

Supporting Information

Formation and evolution of aqSOA from aqueous-phase reactions of phenolic carbonyls: comparison between ammonium sulfate and ammonium nitrate solutions

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This supplementary document contains three appendixes, fifteen figures and one table, 19 pages in total.

S-1 Subtraction of non-OA CO₂⁺

Pieber et al. (2016)¹ suggested that the non-OA CO₂⁺ intensities generated in the AMS chamber can be correlated with the intensities of (NO⁺ + NO₂⁺) by measuring pure NH₄NO₃ at different concentrations. However, such measurements were not made in our study and we assumed the ratio of organic CO₂⁺ obtained in the dark AN experiments is from the non-OA CO₂⁺, which is a reasonable assumption since concentrations of OA components in the solution are low before the lights are turned on. We found that the NO₂⁺ peak is likely interfered by the adjacent organic peak (CH₂O₂⁺) in the organic spectrum of illuminated experiments. Since non-OA CO₂⁺ showed good correlation with NO⁺ (Figure S5), the signal intensity of non-OA CO₂⁺ is obtained as follows:

$$non - OA CO_{2AN}^{+} = 0.07 * NO_{AN}^{+}$$

After modification of the fragmentation table, the organic mass spectra of “ActSyr_AS Dark” and “ActSyr_AN Dark” are comparable to the standard mass spectrum of ActSyr in NIST database as shown in Figure S8, giving us confidence that the data processing and the method that applied to modify the fragmentation table are appropriate. However, the “SyrAld_AN Dark” is actually quite different from “SyrAld_AS Dark”. We note that the AMS detected organic concentration in SyrAld_AN Dark (CE=1) was only around 2 µg/m³ but it was around 40 µg/m³ in SyrAld_AS Dark. The low organic concentration in “SyrAld_AN Dark” likely results in high uncertainty in the mass spectrum and the elemental ratios in AMS analyses. Differences in the initial concentrations of the precursor compound used in SyrAld_AN Dark (30µM) and SyrAld_AS Dark (100µM) as well as the efficiency of the atomizer may contribute to the large differences in organic concentrations in the SyrAld AS Dark and SyrAld_AN Dark experiments. Hence, it is reasonable to consider that the organic concentration in SyrAld_AN Dark is too low to generate a reasonable organic mass spectrum. Because of this, the first 15 min of the reactions for all experiments are not included in the mass spectra of PMF and elemental analysis since the aqSOA concentrations are low making the spectra highly uncertain.

S-2. PMF analysis

The unit mass resolution AMS data were processed with both SQUIRREL 1.57 and PIKA V1.16 analysis toolkits. We have utilized the organic data matrices and the corresponding error matrices from both “SQUIRREL” and “PIKA” for the PMF analyses. m/z ranges of the data from “SQUIRREL” and “PIKA” in PMF analyses are 12 – 450 and 12 - 200, respectively. SQUIRREL analysis is good for the analysis of high-molecular weight ions as it exhibits a more favorable signal to noise ratios; PIKA analysis is good for ion identification and elemental analysis.

The error matrices were pretreated using the PMF Evaluation Toolkit (PET) following the procedure described in *Ulbrich et al.* [2009].² Variables with a signal-to-noise (SNR) ratio less than 0.2 (“bad” variables) were removed and variables with SNR ranging between 0.2 and 2 (“weak” variables) were downweighted by a factor of 2. Since O^+ , HO^+ , H_2O^+ and CO^+ are related proportionally only to CO_2^+ in the fragmentation table, the error values for each of these m/z were multiplied by $\sqrt{5}$ to avoid excessive weighting of CO_2^+ as prescribed by *Ulbrich et al.* [2009].² The data were analyzed using the PMF2 algorithm³ with f_{peak} varying between -1 and 1. The PMF results are evaluated using the PMF Evaluation Tool in Igor Pro developed by *Ulbrich et al.* [2009]² (PET, Version 2.06, http://cires1.colorado.edu/jimenez-group/wiki/index.php/PMF-AMS_Analysis_Guide). The PMF solution was carefully evaluated according to the procedures outlined in Zhang et al. (2011).⁴

For each dataset, the optimal solution was determined after examining the residuals of PMF fits. For all four sets of experiments, $Q/Q_{expected}$ decreased from $p=1$ to $p=3$, beyond which the decreases in $Q/Q_{expected}$ are small. The PMF results for aqSOA formation from all four experiments exhibit three distinct time series with their corresponding factor mass spectral profiles. When the PMF solution is increased to four factors, the addition of one more factor would not enhance the information for the factorization from a residual point of view. Also, adding one more factor will lead to the missing point of FPEAK, which might be due to the relatively small data amount for lab experiments compared with the field data. Splitting more factors from the organic matrices will have more solutions that are not converging. The rotational ambiguity of solutions was examined by changing the parameter FPEAK, and an FPEAK value of 0 was used for all data sets in the PMF analysis on organic mass spectra. The robustness of solutions were evaluated by starting PMF with different initial conditions

(parameter SEED, *i.e.*, Figure S14).

Bootstrapping is performed for the current PMF solution to evaluate the statistical uncertainty of the candidate solution (*i.e.*, Figure S15). We made assessment of the uncertainty of the factors with 100 bootstrapping runs. Black lines in time series (TS) and black sticks in mass spectra (MS) represent the PMF candidate solutions. Overall, the PMF solutions show a similar range in MS and TS to the bootstrapping 1- σ variation bars. The bootstrapping analysis shows our current PMF solution is reasonably robust and appropriate.

S-3. aqSOA yields

The added ammonium sulfate or sulfuric acid was used as an internal standard to relate aerosol concentration ($\mu\text{g m}^{-3}$) measured by AMS to liquid concentration (mg L^{-1}). Organic to inorganic ratio can be measured online by AMS before and after the reactions starts. The organic concentration at time t in the solution can thus be calculated as follows:

$$\frac{(aqOrg)_t}{aqInorg} = \left(\frac{Org}{Inorg} \right)_{AMS}$$

$$(aqOrg)_t = aqInorg (constant) * \left(\frac{Org}{Inorg} \right)_{AMS}$$

The aqSOA can thus be calculated as:

$$aqSOA = (aqOrg)_{t_illu_AMS} - (aqOrg)_{t_dark_AMS}$$

where $(aqOrg)_{t_dark_AMS}$ is determined before each experiment starts. And aqSOA yield can subsequently be calculated:

$$Yield = \frac{(aqOrg)_{t_illu_AMS} - (aqOrg)_{t_dark_AMS}}{ArOH \text{ reacted determined by HPLC}}$$

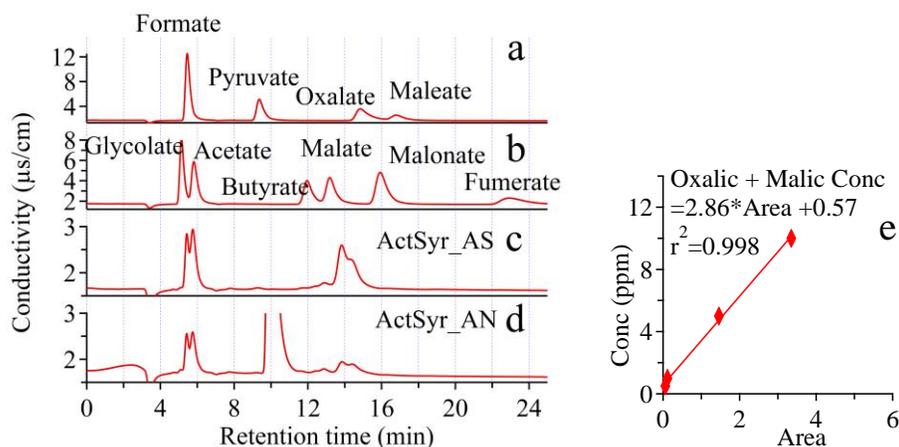


Figure S1. IC chromatographs of a) standard mixture of formic, pyruvic, oxalic, maleic acids; b) standard mixture of acetic, butyric, malic and malonic acids; c) one of the offline samples in ActSyr_AS; d) one of the offline samples in ActSyr_AN; e) calibration curve for quantification of oxalic and malic acids. For the same precursor, organic anions in AS experiment were eluted at similar retention time as the AN one, *i.e.*, the lumped peaks at $t = 6\text{min}$ and $t = 14\text{min}$ in Figures S1c and S1d, indicating the presence of the same organic species in AS and AN experiments. Other organic anions might as well present in the reaction solutions, but they are below the detection limit using the current chromatographic method and hence are not included in the current discussions.

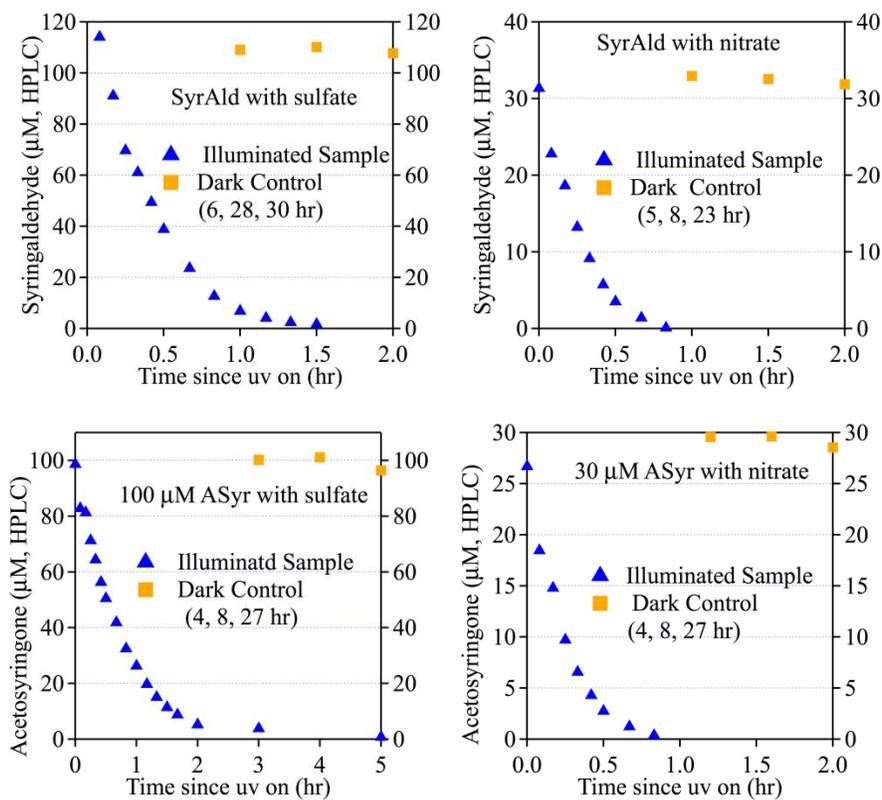


Figure S2 Precursor decay as measured by HPLC in illuminated and dark samples

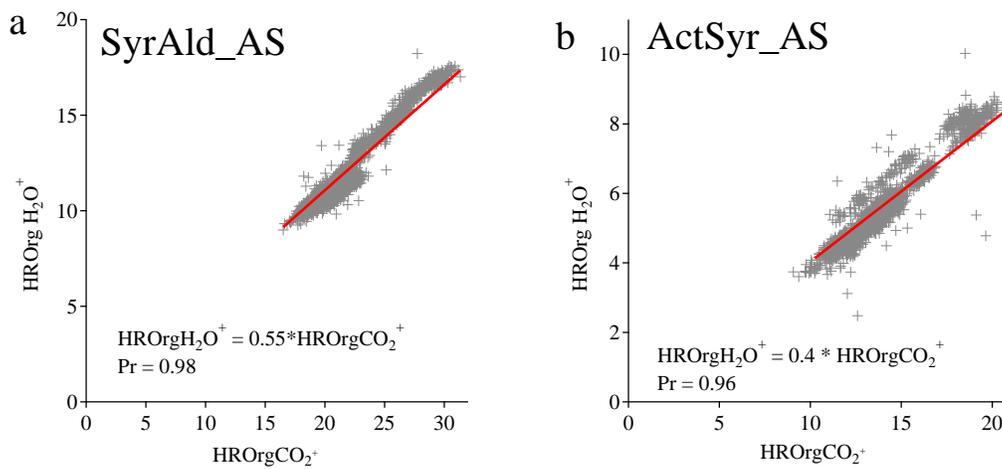


Figure S3. Correlation of Organic H_2O^+ vs. Organic CO_2^+ in a) SyrAld and b) ActSyr experiments.

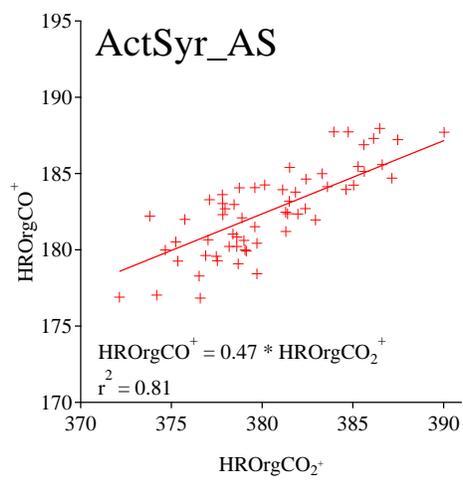


Figure S4. Correlation of Organic CO⁺ vs. Organic CO₂⁺ in ActSyr_AS

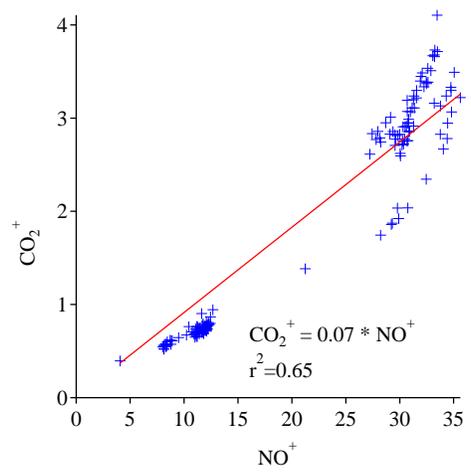
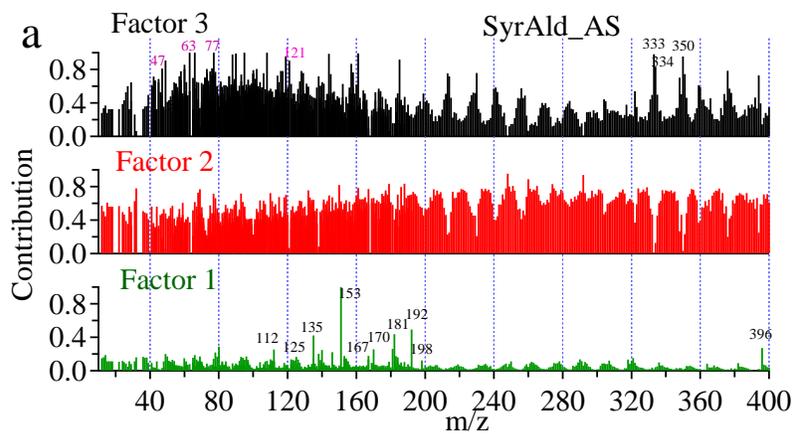


Figure S5. Correlation of non-OA CO₂⁺ vs. NO⁺



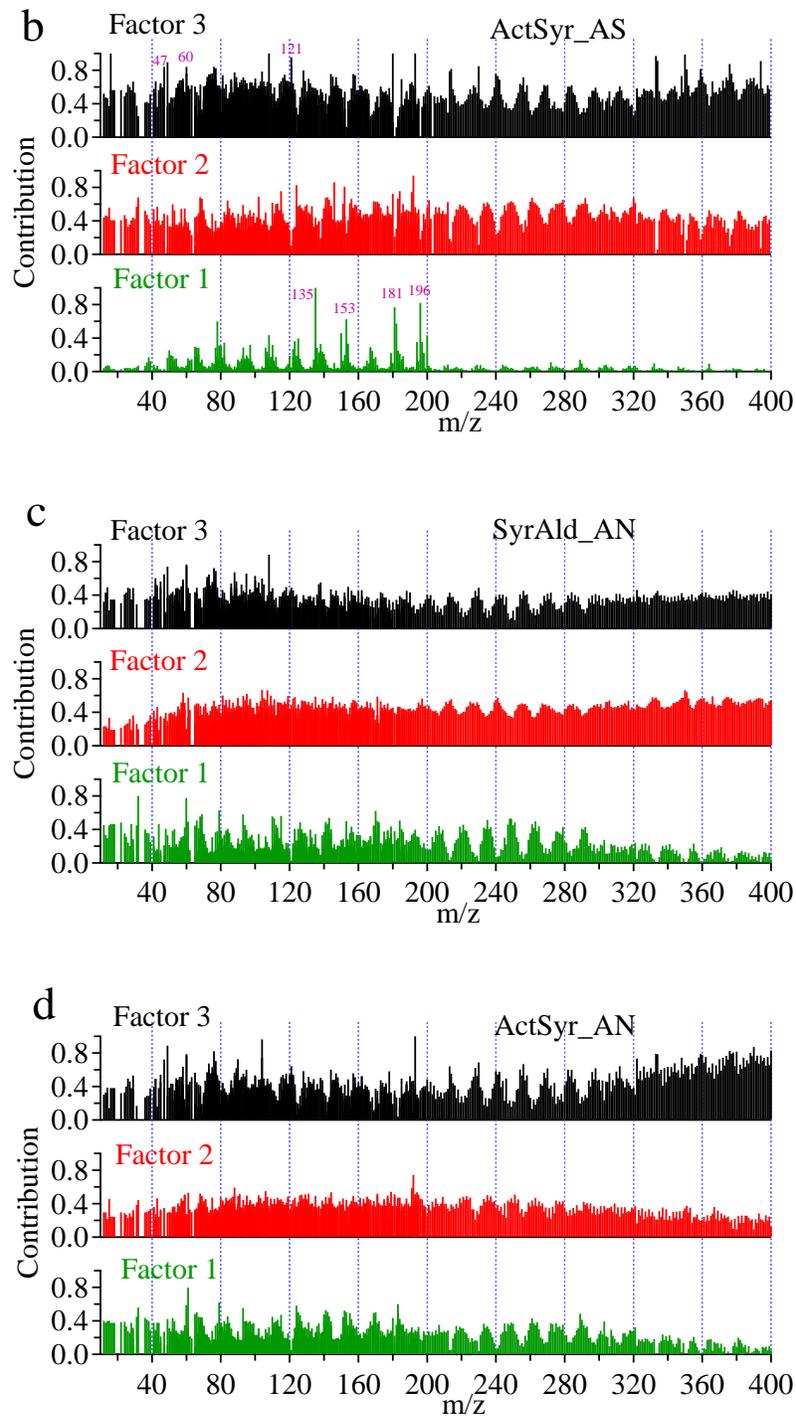


Figure S6. Contribution of each factor to each m/z for: a) SyrAld_AS; b) ActSyr_AS; c) SyrAld_AN; d) ActSyr_AN.

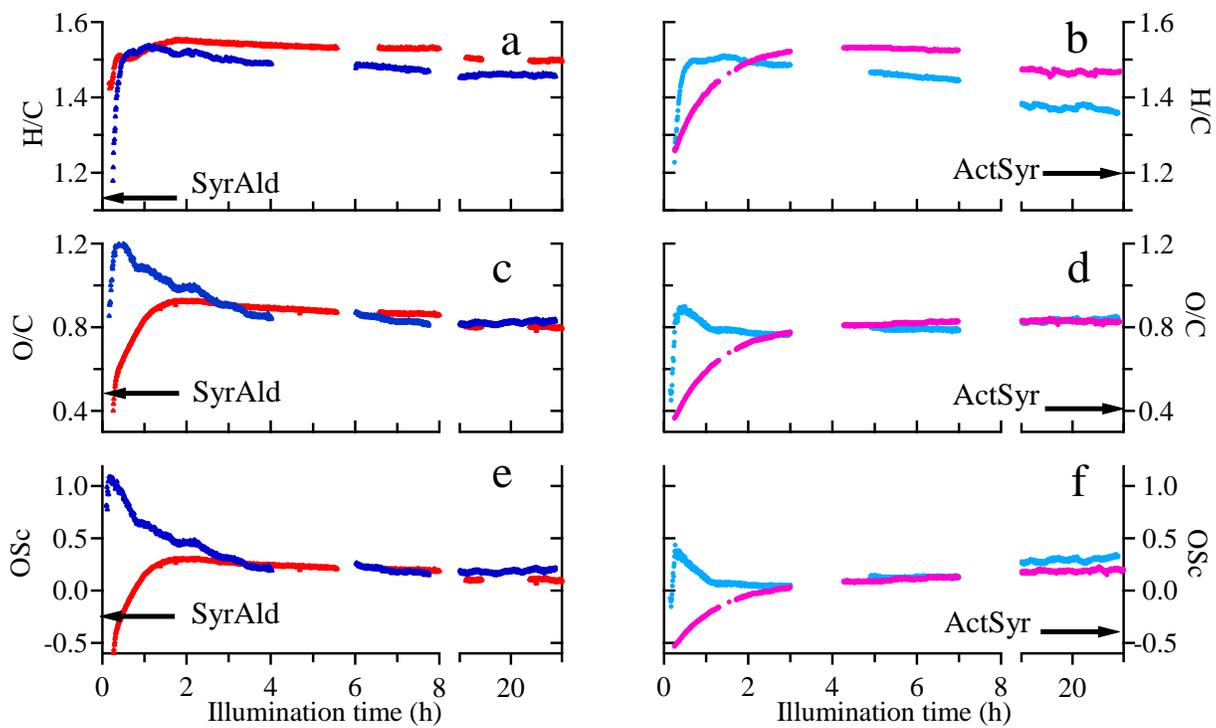


Figure S7 Photodegradation of SyrAld or ActSyr in ammonium sulfate (AS) or ammonium nitrate (AN) solutions: (a) - (d), elemental ratios of aqSOA; (e) - (f) average carbon oxidation states (OS_C) of aqSOA.

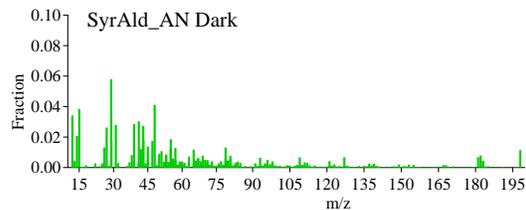
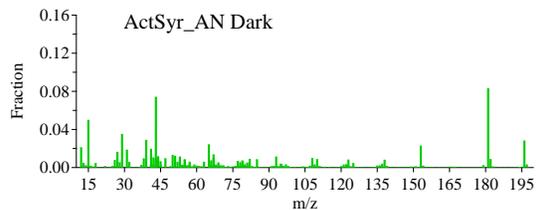
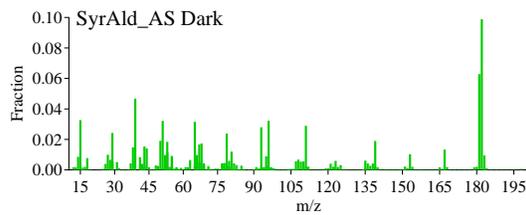
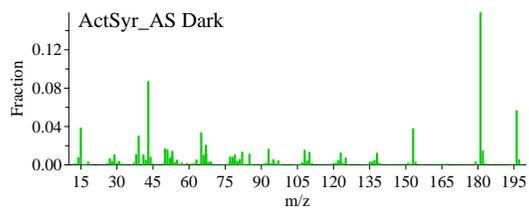
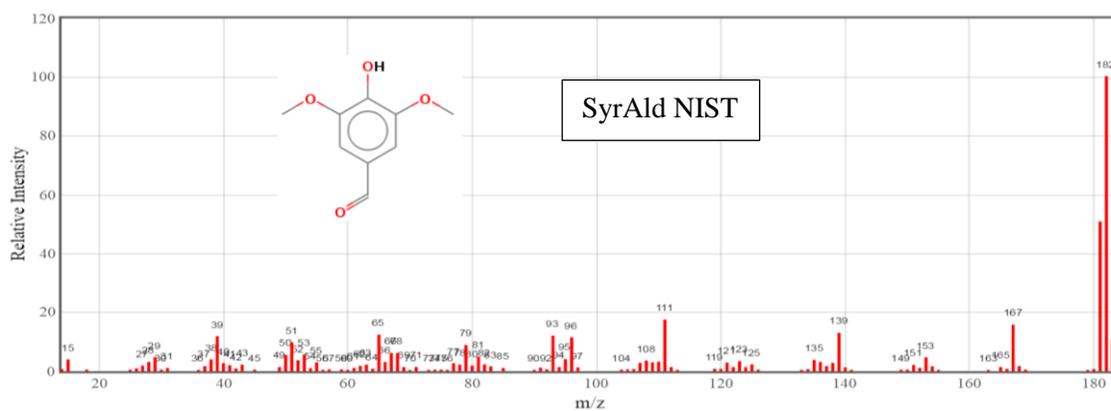
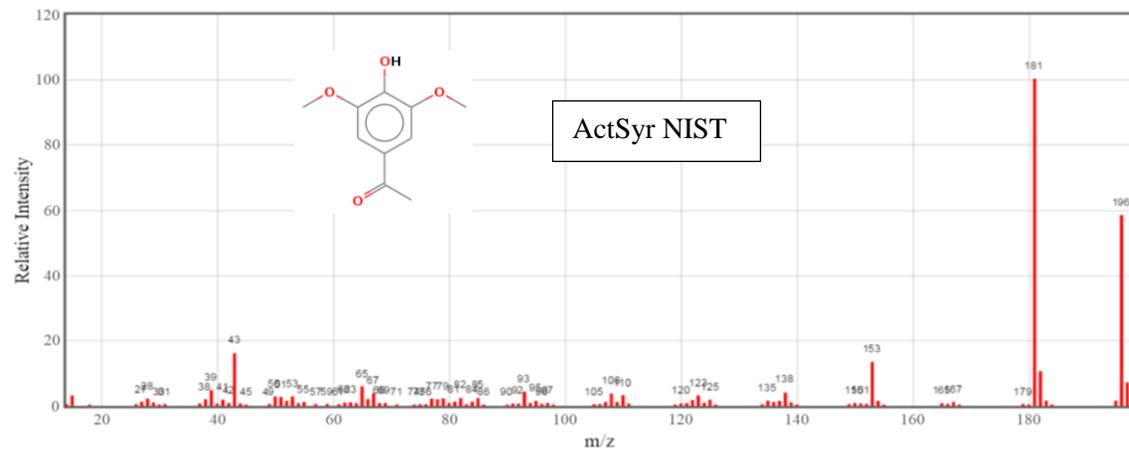


Figure S8. NIST and AMS organic mass spectra of each pure precursor compound mixed with different inorganic salts before illumination.

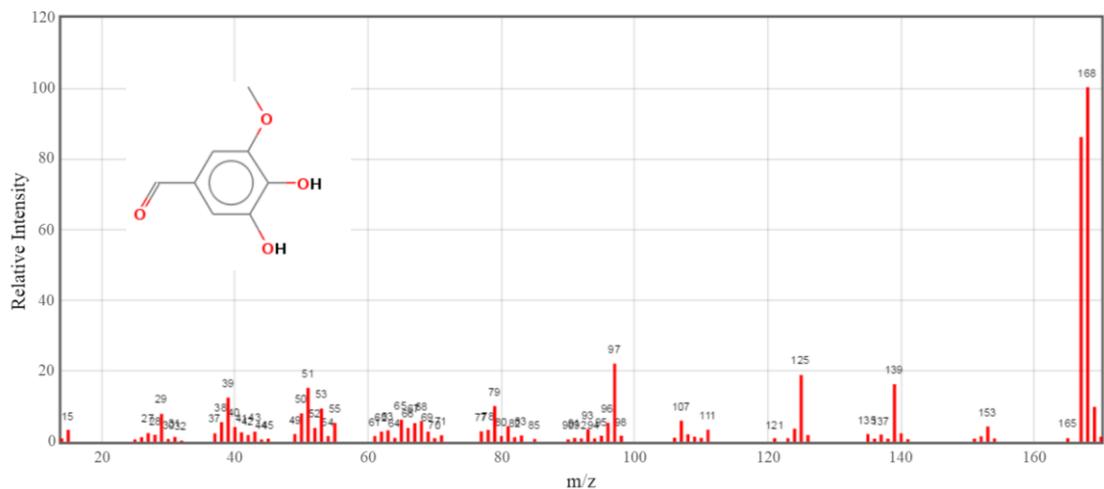


Figure S9. NIST mass spectrum of 3, 4- Dihydroxy-5-methoxybenzaldehyde, C₈H₈O₄ (MW = 168).

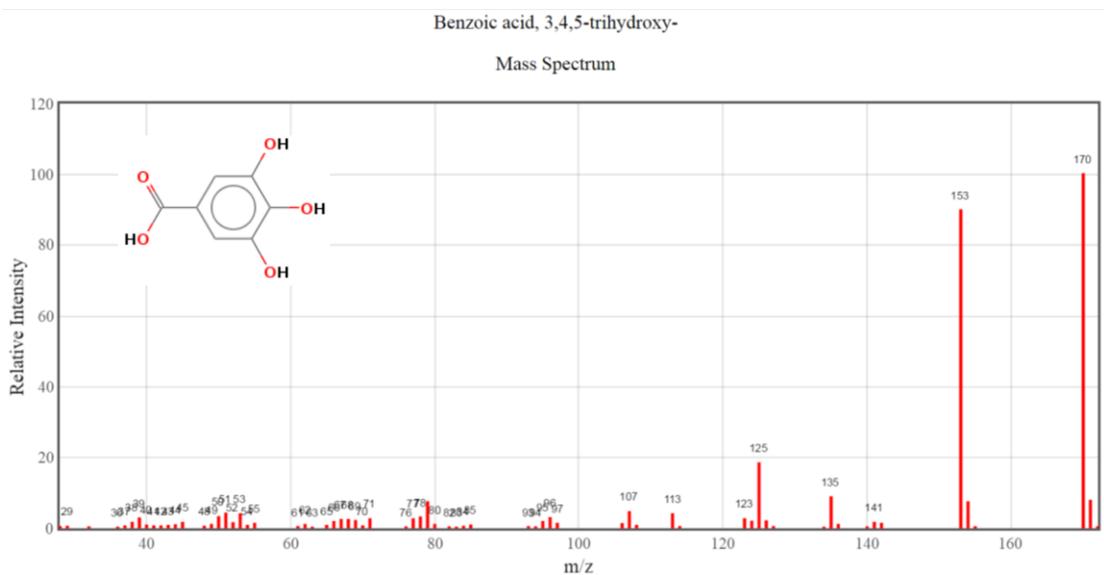


Figure S10. NIST mass spectrum of 3,4,5-Trihydroxybenzoic acid, C₇H₆O₅ (MW = 170).

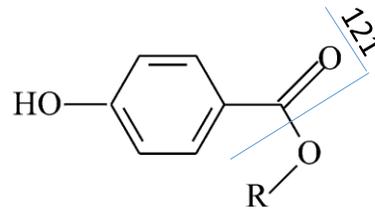


Figure S11. Proposed structure for fragment m/z 121

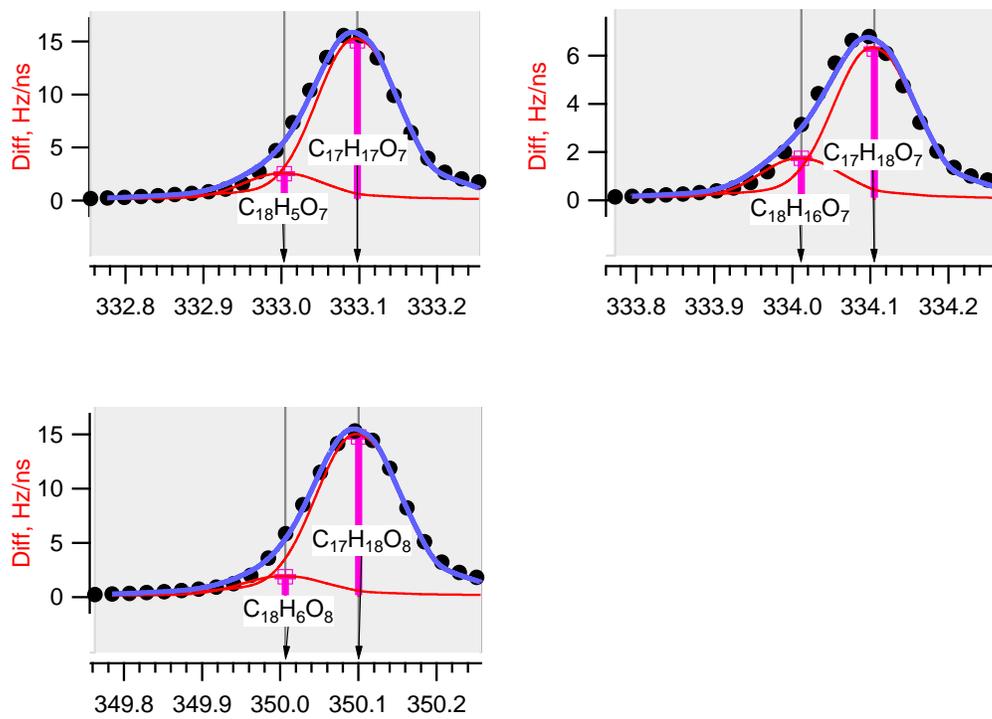
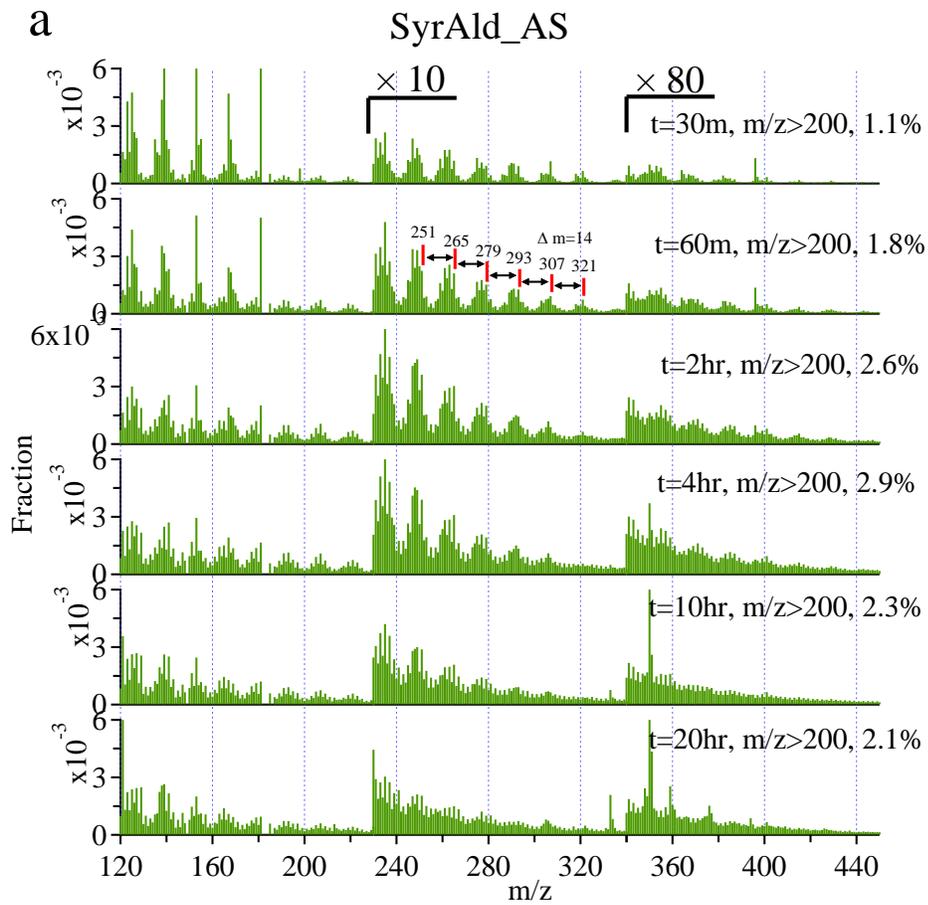
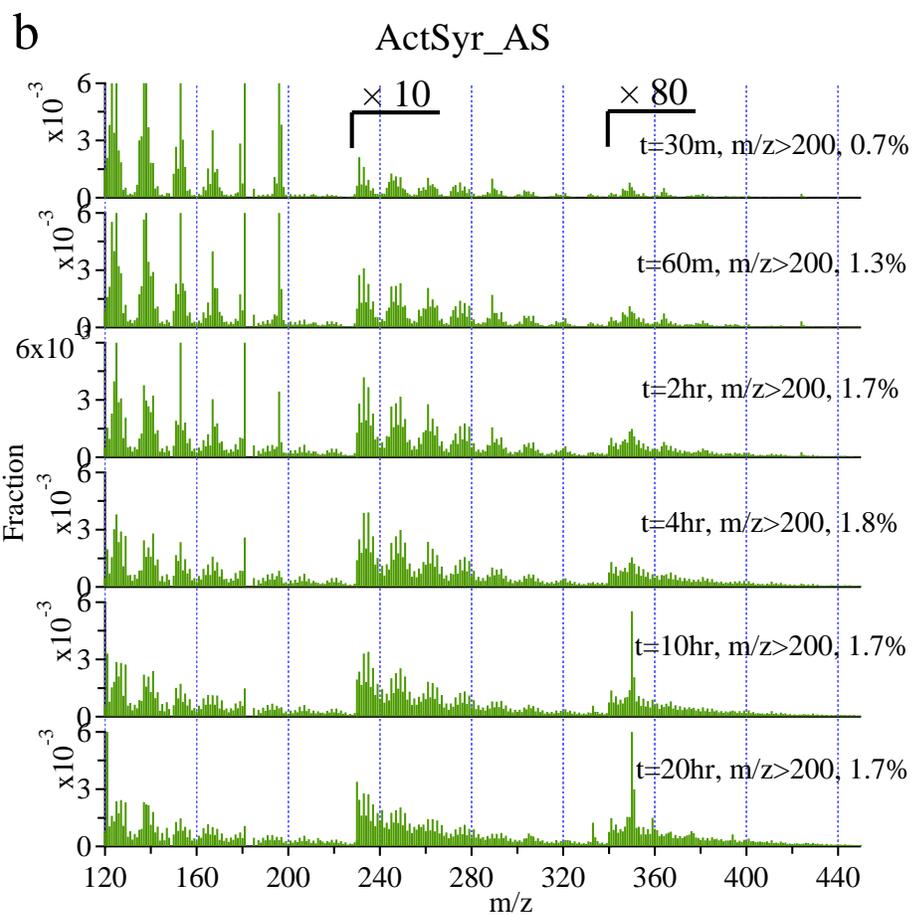
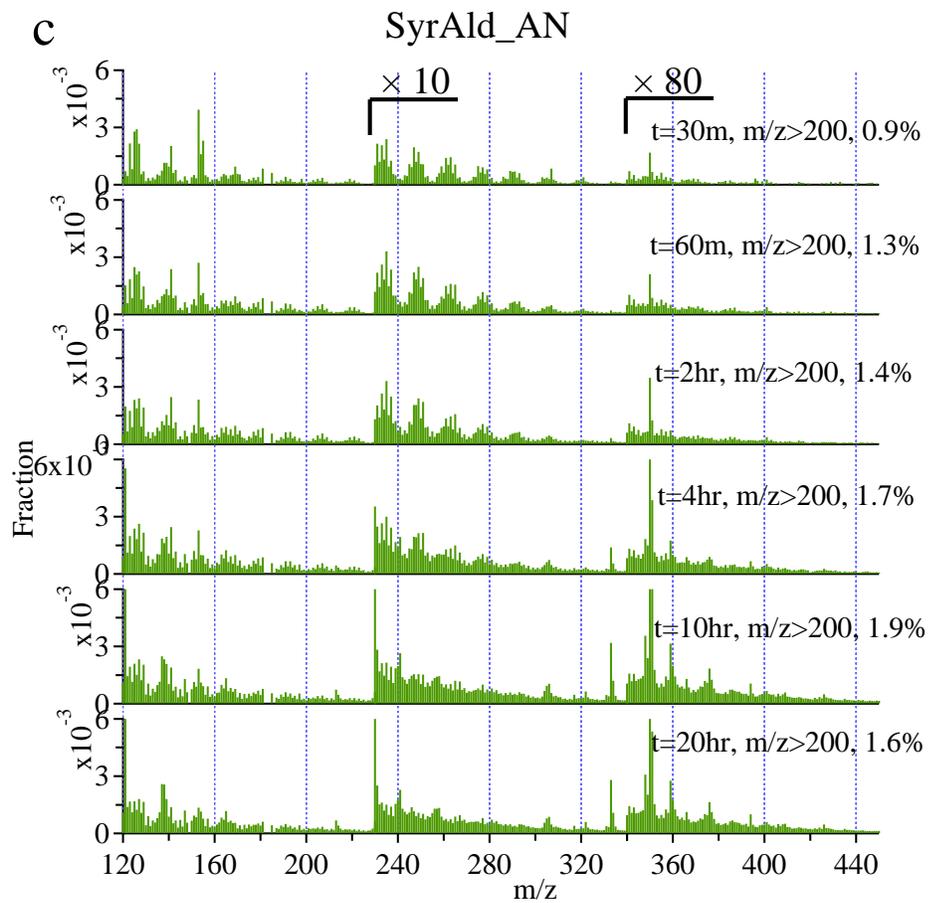


Figure S12. Peak fittings for the dimer compounds







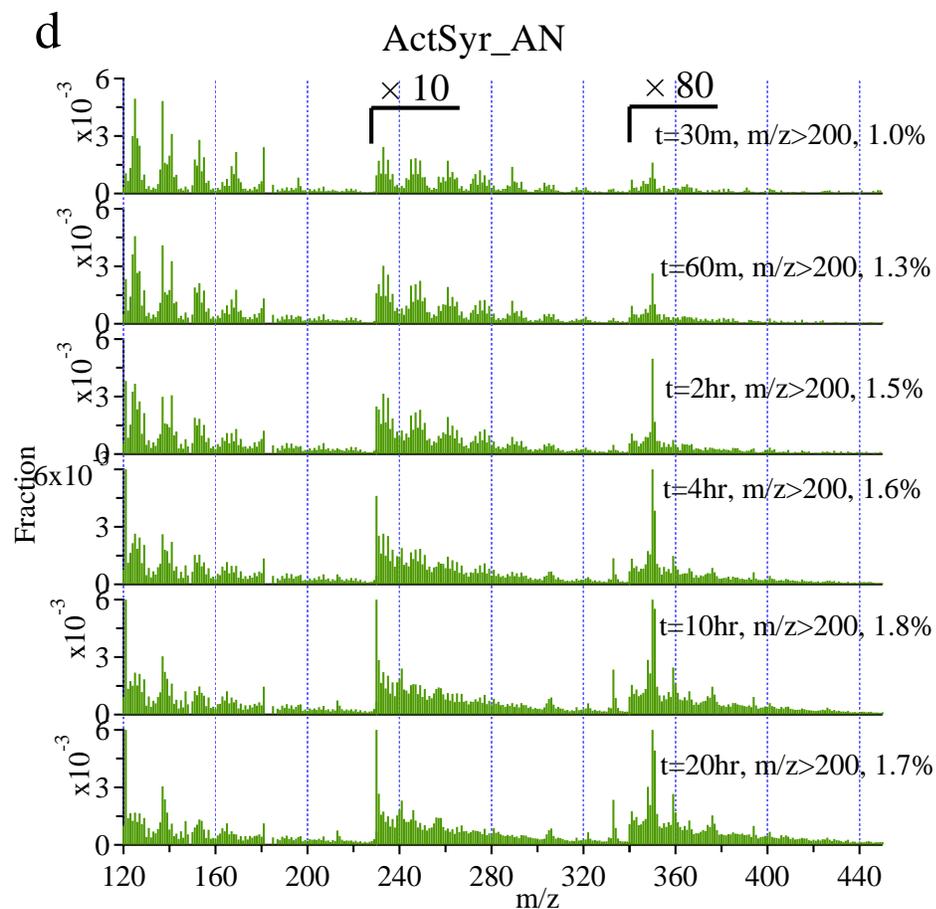


Figure S13. Mass spectra of aqSOA at different time of reactions in (a) SyrAld_AS, (b) ActSyr_AS, (c) SyrAld_AN, and (d) ActSyr_AN experiments.

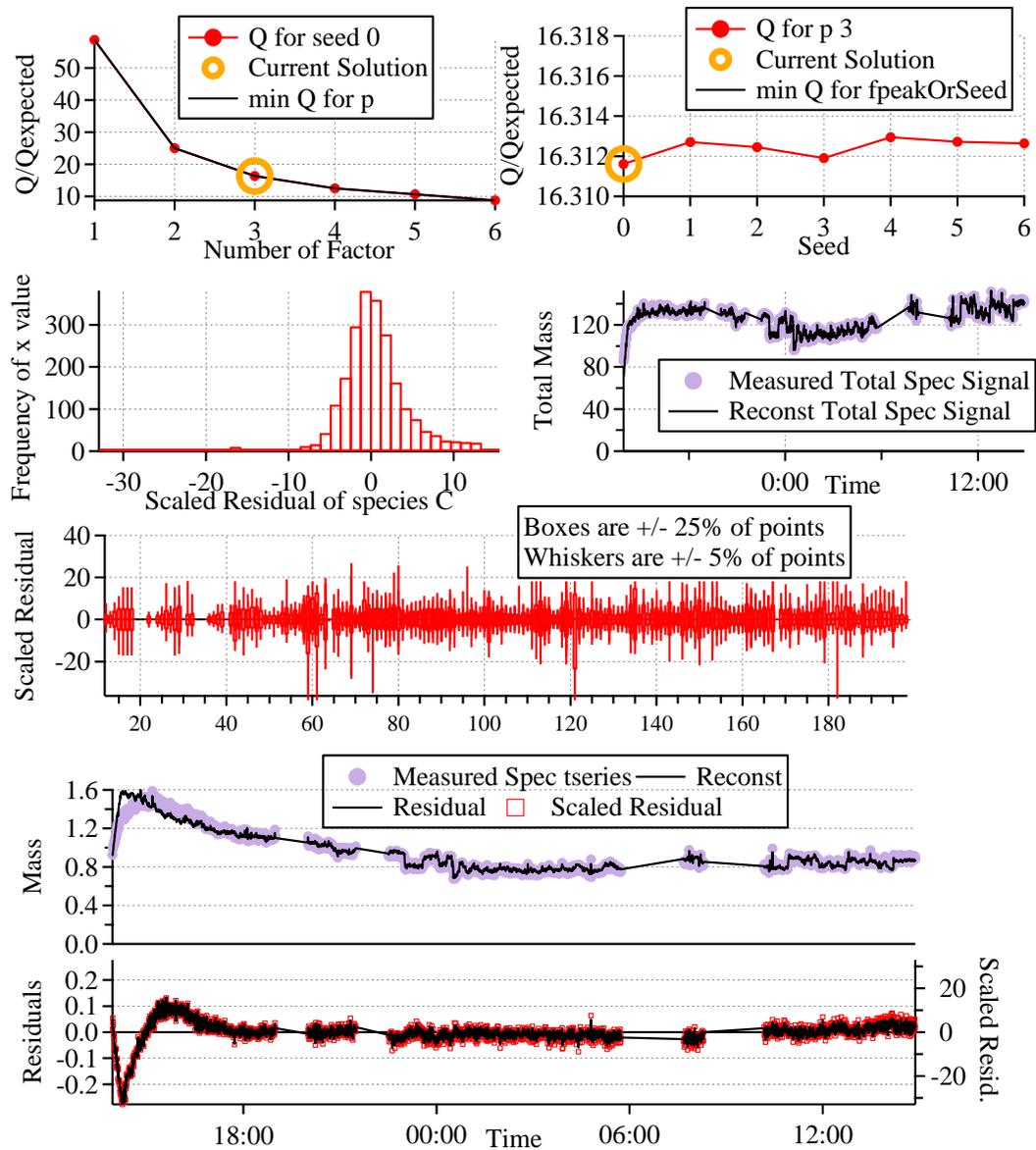


Figure S14 Three-factor solution for PMF analysis of SyrAld_AS, Diagnostic plot, fPeak=0, Seed varies from 0 to 6

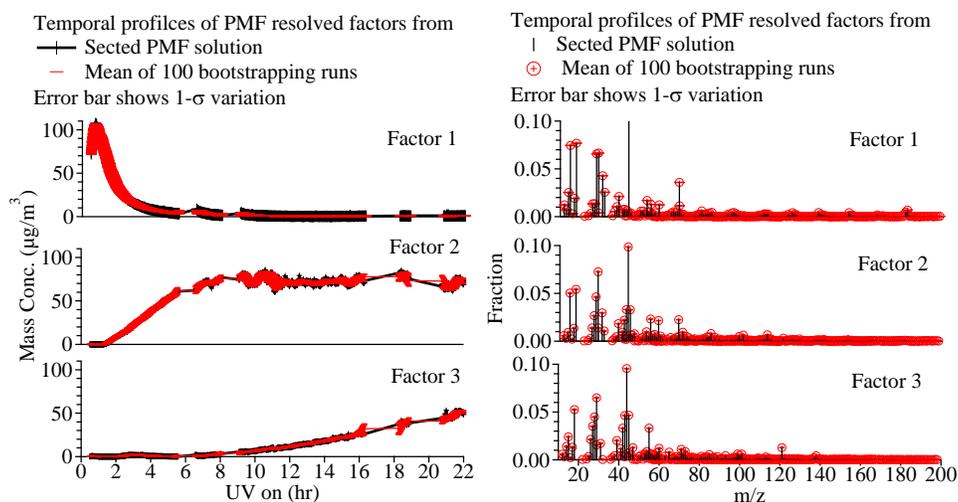


Figure S15 Bootstrapping analysis for the three-factor solution for SyrAld_AS

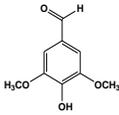
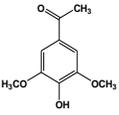
Precursor information Chemical structure Chemical formula O/C, H/C, OS _c	Syringaldehyde (SyrAld)		Acetosyringone (ActSyr)	
				
	C ₉ H ₁₀ O ₄ M.W. 182		C ₁₀ H ₁₂ O ₄ M.W. 196	
	0.44, 1.11, -0.23		0.4, 1.2, -0.4	
Inorganic components and initial concentrations	NH ₄ NO ₃ (AN) 200 µM	(NH ₄) ₂ SO ₄ (AS) 22.7 µM	NH ₄ NO ₃ (AN) 200 µM	(NH ₄) ₂ SO ₄ (AS) 22.7 µM
Initial concentrations of organic	30 µM (5.47ppm)	100 µM (18.22ppm)	30 µM (5.89ppm)	100 µM (19.62ppm)
Apparent first order decay rate (s ⁻¹)	1.3×10 ⁻³	0.87×10 ⁻³	1.4×10 ⁻³	0.41×10 ⁻³
TOC (ppm) when all precursors were consumed	3.3	9.2	3.5	11
OM/OC when all precursors were consumed	2.4	2.3	2.1	2.1
aqSOA(ppm) yield when all precursors were consumed	0.9	0.6	0.8	0.4
O/C, H/C, OS _c when all precursors were consumed	1.1, 1.52, 0.68	0.91, 1.54, 0.28	0.83, 1.49, 0.17	0.68, 1.46, -0.1

Table S1 Information for different experiments

References:

- (1) Pieber, S. M.; El Haddad, I.; Slowik, J. G.; Canagaratna, M. R.; Jayne, J. T.; Platt, S. M.; Prévôt, A. S. H. Inorganic Salt Interference on CO_2^+ in Aerodyne AMS and ACSM Organic Aerosol Composition Studies. *Environ. Sci. Technol.* **2016**. 50(19), 10494–10503.
- (2) Ulbrich, I. M.; Canagaratna, M. R.; Zhang, Q.; Worsnop, D. R.; Jimenez, J. L. Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data. *Atmos. Chem. and Phys.* **2009**. 9(9), 2891–2918.
- (3) Paatero, P., Hopke, P. K., Song, X.-H., & Ramadan, Z.: Understanding and controlling rotations in factor analytic models. *Chemometr and Intell Lab Syst*, 60(1–2), 253–264. 2002.
- (4) Zhang, Q.; Jimenez, J.; Canagaratna, M.; Ulbrich, I.; Ng, N.; Worsnop, D.; Sun, Y. Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review. *Analy. Bioanaly. Chem.* **2011**. 401(10), 3045–3067.