Supporting Information
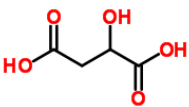
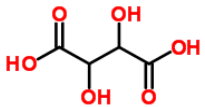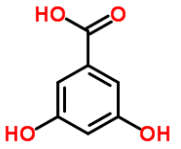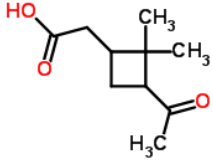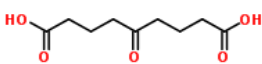**Section S1: Contribution from OH radical**

OH-initiated chemistry may compete with direct photolysis. Sources of OH in aqueous solution of high-NOx SOA include the photolysis of peroxides (ROOH), nitrate ions, and nitrite ions. To gauge the OH production from peroxides in the control and photolyzed aqueous SOA samples, we performed iodo-colorimetric peroxide assays [1,2] using H_2O_2 (Aldrich, 3 wt %) as a standard in the concentration range of $0 - 100$ µM. The results for the control and photolyzed samples were identical within error ~ 3.0 (±0.5) µM. The low concentration of peroxides in SOA is expected due to the suppression of HO_2 chemistry in the high-NOx oxidation. [3] We note that some fraction of the detected peroxide concentration may also originate from the sonication of the SOA samples in water. [4] We used the wavelength-dependent flux from our lamp (Fig. S2), the near UV absorption cross section of methyl hydroperoxide, [5] and a quantum yield of unity to estimate the rate of OH production from peroxides. The rate was low; photolysis of peroxides generated less than 0.6 µM in total over the entire timescale of the photolysis. Assuming prompt and complete reaction of OH with organics under 1:1 stoichiometry (~ 200 g/mol average molar mass of SOA compounds) we estimate < 0.1 % loss of organics resulting from peroxide photolysis and OH chemistry.

Likewise, negative ion mode IC measurements were used to estimate the rate of OH production from nitrate and nitrite ions present in solution. The measured concentrations of nitrate ($[NO_3^-]$ ~ 1.5 (±0.2) µM) and nitrite ions ($[NO_2^-]$ ~ 0.8 (±0.2) µM) were identical within error in control and photolyzed samples, indicating that photolysis of organic nitrates was not a significant source of these anions within 4 h irradiation. Our results agree with the available

1   literature sources , which suggest the nitrite ion yield is negligible and the nitrate ion yield is

2   below 0.1 in aqueous photolysis of organic nitrates at neutral pH. [6-8] Similar to the estimation

3   from peroxides, calculations using the known OH quantum yields [9, 10] and absorption cross

4   sections [11, 12] for nitrate and nitrite ions, predicted small loss of organics from OH chemistry

5   from the photolysis of nitrate ($< 0.1\%$) and nitrite ($< 0.2\%$) during the 4 h photolysis under our

6   lamp flux. Considering all plausible sources for OH, we conclude that the contribution of OH

7   chemistry to the changes in composition of aqueous isoprene SOA under the studied photolytic

8   conditions are negligible ($< 1\%$) assuming no OH recycling from the photolysis of organics.

9

1 **Table S1:** Positive ion mode ESI characterization of organic mono- and di-acid standards in
2 aqueous isoprene SOA sample matrix. Collision induced dissociation (CID) energy is the
3 threshold energy when accompanying loss fragments are produced. Loss fragments are neutral
4 compounds ejected from the CID of the monomer standard or its dimer.
5

Standard	Structure	CID Energy	Loss Fragments
malic acid $(C_4H_6O_5)$ Detected as Na^+ ion	 134.022 Da	Monomer (23 units) Dimer (0-8 units)	Monomer (CO) Dimer (H_2O, CH_2O_3, C_4H_6O)
tartaric acid $(C_4H_6O_6)$ Detected as H^+ ion	 150.016 Da	Monomer (18 units) Dimer (0 units)	Monomer (C_2H_2O, H_2O) Dimer (CH_2O_3, $C_4H_6O_6$)
3,5-dihydroxy benzoic acid $(C_7H_6O_4)$ Detected as H^+ ion	 154.027 Da	Monomer (16 units) Dimer (N/A)	Monomer (CO_2, H_2O) Dimer (N/A)
pinonic acid $(C_{10}H_{16}O_3)$ Detected as both Na^+ and H^+ ions	 184.110 Da	Monomer (25 units) Dimer (10 units)	Monomer (N/A) Dimer (H_2O, C_4H_6O)
5-oxoazelaic acid $(C_9H_{14}O_4)$ Detected as Na^+ ion	 186.089 Da	Monomer (28 units) Dimer (0 units)	Monomer (H_2O) Dimer ($C_9H_{14}O_4$)

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7

1   **Table S2:** Neutral composition and concentrations of compounds degraded from (a) photolysis
2   and (b) hydrolysis. Entries highlighted in gray are observed in duplicate photolysis trials and
3   average concentrations are reported. Peaks are sorted by increasing number of carbon. The rates
4   of degradation for select compounds, listed in Table 2, in the main text are derived from linear
5   fits of concentration vs. time profiles.
6

| a. Photolysis Sample | | | | Conc. 0h ($\mu g\ mL^{-1}$) | Conc. 1h ($\mu g\ mL^{-1}$) | Conc. 2h ($\mu g\ mL^{-1}$) | Conc. 4h ($\mu g\ mL^{-1}$) |
C	H	O	N				
7	10	6	0	1.06	0.23	0.10	0.00
8	12	7	0	1.02	0.29	0.14	0.12
8	12	8	0	0.06	0.05	0.00	0.00
8	13	9	1	0.88	0.40	0.25	0.12
9	14	8	0	5.51	1.49	1.16	0.78
10	14	9	0	0.38	0.06	0.00	0.00
10	16	9	0	0.70	0.58	0.50	0.26
10	15	10	1	0.82	0.11	0.00	0.00
11	16	9	0	6.52	1.55	0.92	0.56
11	16	10	0	0.96	0.12	0.00	0.00
11	17	11	1	0.25	0.22	0.22	0.00
12	20	10	0	2.65	1.49	1.33	0.94
12	20	8	0	0.71	0.34	0.27	0.30
12	20	9	0	0.26	0.13	0.11	0.00
12	18	10	0	7.94	2.45	1.47	1.18
12	19	12	1	1.70	0.45	0.29	0.08
12	19	9	1	0.06	0.05	0.00	0.00
12	21	10	1	0.52	0.04	0.00	0.00
12	19	11	1	0.22	0.08	0.05	0.00
12	17	12	1	0.23	0.15	0.06	0.00
13	22	9	0	0.11	0.06	0.02	0.00
13	20	7	0	2.17	1.14	1.01	0.80
13	18	8	0	0.11	0.11	0.10	0.00
13	18	9	0	0.15	0.10	0.09	0.00
13	20	10	0	6.37	2.20	1.79	1.37
13	20	11	0	3.13	0.48	0.37	0.13
13	22	8	0	0.36	0.20	0.10	0.00
13	18	11	0	0.53	0.49	0.33	0.14
13	19	11	1	0.26	0.05	0.00	0.00
13	19	12	1	0.16	0.09	0.05	0.00
13	19	13	1	0.41	0.19	0.08	0.00
14	20	9	0	0.27	0.18	0.15	0.05
14	22	10	0	2.93	1.48	1.28	0.85
14	22	11	0	23.33	11.74	10.35	8.33
14	24	9	0	0.09	0.06	0.00	0.00

14	20	10	0	1.15	0.17	0.09	0.00
14	22	9	0	2.41	1.31	0.95	0.59
14	22	12	0	0.40	0.24	0.21	0.14
14	21	13	1	2.20	0.65	0.58	0.36
14	23	10	1	0.09	0.06	0.00	0.00
14	21	11	1	0.14	0.06	0.00	0.00
14	23	11	1	0.14	0.06	0.00	0.00
14	25	11	1	0.73	0.05	0.00	0.00
14	21	14	1	0.21	0.10	0.07	0.00
15	24	9	0	0.53	0.17	0.09	0.00
15	22	12	0	3.33	1.76	1.48	1.35
15	24	10	0	0.71	0.14	0.12	0.10
15	22	9	0	0.10	0.05	0.00	0.00
15	22	10	0	0.53	0.32	0.25	0.14
15	24	11	0	1.45	0.93	0.70	0.61
15	22	13	0	0.55	0.28	0.09	0.00
15	23	14	1	0.10	0.06	0.00	0.00
16	24	11	0	0.50	0.23	0.16	0.12
16	24	12	0	1.83	0.89	0.72	0.46
16	24	10	0	0.26	0.14	0.05	0.00
16	26	10	0	0.12	0.07	0.00	0.00
16	26	11	0	0.33	0.09	0.09	0.00
16	26	12	0	0.10	0.04	0.00	0.00
16	24	13	0	2.32	1.73	1.39	0.93
16	26	13	0	0.71	0.31	0.20	0.00
16	23	15	1	0.14	0.05	0.00	0.00
16	25	15	1	0.33	0.03	0.00	0.00
16	20	8	2	0.09	0.04	0.00	0.00
17	26	11	0	0.32	0.08	0.04	0.00
17	26	13	0	1.84	0.81	0.59	0.41
17	28	10	0	0.09	0.06	0.00	0.00
17	26	10	0	0.33	0.07	0.00	0.00
17	24	12	0	0.06	0.05	0.04	0.00
17	26	12	0	1.51	0.86	0.54	0.21
17	24	13	0	0.15	0.08	0.06	0.00
17	24	14	0	0.14	0.05	0.00	0.00
17	26	14	0	0.88	0.45	0.21	0.12
18	28	14	0	3.48	1.53	1.19	0.88
18	28	10	0	0.10	0.06	0.00	0.00
18	28	12	0	0.73	0.15	0.00	0.00
18	28	13	0	1.48	0.28	0.26	0.15
18	28	11	0	0.09	0.04	0.00	0.00
18	30	11	0	0.10	0.05	0.00	0.00

18	26	12	0	0.08	0.05	0.00	0.00
18	28	12	0	0.59	0.18	0.14	0.00
18	26	14	0	0.19	0.11	0.08	0.00
18	26	15	0	0.07	0.04	0.00	0.00
19	28	13	0	0.10	0.04	0.00	0.00
19	30	13	0	0.17	0.04	0.00	0.00
19	28	14	0	0.11	0.11	0.06	0.00
19	30	14	0	0.34	0.13	0.00	0.00

| b. Control Sample | | | | Conc. 0h | Conc. 1h | Conc. 2h | Conc. 4h |
C	H	O	N	(μg mL^{-1})	(μg mL^{-1})	(μg mL^{-1})	(μg mL^{-1})
9	12	5	0	0.14	0.13	0.12	0.00
9	14	4	0	0.11	0.06	0.06	0.00
9	14	5	0	0.09	0.08	0.08	0.07
9	12	7	0	0.61	0.48	0.37	0.25
9	17	8	1	0.48	0.36	0.31	0.19
10	16	6	0	1.40	1.38	1.37	1.30
10	19	8	1	1.09	1.01	0.78	0.71
13	23	9	1	0.16	0.10	0.09	0.00
13	23	10	1	0.15	0.13	0.11	0.10
14	20	10	0	1.14	0.98	0.82	0.76
14	25	11	1	0.72	0.60	0.53	0.47
16	26	12	0	0.10	0.06	0.06	0.06
16	22	13	0	0.11	0.10	0.08	0.05

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2

1 **Table S3:** Neutral composition and concentrations of compounds produced by (a) photolysis and
2 (b) hydrolysis. Entries highlighted in gray are observed in duplicate photolysis trials and average
3 concentrations are reported. Peaks are sorted by increasing number of carbon. The rates of
4 degradation for select compounds, listed in Table 3, in the main text are derived from linear fits
5 of concentration vs. time profiles.
6

a. Photolysis Sample				Conc. 0h ($\mu g\ mL^{-1}$)	Conc. 1h ($\mu g\ mL^{-1}$)	Conc. 2h ($\mu g\ mL^{-1}$)	Conc. 4h ($\mu g\ mL^{-1}$)
C	H	O	N				
3	4	5	2	0.00	0.22	0.36	0.49
5	12	4	0	0.00	0.04	0.16	0.26
5	11	6	1	0.00	0.12	0.40	0.61
5	6	7	2	0.35	1.38	1.48	1.93
6	14	6	0	0.00	0.09	0.12	0.14
6	8	4	0	0.04	0.13	0.22	0.45
6	6	8	2	0.17	0.78	0.89	1.43
7	12	6	0	0.00	0.14	0.18	0.52
7	12	5	0	0.00	0.55	1.16	2.04
7	12	4	0	0.00	0.15	0.17	0.17
7	10	5	0	0.03	0.33	0.79	1.04
7	8	9	2	0.09	0.67	0.82	1.20
7	10	9	2	0.30	2.39	3.74	5.44
7	8	8	2	0.00	0.44	0.50	0.78
8	12	4	0	0.00	0.12	0.17	0.24
8	12	6	0	0.60	1.81	3.08	4.59
8	16	3	0	0.00	0.09	0.22	0.22
8	16	4	0	0.00	0.09	0.11	0.19
8	14	5	0	0.00	0.14	0.16	0.17
8	10	5	0	0.03	0.05	0.19	0.86
8	12	5	0	0.11	0.56	0.59	0.82
8	14	6	0	0.00	0.16	0.20	0.23
8	15	6	1	0.00	0.07	0.14	0.18
8	15	7	1	0.00	0.08	0.13	0.15
8	15	6	1	0.00	0.04	0.14	0.32
8	10	8	2	0.16	1.07	1.40	1.57
8	10	10	2	0.42	2.86	4.07	5.85
9	16	7	0	0.00	0.32	0.42	0.59
9	12	3	0	0.00	0.03	0.07	0.32
9	14	3	0	0.00	0.03	0.06	0.21
9	16	5	0	0.00	0.14	0.15	0.23
9	12	6	0	0.05	0.16	0.20	0.23
9	14	6	0	3.45	4.46	5.97	6.87
9	12	7	0	0.08	0.29	0.40	0.43
9	12	10	2	0.39	5.37	8.01	12.03

C	H	O	N				
9	12	11	2	0.00	0.08	0.13	0.16
10	16	5	0	0.24	0.55	0.74	1.00
10	20	4	0	0.12	0.67	1.29	1.70
10	20	5	0	0.00	0.13	0.17	0.34
10	14	7	0	0.55	0.68	0.80	1.22
10	18	5	0	0.00	0.04	0.07	0.18
10	18	6	0	0.00	0.07	0.07	0.12
10	14	8	0	0.38	1.09	1.13	1.81
10	12	10	2	0.00	0.21	0.34	0.43
10	14	10	2	0.00	0.52	1.04	1.18
11	16	6	0	0.16	0.28	0.48	0.54
11	16	8	0	1.23	1.99	3.12	5.42
11	18	7	0	0.17	0.37	0.42	0.49
11	14	9	2	0.00	0.19	0.20	0.26
12	18	5	0	0.00	0.16	0.26	0.35
12	18	6	0	0.05	0.09	0.12	0.16
12	18	8	0	1.16	1.29	1.33	1.49
12	18	9	0	3.45	4.15	4.61	4.73

| b. Control Sample | | | | Conc. 0h | Conc. 1h | Conc. 2h | Conc. 4h |
C	H	O	N	$(\mu g\ mL^{-1})$	$(\mu g\ mL^{-1})$	$(\mu g\ mL^{-1})$	$(\mu g\ mL^{-1})$
8	14	7	0	3.36	3.76	3.82	3.83
12	14	8	0	0.13	0.15	0.19	0.20
12	18	8	0	1.15	1.17	1.27	1.41
12	20	10	0	3.46	3.73	3.91	4.22
15	22	11	0	0.58	0.68	0.74	0.89

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2   **Figure S1:** Relative contribution of OH and O_3 chemistry to the high-NOx photooxidation of
3   isoprene. The rate of the O_3 + isoprene reaction, $R_{O3} = k_{O3}[O_3][ISO]$ was calculated from the
4   measured concentrations of O_3 (ozone photometer) and isoprene (PTR-ToF-MS). The rate of
5   disappearance of isoprene was calculated by numerically differentiating the measured isoprene
6   concentration. The rate of the OH + isoprene reaction could then be calculated as the difference,
7   $R_{OH} = -d[ISO]/dt - R_{O3}$. The results show that ozone did not make a significant contribution to
8   isoprene oxidation under present conditions.
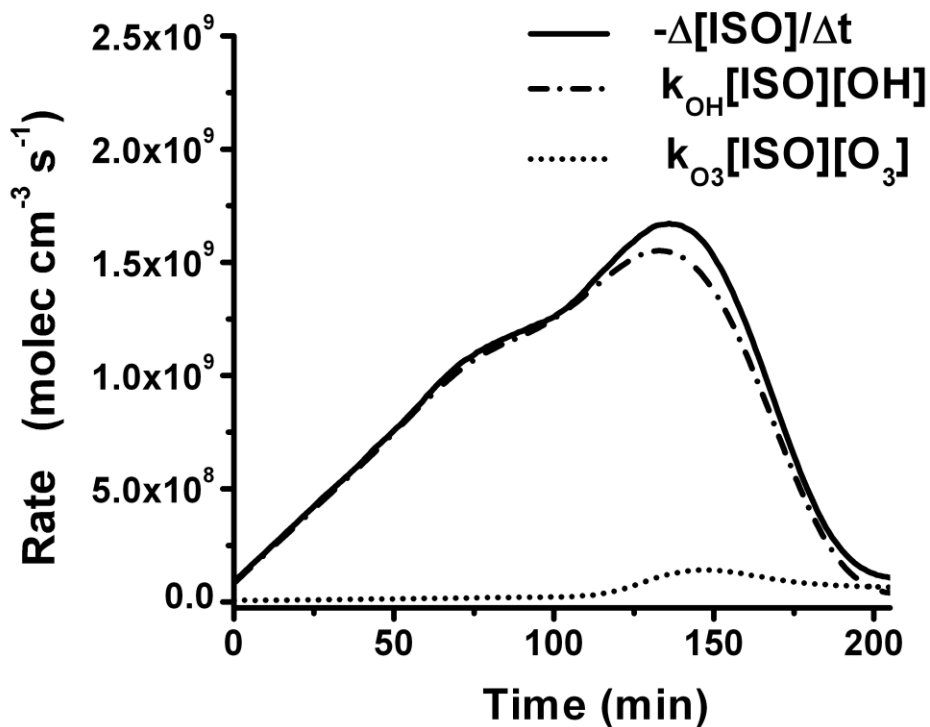
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1   **Figure S2:** Time evolution of (a) oxidants and particles and (b) select VOC in the high-NOx
2   photooxidation reaction including: isoprene (ISO), the sum of isobaric methylvinylketone and
3   methacrolein (MVK+MAC), methacrylic acid (METH), glycolaldehyde (GLYCOL),
4   hydroxyacetone (HAC), and methylglyoxal (MGLY). Gray shading represents the error between
5   repeated experiments.
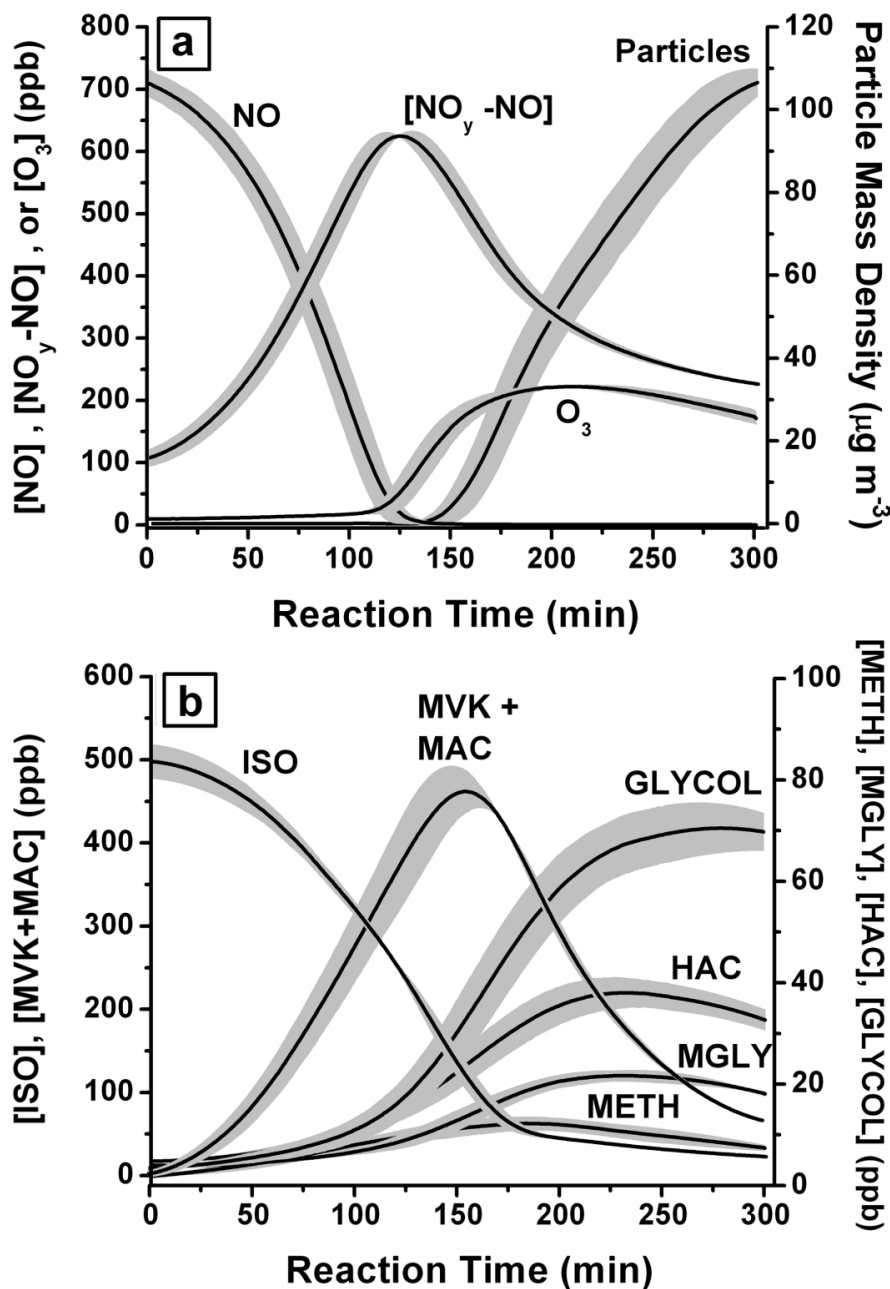
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1 **Figure S3:** Characterization of (a) the flux from the photolysis lamp compared modeled solar
2 flux under summer clear-sky conditions and (b) the temperature change of an aqueous sample
3 under the lamp for the 0 – 4 h photolysis time period used in this work. The solar flux was
4 calculated using the "Quick TUV" calculator,
5 http://cprm.acd.ucar.edu/Models/TUV/Interactive_TUV/, using the following parameters: SZA =
6 0, 300 Dobson overhead ozone, surface albedo of 0.1, ground elevation and altitude = 0 km.
7
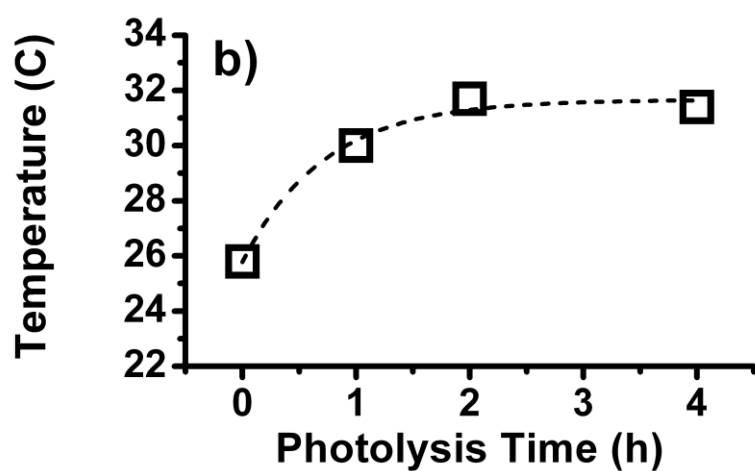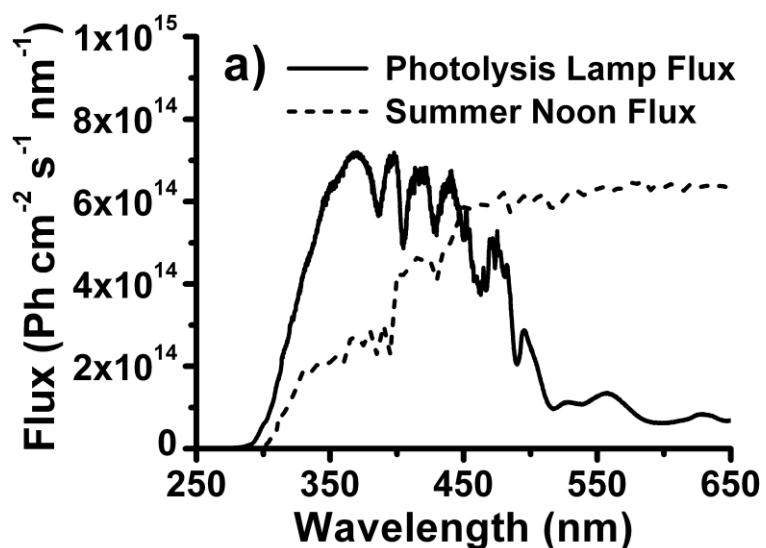
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1   **Figure S4:** Complimentary figure to Figure 1 in the main text. Positive ion mode ESI mass
2   spectra of the aqueous SOA extract in the dark control (panels on the left) and photolysis (panels
3   on the right) experiments, normalized with respect to the most intensive peak in the sample
4   without conversion to mass. Note the breaks in the vertical axis. Red peaks cannot be assigned to
5   molecules comprised of C, H, O and N atoms.
6
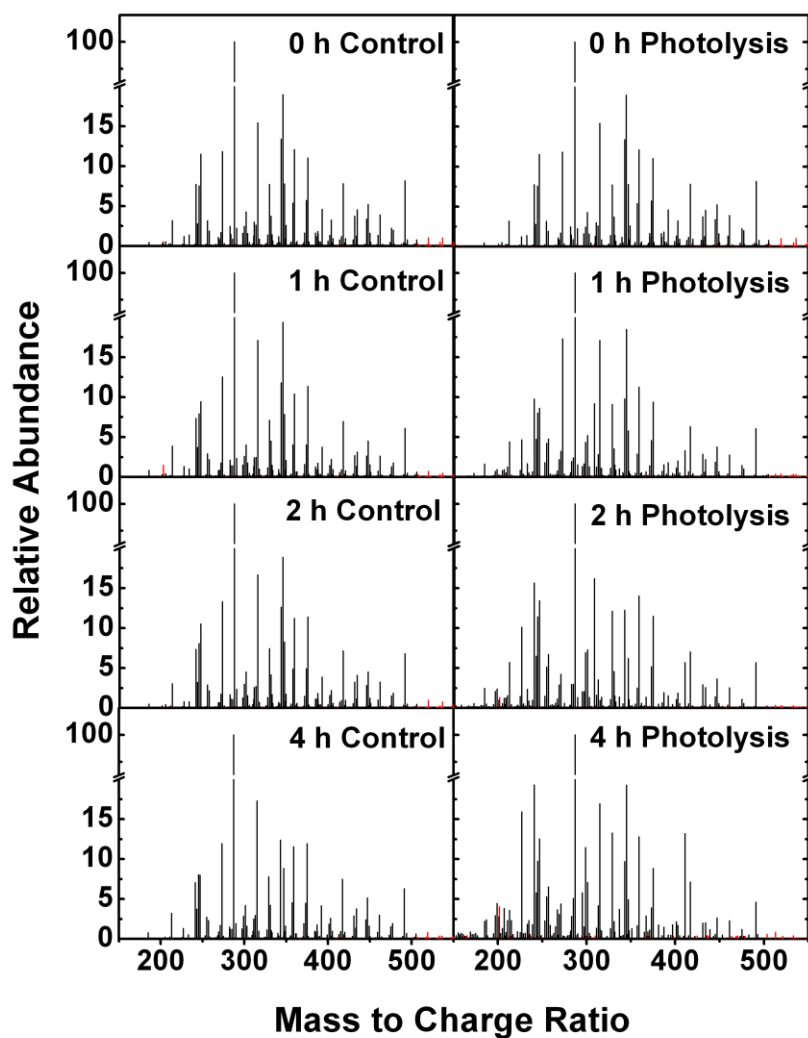
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1   **References:**
2   1   K. S. Docherty, W. Wu, Y. B. Lim and P. J. Ziemann, *Environ. Sci. Technol.*, 2005, **39**,
3   4049-4059.
4   2   D. K. Banerjee and C. C. Budke, *Anal. Chem.*, 1964, **36**, 792-796.
5   3   B. J. Finlayson-Pitts and J. N. Pitts, *Chemistry of the Upper and Lower Atmosphere:*
6   *Theory, Experiments, and Applications*, Academic Press, San Diego, CA, 2000.
7   4   A. S. Hasson and S. E. Paulson, *Journal of Aerosol Science*, 2003, **34**, 459-468.
8   5   C. M. Roehl, Z. Marka, J. L. Fry and P. O. Wennberg, *Atmos. Chem. Phys.*, 2007, **7**, 713-
9   720.
10   6   F. Monteil-Rivera, Z. Radovic-Hrapovic, A. Halasz, L. Paquet, G. Ampleman, S.
11   Thiboutot and J. and Hawari, *Environ. Eng. Sci.*, 2011, **28**, 71-79.
12   7   H. Engelhardt, J. Meister and P. Kolla, *Chromatographia*, 1993, **35**, 5-12.
13   8   W. R. Haag, R. J. Spanggord, T. Mill, R. T. Podoll, T.-W. Chou, D. S. Tse and J. C.
14   Harper, *Chemosphere*, 1991, **23**, 215-230.
15   9   R. Zellner, M. Exner and H. Herrmann, *J. Atmos. Chem.*, 1990, **10**, 411-425.
16   10   O. C. Zafiriou and R. Bonneau, *Photochem. Photobio.*, 1987, **45**, 723-727.
17   11   J. S. Gaffney, N. A. Marley and M. M. Cunningham, *Environ. Sci. Technol.*, 1992, **26**,
18   207-209.
19   12   Y. Zuo and Y. Deng, *Chemosphere*, 1998, **36**, 181-188.
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