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Supplement of

Aging of secondary organic aerosol from small aromatic VOCs: changes in chemical composition, mass yield, volatility and hygroscopicity

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1 **S1 Modification of Standard Fragmentation Table**

2 Several adjustments were made to the standard fragmentation table (Allan et al., 2004) for the
3 analysis of HR and UMR data. Most importantly, a significant adjustment was made to the
4 treatment of water fragmentation (Section S1.2) and to the fraction of observed H₂O attributed to
5 organics (Section S1.3).

7 **S1.1 Air Fragmentation**

8 The fragmentation pattern of air at m/z 44 (CO₂⁺), m/z 29 (N¹⁵N⁺), m/z 18 (H₂O⁺) and m/z 16
9 (O⁺) was calculated using difference spectra (signal – background) at UMR during filter
10 measurements, which were taken at the beginning (before aerosol formation) and at the end of
11 every experiment. H₂O⁺, N¹⁵N⁺ and CO₂⁺ were calculated as constant fractions of the N₂⁺ signal
12 at m/z 28. O⁺ was calculated as a constant fraction of N⁺. When the fractions were different at the
13 beginning and end of the experiments, a linear function was used to approximate the time-
14 dependent fraction throughout the experiment. In all cases the calculated fractions did not differ
15 greatly from the standard values.

17 **S1.2 Water Fragmentation**

18 Water dominates the signal in the background (closed) spectrum at m/z 16 (O⁺), m/z 17 (HO⁺)
19 and m/z 18 (H₂O⁺). It is standard practice to determine the water fragmentation pattern from
20 linear regressions to the closed signal of m/z 16 vs. m/z 18 and m/z 17 vs. m/z 18. In this way the
21 O⁺/H₂O⁺ and HO⁺/H₂O⁺ ratios were determined for each experiment; the values, summarized in
22 Table S1, differ slightly from the default values of 4% and 25% for O⁺/H₂O⁺ and HO⁺/H₂O⁺,
23 respectively. However, this treatment of water fragmentation does not account for the H-atoms
24 which were bound to HO⁺ and O⁺ before fragmentation. Therefore, H was added to the standard
25 fragmentation table to obtain an H:O ratio of 2 in the total signal of H₂O determined by AMS
26 data analysis (Canagaratna et al., 2014). This addition of H is made in three locations in the
27 fragmentation table (water, organics and sulfate) because observed particle-phase H₂O is divided
28 between these species. The resulting changes in mass of water, organics and sulfate are low due
29 to the low atomic weight of H. But, the addition of H changes the organic H:C ratio calculated in

1 elemental analysis of the organic aerosol (OA) and therefore the average carbon oxidation state
2 (\overline{OS}_C) estimated from O:C and H:C ratios ($\overline{OS}_C \sim 2 \times \text{O:C} - \text{H:C}$) (Kroll et al., 2011).

3

4 **S1.3 Organic Fragmentation**

5 Important changes were also made to the organic fragmentation table. Based on the
6 recommendation by Aiken et al. (2008), the following fragmentation pattern should be used
7 relative to the m/z 44 (or CO_2^+ for HR analysis) signal: m/z 28 (CO^+) = 100%, m/z 18 (H_2O^+) =
8 22.5%. Since the experiments presented here contained isotopically labeled species, organic
9 H_2O^+ was instead set as a function of the ($^{13}\text{CO}_2^+ + \text{CO}_2^+$) signal. When using 22.5%, the mass
10 attributed to particulate water correlated with organic mass during the experiment, which is
11 unexpected in these dry experiments (RH was less than 10%). There may be some water in the
12 particles if the ammonium sulfate seed particles were not dried completely; however, the
13 particle-phase water signal should not correlate with total organic signal. Thus, the ratio of
14 organic H_2O^+ to $^{13}\text{CO}_2^+ + \text{CO}_2^+$ was chosen so that the mass of water does not correlate with the
15 mass of organics ($R < 0.01$). The ratios of organic H_2O^+ to ($^{13}\text{CO}_2^+ + \text{CO}_2^+$) are provided in
16 Table 2 and ranged from 0.3 to 2.4, higher than the ratio of 0.225 in the default fragmentation
17 table. Calibration experiments suggest that polyacids, diacids and multifunctional organic
18 molecules have $\text{H}_2\text{O}^+/\text{CO}_2^+$ ratios of 1, 2 and 0.5-1.5, respectively when analyzed with the AMS,
19 and polyols have $\text{H}_2\text{O}^+/\text{CO}_2^+$ exceeding 10 (Canagaratna et al., 2014). Thus, the observation of
20 high $\text{H}_2\text{O}^+/\text{CO}_2^+$ in these experiments may point to an importance of these functional groups in
21 the OA produced. Increasing the amount of organic H_2O significantly increased organic mass as
22 well as O:C in these experiments; it does not increase the approximated oxidation state.

23 A relative ionization efficiency (RIE) of 2.0 was used for all H_2O including the organic H_2O .
24 This RIE is the ionization efficiency which has been determined for H_2O (Mensah et al., 2011)
25 and is correct to use for the H_2O fragments from dehydration of organics if and only if H_2O
26 ionizes after fragmentation. If the organic molecule is ionized and then dehydrates and results in
27 H_2O^+ , an RIE of 1.4 should be used (the RIE of organics). The only place where this uncertainty
28 (whether fragmentation follows or precedes ionization) affects the presented results is in the
29 calculated ratios of $\text{H}_2\text{O}^+/(^{13}\text{CO}_2^+ + \text{CO}_2^+)$ presented in Table 2; these ratios would be higher by a
30 factor of (2.0/1.4) if dehydration follows ionization. The ratio of $^{13}\text{CO}^+$ to $^{13}\text{CO}_2^+$ was close to 1

1 throughout the experiments (Table 2), so the ratio $\text{CO}^+/\text{CO}_2^+ = 1$ from the standard fragmentation
2 table was used.

3 **S1.4 Treatment of NO^+ and NO_2^+**

4 In these experiments, no inorganic nitrate is introduced or anticipated. Hence the ions assigned to
5 the nitrate family in the HR analysis (NO^+ , NO_2^+) are presumed to be due to organic nitrates and
6 were added to the total organic aerosol mass in the HR batch table. The relative ionization
7 efficiency (RIE) of 1.0 is used to quantify the contribution from these fragments. The elemental
8 analysis examines the oxidation state of the carbon atoms; hence, nitrate fragments (NO^+ , NO_2^+)
9 were **not** included in the calculation of O:C and H:C.

10

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1 Table S1. Details on AMS data analysis

Expt #	O/H ₂ O	HO/H ₂ O	AB (×10 ⁵)	Org < 106 ratio	v/w	CE _{BP}	CE _{TD}	ρ _{org,BP}	ρ _{org,TD}
1	0.027	0.229	5.28	0.966	0.427	0.20	0.20	1.275	1.400
2	0.017	0.232	5.36	0.977	0.478	0.35	0.30	1.350	1.400
3	0.028	0.223	5.33	0.959	0.466	0.25	0.25	1.375	1.425
4	0.020	0.238	5.48	0.970	0.490	0.25	0.25	1.350	1.450
5	0.016	0.234	5.04	0.959	0.504	0.30	0.30	1.325	1.375
6	0.042	0.238	5.09	0.961	0.531	0.25	0.25	1.275	1.375
7	0.036	0.269	4.84	0.971	0.490	0.25	0.25	1.375	1.475
8	0.037	0.227	4.80	0.968	0.504	0.20	0.20	1.325	1.400
9	0.022	0.234	5.05	0.974	0.705	0.40	0.35	1.425	1.400

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1 Table S2. Evaporation model inputs for each experiment

2

Expt.	Diameter ^a (nm)	Concentration ^b ($\mu\text{g m}^{-3}$)	OA Density (kg m^{-3})
1	298	42.8	1.28
2	234	6.4	1.35
3	275	51.4	1.38
4	228	26.0	1.35
5	234	11.8	1.33
6	243	94.4	1.28
7	285	41.5	1.38
8	266	30.1	1.33
9	251	22.8	1.43

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^aAverage volumetric mode diameter of the bypass line.

4

^bAverage CE corrected concentration of the bypass line .

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6

7 Enthalpy of Vaporization and Accommodation Coefficient Sensitivity Analysis

8 Table S3. Normalized shifting factors for all tested values of ΔH_{vap}

Normalized Shifting Factors			
Expt	$\Delta H_{\text{vap}} = 20 \text{ kJ}$	$\Delta H_{\text{vap}} = 80 \text{ kJ}$	$\Delta H_{\text{vap}} = 120 \text{ kJ}$
1	0.36	0.31	0.29
2	0.08	0.04	0.01
3	0.57	0.31	0.16*
4	0.50	0.25	0.27*
5	0.74*	0.52	0.57
6	0.93	0.53	0.61*
7	1.0	1.00	1.00*
8	0.38*	0.23	0.13
9	0.22*	0.14	0.07

9

* The sum of squared residuals exceeding 0.10

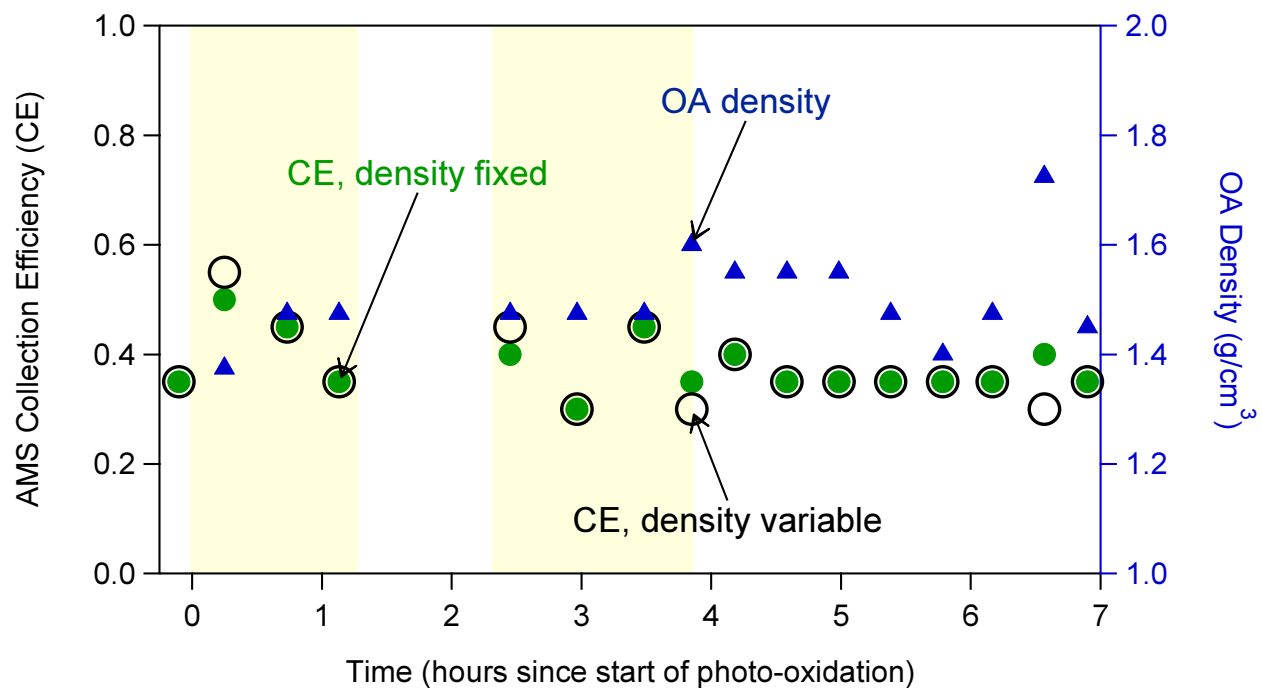
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1 **Table S4** Shifting factors and SSR values for the most volatile (Expt. 7) and least volatile (Expt.
 2 9) experiments in our dataset estimated using different values of accommodation coefficient.

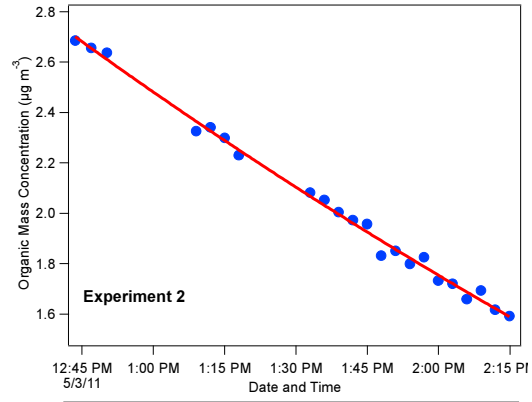
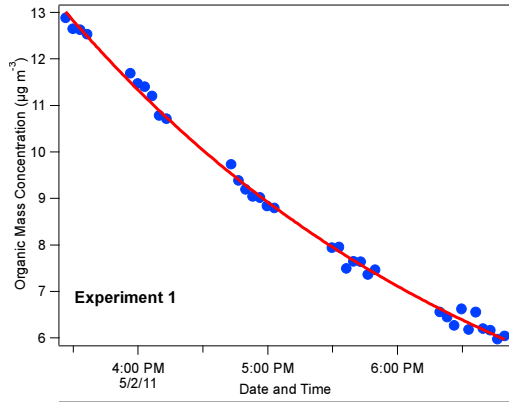
α_m	Shifting Factors			Sum of the Squared Residuals	
	Expt 7	Expt 9	Ratio (Expt 7 / Expt 9)	Expt 7	Expt 9
0.01	1.95	0.32	6.14	0.09	0.079
0.1	0.21	0.03	6.24	0.09	0.078
1.0	0.04	0.006	7.04	0.10	0.075

3

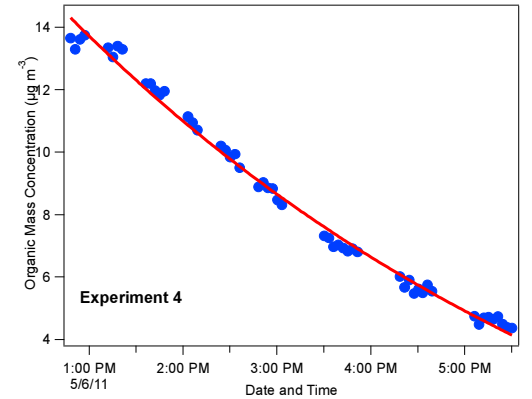
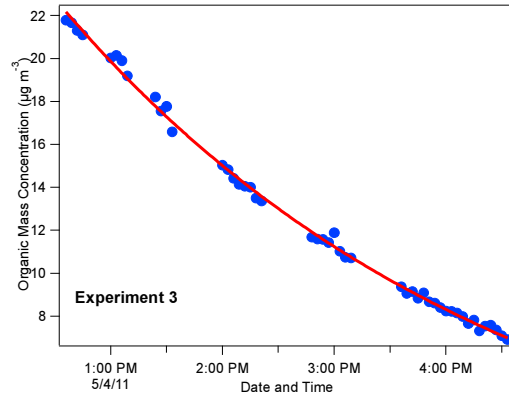
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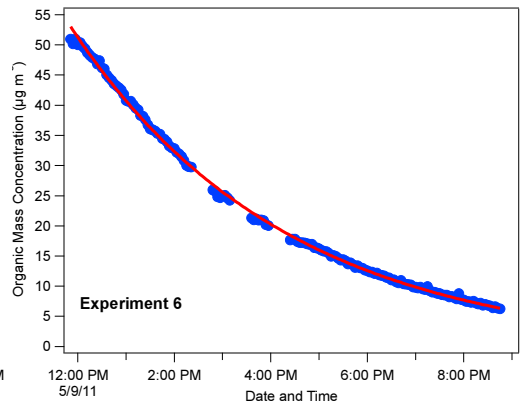
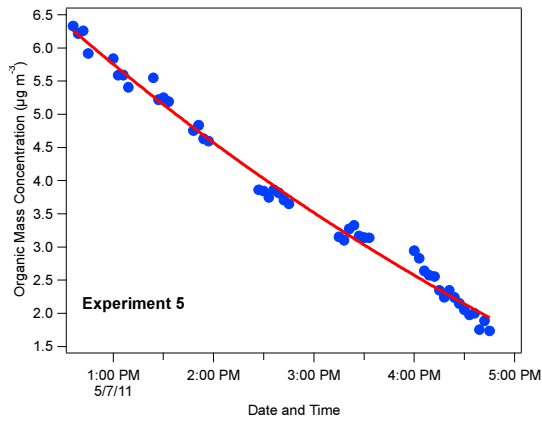
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 2 Figure S1. Estimated CE (solid green and open black circles) and OA density did not change
 3 much over the course of an experiment (shown here is experiment 9). The algorithm used is not
 4 as sensitive to OA density, and fixing the density at 1.5 g cm⁻³ changes the CE values only
 5 slightly for some, and not at all for other time periods.
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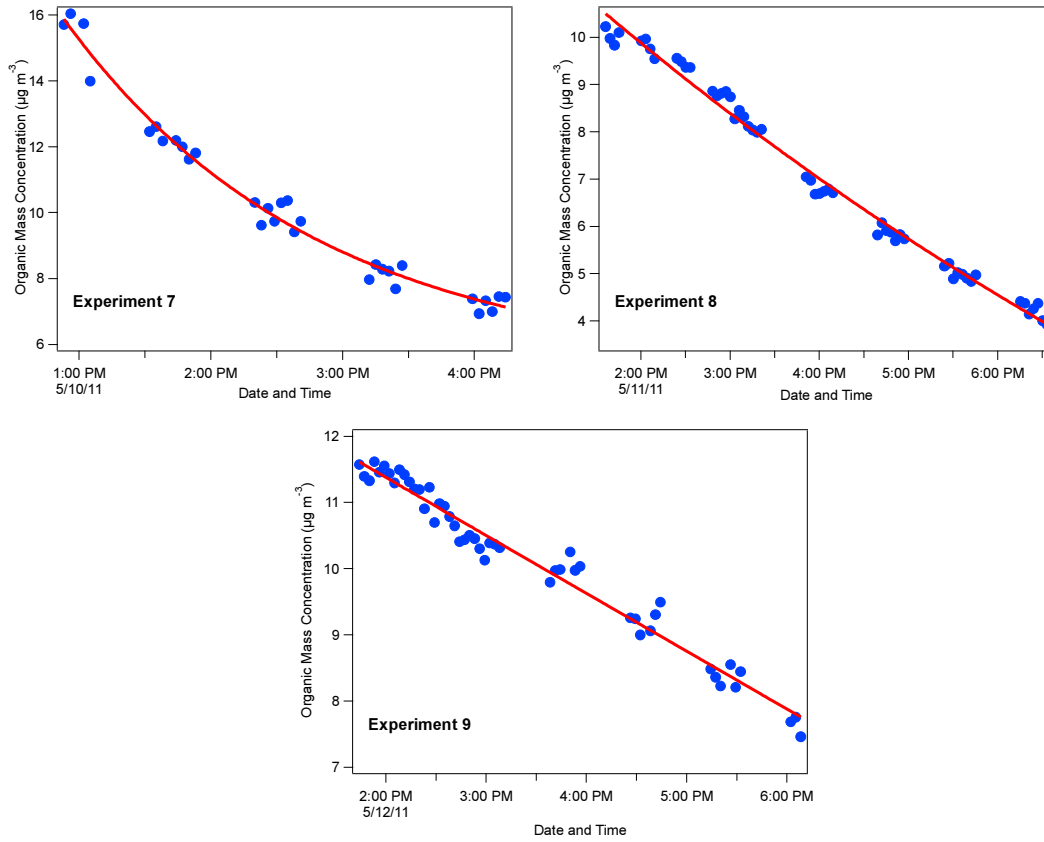


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4 Figure S2. The interpolated fits to the bypass data are shown for each experiment. The blue
5 circles represent the measured organic mass concentration from the bypass line and the red lines
6 represent the interpolated fit, normally an exponential decay.

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