05	0.10	0.50	1.00
Percent of Peaks Assigned		30	48	62	58
Negative ESI Mode	⟨O/C⟩ Before UV	0.53	0.52	0.49	0.50
	⟨O/C⟩ 2 hr UV	0.54	0.53	0.54	0.55
	⟨O/C⟩ 24 hr UV	-	-	0.57	0.57
	⟨H/C⟩ Before UV	1.55	1.54	1.55	1.55
	⟨H/C⟩ 2 hr UV	1.56	1.55	1.55	1.54
	⟨H/C⟩ 24 hr UV	-	-	1.53	1.53
	⟨DBE⟩ Before UV	3.54	3.56	3.85	4.10
	⟨DBE⟩ 2 hr UV	3.34	3.22	3.37	3.73
	⟨DBE⟩ 24 hr UV	-	-	3.23	3.27
	⟨OM:OC⟩ Before UV	1.83	1.80	1.78	1.79
	⟨OM:OC⟩ 2 hr UV	1.83	1.83	1.84	1.85
	⟨OM:OC⟩ 24 hr UV	-	-	1.88	1.88
	⟨#C⟩ Before UV	11.41	11.35	12.89	14.08
	⟨#C⟩ 2 hr UV	10.75	9.89	10.63	11.93
	⟨#C⟩ 24 hr UV	-	-	9.51	9.69
SOA Precursor Concentration (ppm)		0.05	0.10	0.50	1.00
Percent of Peaks Assigned		19	22	22	21
Positive ESI Mode	⟨O/C⟩ Before UV	0.42	0.41	0.39	0.39
	⟨O/C⟩ 2 hr UV	0.40	0.42	0.43	0.44
	⟨O/C⟩ 24 hr UV	-	-	0.43	0.45
	⟨H/C⟩ Before UV	1.58	1.60	1.59	1.59
	⟨H/C⟩ 2 hr UV	1.57	1.60	1.61	1.59
	⟨H/C⟩ 24 hr UV	-	-	1.55	1.54
	⟨DBE⟩ Before UV	3.45	3.31	3.69	3.80
	⟨DBE⟩ 2 hr UV	3.60	3.04	3.11	3.35
	⟨DBE⟩ 24 hr UV	-	-	3.26	3.15
	⟨OM:OC⟩ Before UV	1.67	1.66	1.64	1.64
	⟨OM:OC⟩ 2 hr UV	1.66	1.68	1.70	1.71
	⟨OM:OC⟩ 24 hr UV	-	-	1.69	1.73
	⟨#C⟩ Before UV	11.53	11.42	12.94	13.57
	⟨#C⟩ 2 hr UV	10.57	10.58	10.62	11.23
	⟨#C⟩ 24 hr UV	-	-	9.93	9.31

Table S2. Effect of concentration on average values calculated from limonene SOA mass spectra. The data was obtained in a separate set of experiments. SOA was extracted into a stock solution and diluted to a different dilution level. The approximate concentration was estimated from SMPS data, assuming a molecular weight of 200 g mol^{-1} and a density of 1.2 g cm^{-3}. Data was collected only in the ESI (+) mode.

	Dilution Factor (~ Concentration)	⟨O/C⟩	⟨H/C⟩	⟨DBE⟩	⟨OM:OC⟩	⟨#C⟩
Positive ESI Mode	0.0001 ($1.2 * 10^{-5}$ M)	0.43	1.61	4.35	1.70	16.8
	0.001 ($1.2 * 10^{-4}$ M)	0.43	1.57	5.52	1.70	21.0
	0.1 ($1.2 * 10^{-3}$ M)	0.44	1.58	6.02	1.71	23.9
	1 ($1.2 * 10^{-2}$ M)	0.43	1.58	6.62	1.71	27.1

Table S3. Effect of limonene/O_3 mixing ratios on estimated percent fractions of carbonyls and carboxyls in the limonene SOA extract. The ion current was subdivided by compounds known to contain carbonyl, carboxyl, both carbonyl and carboxyl, or neither group. Only compounds with MW < 500 g/mol were included in the analysis. The top and bottom sections of the table were calculated from ESI (-) and (+) mass spectra, respectively.

		Carbonyl	Carboxyl	Both	Other	Total ion Signal
Negative ESI Mode	0.05 ppm	4.31	13.41	65.44	16.84	11653
	0.1 ppm	4.24	11.22	69.97	14.56	19407
	0.5 ppm	5.97	9.29	72.83	11.91	28154
	1 ppm	6.19	8.24	74.01	11.57	28928
		Carbonyl	Carboxyl	Both	Other	Total Ion Signal
Positive ESI Mode	0.05 ppm	8.43	21.01	51.73	18.83	6125
	0.1 ppm	5.86	22.06	64.56	7.51	18623
	0.5 ppm	7.35	16.67	66.55	9.44	29316
	1 ppm	8.09	13.88	69.31	8.73	32910

Table S4. Effect of photolysis on estimated fraction of carbonyls and carboxyls in the limonene SOA extract for each of the concentrations studied. Percent ion current was calculated from limonene SOA before photolysis, after 2 hours of photolysis, and after 24 hours of photolysis (only in the case of 0.5 ppm samples). The ion current was subdivided by compounds found to contain carbonyl, carboxyl, both carbonyl and carboxyl, or neither group. Only compounds with MW < 500 amu were included in the analysis. The top and bottom sections of the table were calculated from ESI (-) and (+) mass spectra, respectively. The loss of carbonyls to photolysis is less apparent at lower limonene/O_3 concentrations (their relative amounts actually increase in the 0.05 ppm data set)

	1 ppm	Carbonyl	Carboxyl	Both	Neither	Total Ion Signal
(-) ESI Mode	No Photolysis	6.2	8.2	74.0	11.6	28000
	2 hr Photolysis	5.7	12.5	62.2	19.6	28500
	24 hr Photolysis	4.4	11.3	64.5	19.9	15500
(+) ESI Mode	No Photolysis	8.1	13.9	69.3	8.7	29500
	2 hr Photolysis	4.7	25.4	55.7	14.2	24000
	24 hr Photolysis	3.2	19.1	58.0	19.7	5000

	0.5 ppm	Carbonyl	Carboxyl	Both	Neither	Total Ion Signal
(-) ESI Mode	No Photolysis	6.0	9.3	73.0	11.9	28000
	2 hr Photolysis	4.4	14.0	65.5	16.1	28500
	24 hr Photolysis	4.6	12.1	63.5	19.9	15500
(+) ESI Mode	No Photolysis	7.4	16.7	66.6	9.4	29500
	2 hr Photolysis	4.1	31.8	52.7	11.4	24000
	24 hr Photolysis	8.9	20.7	51.7	18.7	5000

	0.1 ppm	Carbonyl	Carboxyl	Both	Neither	Total Ion Signal
(-) ESI Mode	No Photolysis	4.2	11.2	70.0	14.6	19500
	2 hr Photolysis	3.9	13.9	66.5	15.7	16500
(+) ESI Mode	No Photolysis	5.6	22.7	64.1	7.6	18000
	2 hr Photolysis	7.9	30.7	47.5	13.9	8000

	0.05 ppm	Carbonyl	Carboxyl	Both	Neither	Total Ion Signal
(-) ESI Mode	No Photolysis	4.3	13.4	65.4	16.8	11500
	2 hr Photolysis	5.6	20.3	55.3	18.9	6000
(+) ESI Mode	No Photolysis	8.4	21.0	51.7	18.8	6000
	2 hr Photolysis	12.9	27.8	37.3	21.9	3000

Table S5. Average values of O/C, H/C, DBE, #C and percent ion current calculated for limonene SOA compounds after 2 hours of photolysis **directly on a filter** (the corresponding table for the aqueous extract of SOA is given in the text). The SOA compounds have been grouped according to their ratio of relative abundance in the photolyzed mass spectra to relative abundance in non-photolyzed mass spectra. The top and bottom sections of the table were calculated from ESI (-) and (+) mass spectra, respectively. On the whole, the trends for the on-filter and aqueous photolysis are similar.

		1ppm Filter 2 hr Photolysis					**0.5 ppm Filter 2 hr Photolysis**				
		⟨O/C⟩	⟨H/C⟩	⟨DBE⟩	⟨#C⟩	% Ion Current	⟨O/C⟩	⟨H/C⟩	⟨DBE⟩	⟨#C⟩	% Ion Current
Negative ESI Mode	New Compounds	0.50	1.49	5.98	19.7	7	0.49	1.52	5.10	17.1	1
	Increased Relative Abundance	0.54	1.51	5.09	16.5	14	0.54	1.48	4.48	13.3	2
	No Change	0.53	1.54	3.90	12.8	75	0.54	1.53	3.87	12.4	71
	Decreased Relative Abundance	0.44	1.41	3.78	9.6	3	0.46	1.55	3.88	13.1	23
	Destroyed Compounds*	0.48	1.59	4.01	14.5	10*	0.48	1.59	4.27	15.7	11*
Positive ESI Mode	New Compounds	0.44	1.58	5.17	19.4	8	0.43	1.61	4.52	17.8	10
	Increased Relative Abundance	0.47	1.62	3.15	10.9	12	0.45	1.64	3.00	10.7	39
	No Change	0.44	1.59	3.96	14.5	66	0.43	1.60	4.11	15.6	41
	Decreased Relative Abundance	0.35	1.58	4.27	15.9	5	0.30	1.57	3.68	12.6	2
	Destroyed Compounds*	0.40	1.52	6.75	25.5	11*	0.38	1.40	7.39	23.7	9*