Supplement:

Real-time, controlled OH-initiated oxidation of biogenic secondary organic aerosol

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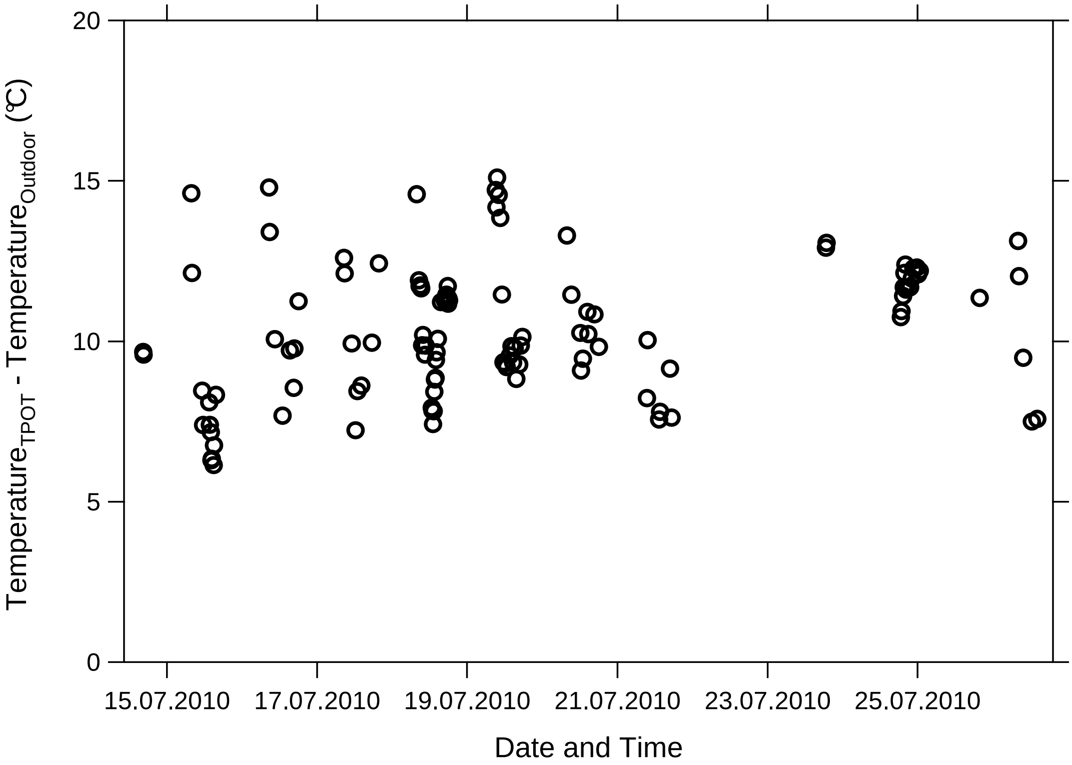


Figure S1. Difference between TPOT lamp housing and outdoor air temperatures.

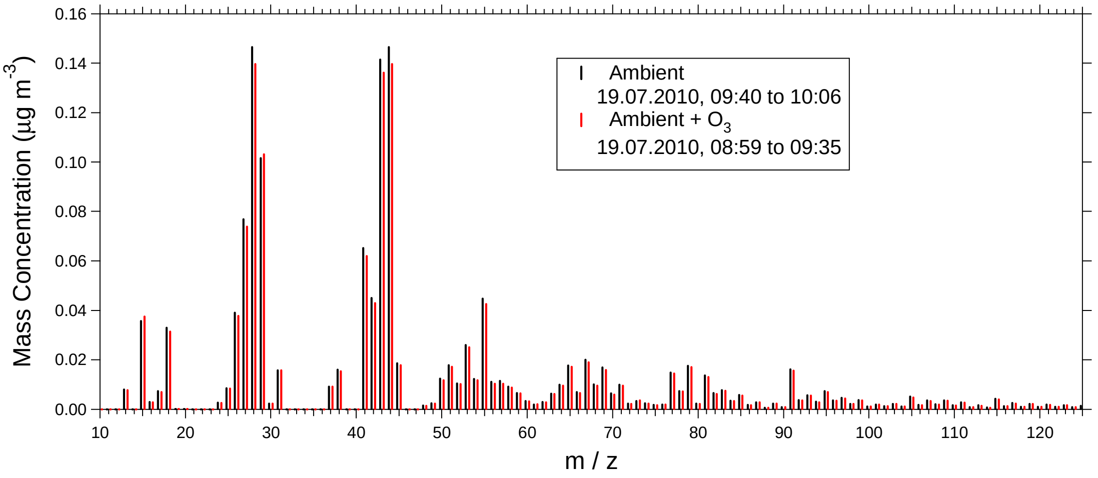


Figure S2. Sample mass spectra showing the effect of O_3 exposure on the organic mass spectrum. The O_3 concentration is ~1100 ppbv, which is the highest concentration used during the study. Spectra are obtained in sequence rather than as an average of alternating spectra. Therefore the slight mass decrease across the spectra (5% of organic mass) is likely influenced by changes in the ambient particle concentration. Mass increases of a similar magnitude are observed for some other control experiments of this type. In no case do mass increases or decrease exceed 5%.

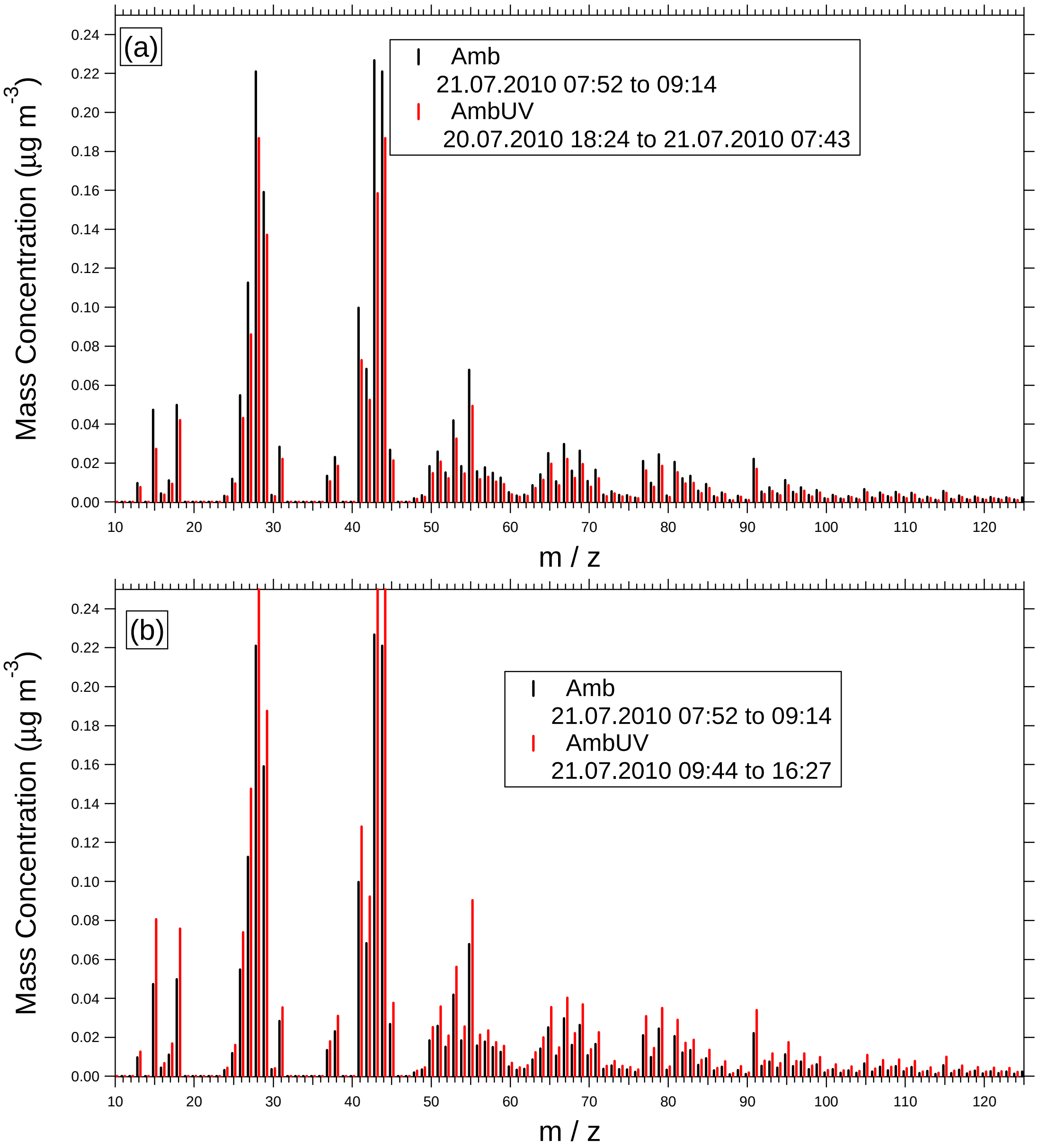


Figure S3. Sample organic mass spectra showing the effect of volatilization resulting from a 4 °C temperature increase on organic aerosol mass spectra. The two AmbUV spectra are the same as those displayed below in the AmbUV/AmbUVOH comparison in Fig. S4. Amb and AmbUV spectra are obtained in sequence.

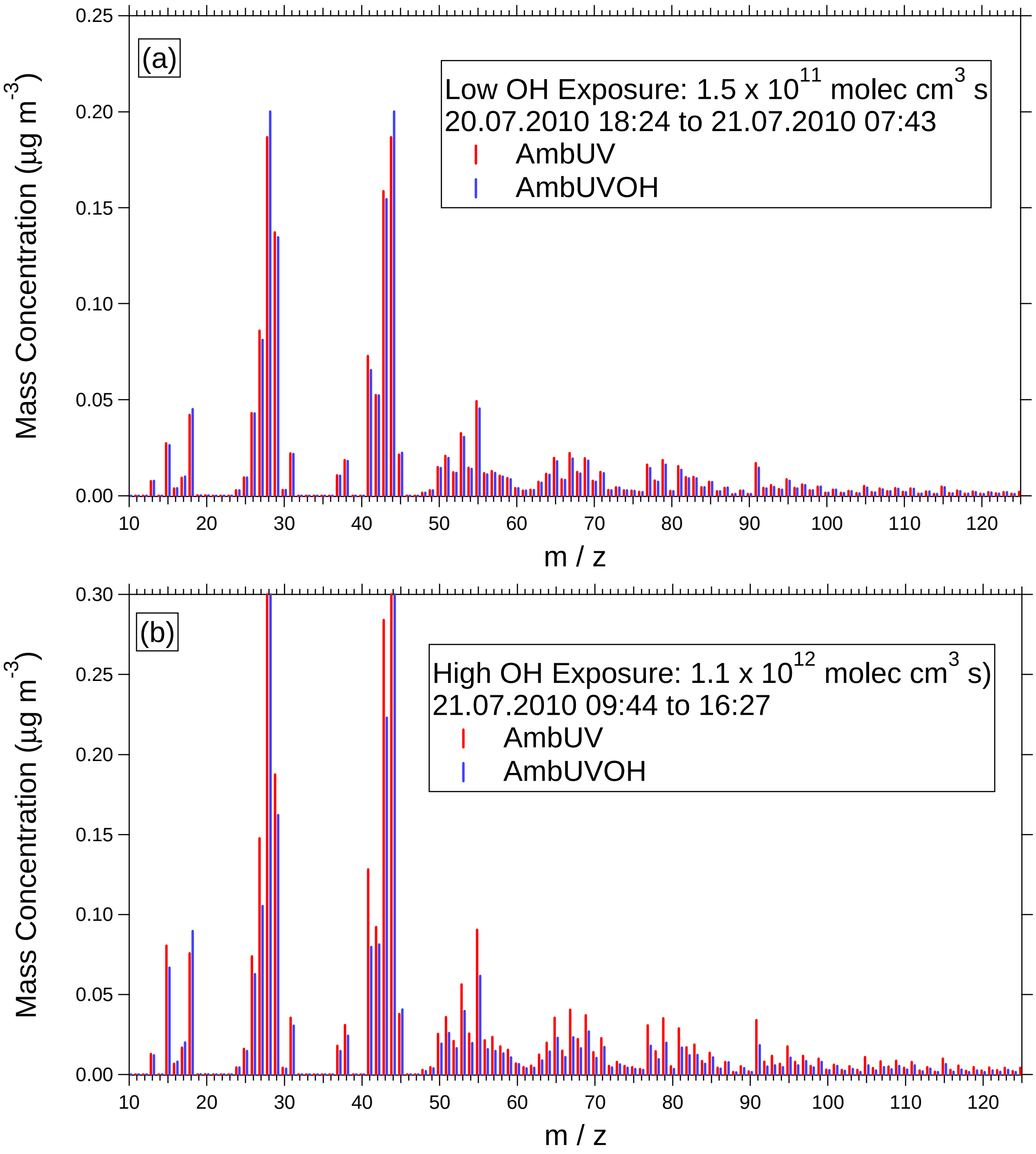


Figure S4. Sample organic mass spectra showing the effect of OH oxidation. The two AmbUV spectra are the same as those displayed in Fig. S3. AmbUV and AmbUVOH spectra are collected alternately (12 min per spectra) and averaged over the entire time period shown.

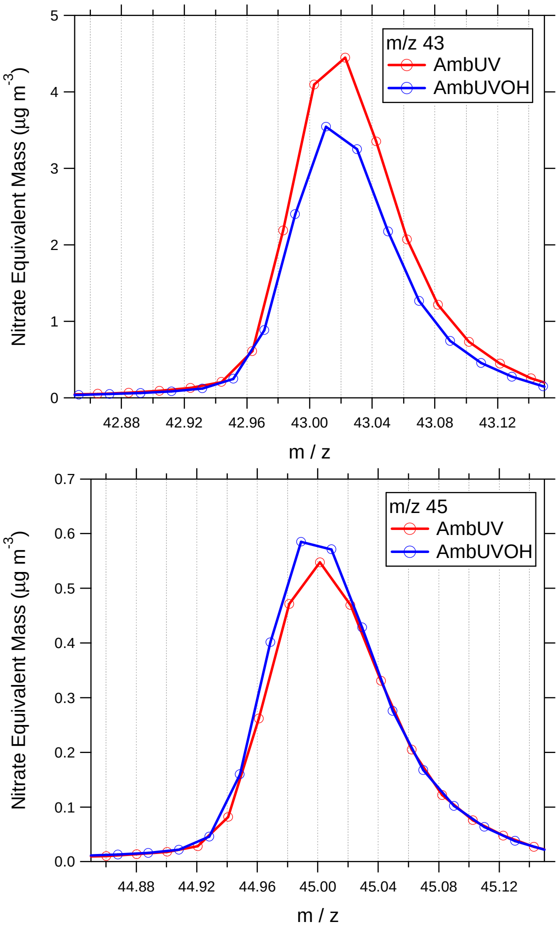
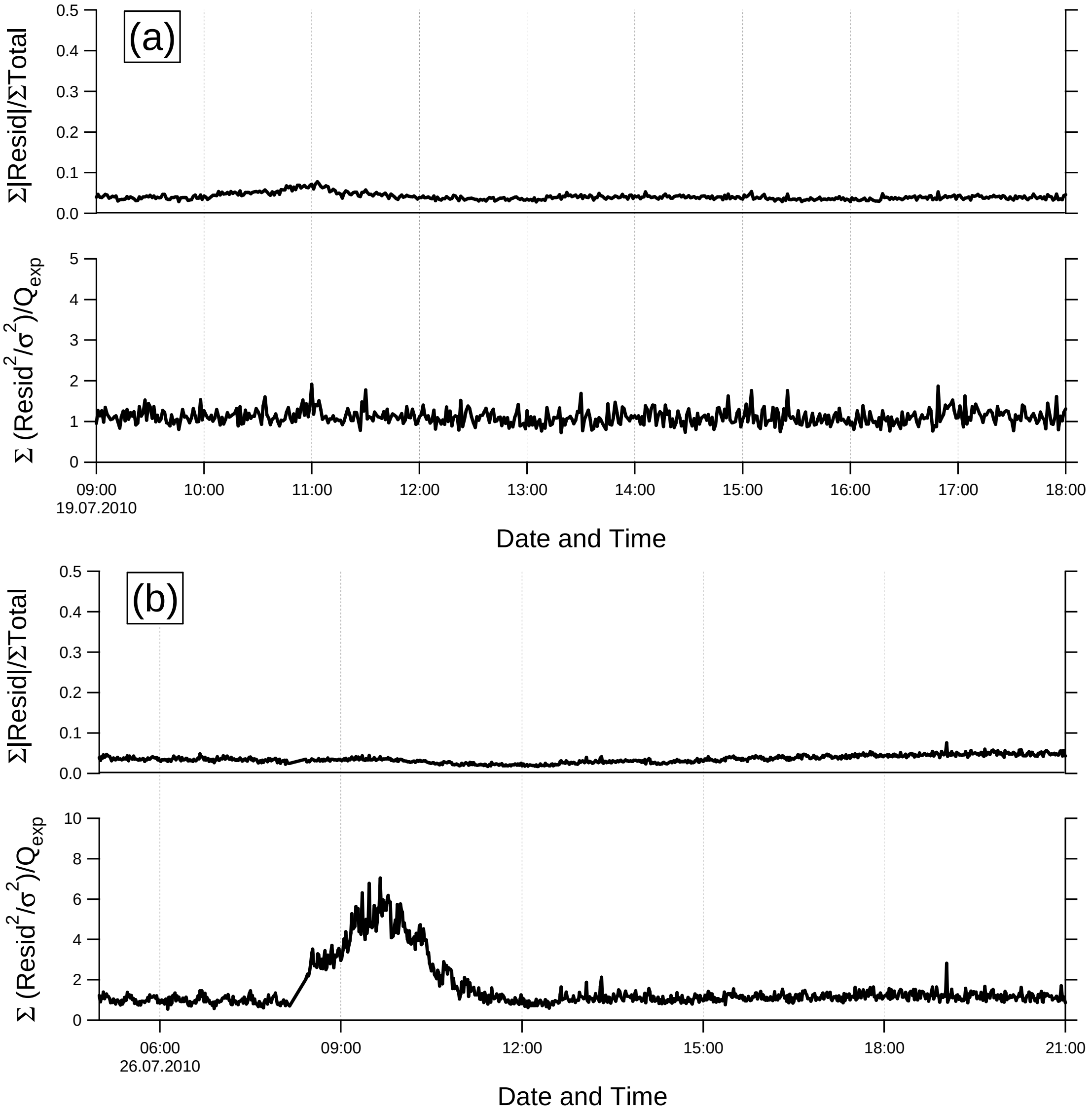


Figure S5. Expanded view of *m/z* 43 and 45 for the AmbUV and AmbUVOH conditions for the period shown in Fig. S4b (OH exposure of ~1.1 x 10^{12} molec cm^{-3} s). Although the C-ToF-AMS does not have the mass resolution to quantitatively distinguish ions occurring at the same nominal *m/z*, analysis of the raw spectral data supports HCO_2^+ as a strong contributor to *m/z* 45. The peak intensity at *m/z* 45 occurs at 45.00 amu (exact mass of HCO_2^+ = 45.00 amu). This can be compared with *m/z* 44 (peak intensity at 43.99 amu), which is known to be dominated by CO_2^+ (exact mass 43.99 amu). A further comparison with *m/z* 43 (peak intensity at 43.02 amu), which is likely dominated by the $C_2H_3O^+$ ion (exact mass 43.02 amu), suggests that sufficient *m/z* resolution is available to rule out dominant contributions from ions such as CH_3NO^+ (45.02 amu), $C_2H_5O^+$ (45.03 amu), and $C_2H_7N^+$ (45.06) amu. The CHS^+ (44.98 amu) and HN_2O^+ (45.01 amu) ions are more difficult to rule out based on the spectra, but are not consistent with observed trends towards oxidation (CHS^+) and organonitrate consumption during oxidation (HN_2O^+), discussed below.


(a)
Σ|Resid|/ΣTotal
0.0
0.1
0.2
0.3
0.4
0.5
Σ (Resid²/σ²)/Q_exp
0
1
2
3
4
5
09:00
19.07.2010
10:00
11:00
12:00
13:00
14:00
15:00
16:00
17:00
18:00
Date and Time
(b)
Σ|Resid|/ΣTotal
0.0
0.1
0.2
0.3
0.4
0.5
Σ (Resid²/σ²)/Q_exp
0
2
4
6
8
10
06:00
26.07.2010
09:00
12:00
15:00
18:00
21:00
Date and Time

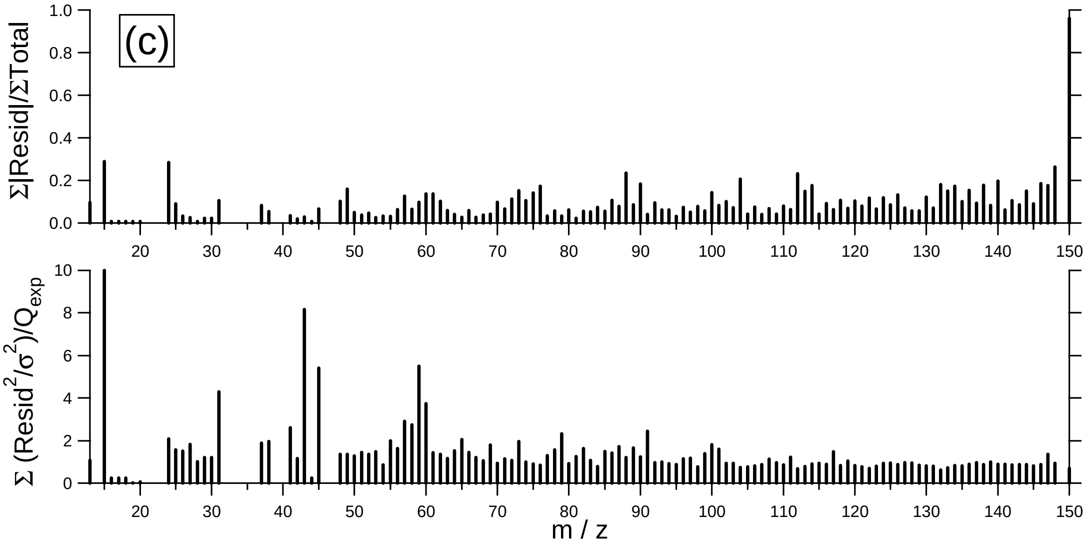


Figure S6. PMF residuals for the time series (a,b) and mass spectrum (c). Time series are shown for the periods displayed in Fig. 9a (a) and Fig. 9b (b), while mass spectral residuals are averaged over the entire dataset.

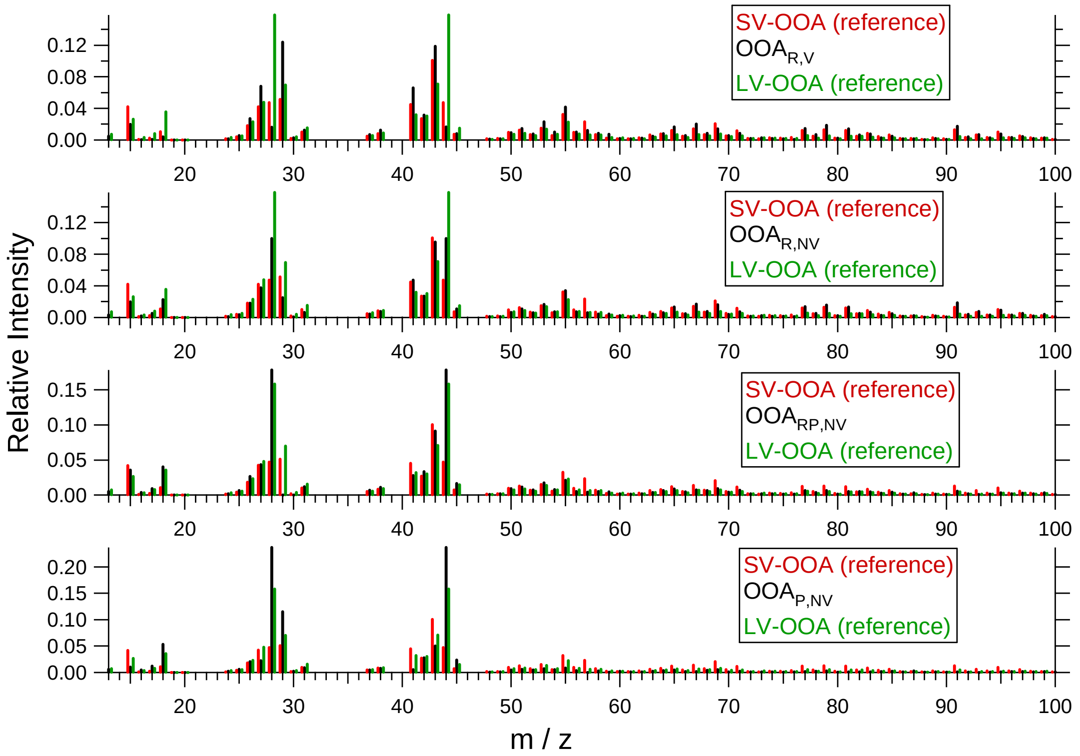


Figure S7. Mass spectral comparison of OOA spectra retrieved from PMF analysis of TPOT data with reference OOA spectra (Ng et al., 2011) obtained from the AMS Spectral Database (Ulbrich et al., 2009).

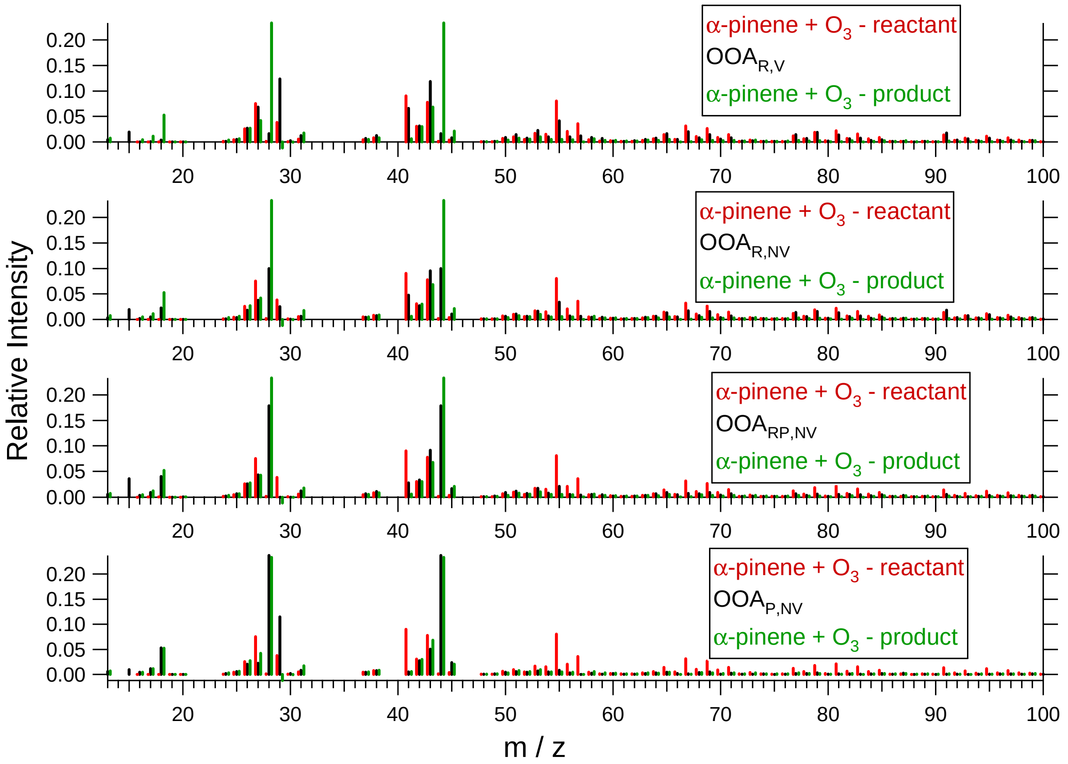


Figure S8. Mass spectral comparison of OOA spectra retrieved from PMF analysis of TPOT data with reactant and product spectra of oxidized OA from α-pinene ozonolysis (George and Abbatt, 2010).

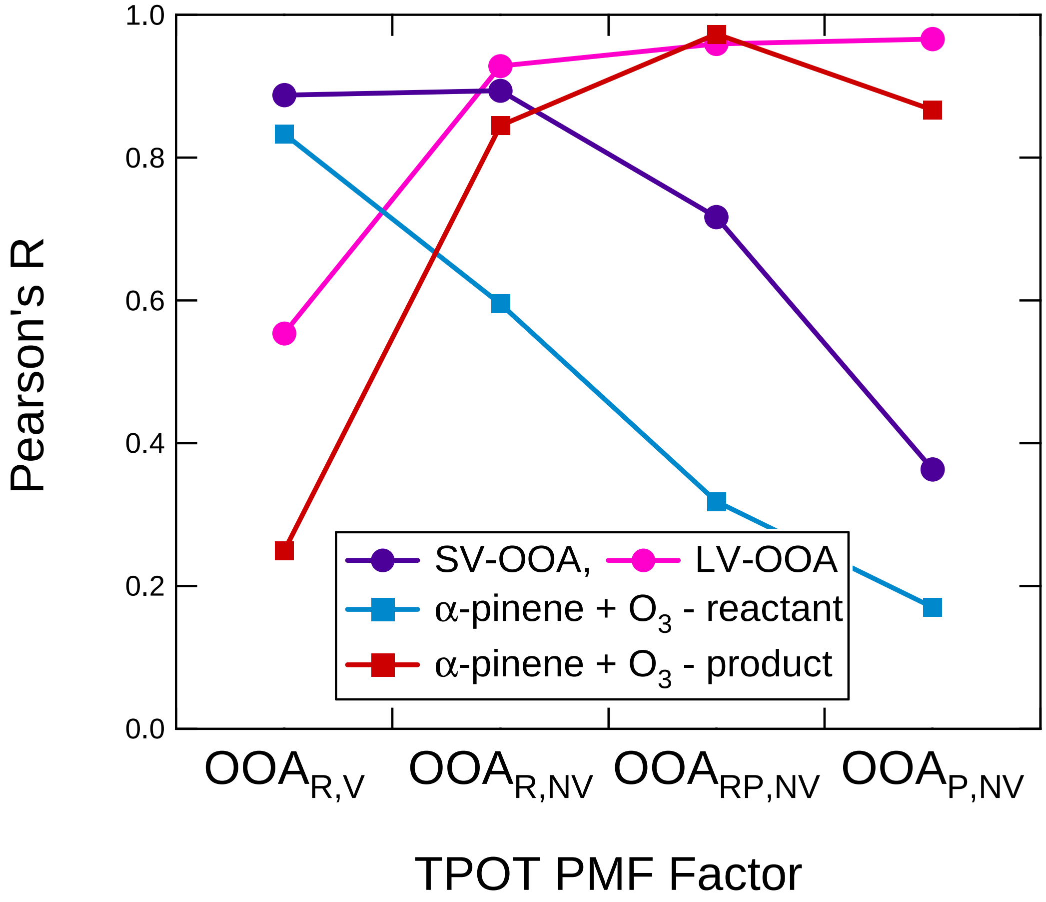


Figure S9. Correlation coefficients (Pearson's R) for the mass spectral comparison of TPOT PMF factors with reference spectra shown in Fig. S0. SV-OOA and LV-OOA reference spectra are from Ng et al., (2011) obtained from the AMS Spectral Database (Ulbrich et al., 2009). α-pinene ozonolysis factors are from George and Abbatt (2010).

Start	Stop	Org (μg m^{-3})	f_{43}	f_{44}
17.07.2010 11:05:00	17.07.2010 12:11:00	0.92	0.11	0.10
17.07.2010 14:21:00	17.07.2010 15:20:00	1.06	0.097	0.098
19.07.2010 08:59:00	19.07.2010 10:04:00	1.40	0.098	0.10
19.07.2010 11:41:00	19.07.2010 13:05:00	1.55	0.094	0.11
19.07.2010 15:19:00	19.07.2010 16:09:00	1.67	0.088	0.11
20.07.2010 07:55:00	20.07.2010 09:19:00	2.36	0.097	0.098
20.07.2010 13:02:00	20.07.2010 14:25:00	3.06	0.093	0.095
20.07.2010 16:40:00	20.07.2010 18:04:01	2.01	0.097	0.10
21.07.2010 07:52:00	21.07.2010 09:14:01	2.16	0.10	0.10
21.07.2010 12:17:00	21.07.2010 13:40:00	2.74	0.099	0.10
21.07.2010 16:54:01	21.07.2010 18:21:00	2.41	0.098	0.11
26.07.2010 08:25:01	26.07.2010 09:48:01	7.89	0.069	0.092
26.07.2010 12:32:01	26.07.2010 14:01:00	5.34	0.073	0.12
26.07.2010 17:13:00	26.07.2010 18:41:00	3.79	0.08	0.11

Table S1. Sampling times, organic mass loadings, f_{43}, and f_{44} for the Amb condition.

			AmbUV Condition			AmbUVOH Condition		
Start	Stop	OH Exposure	Org	f_{43}	f_{44}	Org	f_{43}	f_{44}
16.07.2010 18:20:00	17.07.2010 08:00:00	1.3e+12	0.59	0.092	0.12	0.5	0.086	0.23
17.07.2010 08:43:00	17.07.2010 14:19:01	1.3e+12	0.79	0.091	0.099	0.68	0.083	0.18
17.07.2010 12:20:00	17.07.2010 14:19:01	1.3e+12	0.76	0.087	0.098	0.67	0.081	0.17
17.07.2010 19:59:00	17.07.2010 22:32:00	1.8e+12	0.98	0.082	0.11	0.85	0.067	0.19
17.07.2010 22:47:00	18.07.2010 07:56:00	1.8e+12	0.9	0.089	0.1	0.74	0.071	0.19
19.07.2010 10:06:00	19.07.2010 13:01:00	1.7e+12	1.2	0.09	0.11	0.93	0.073	0.19
19.07.2010 16:13:00	19.07.2010 18:10:00	1.9e+10	1.5	0.084	0.12	1.6	0.084	0.12
19.07.2010 18:36:01	20.07.2010 05:18:00	1.5e+11	1.4	0.085	0.11	1.4	0.083	0.13
19.07.2010 18:38:00	21.07.2010 07:46:00	1.5e+11	1.7	0.09	0.11	1.7	0.088	0.12
20.07.2010 05:55:00	20.07.2010 18:21:00	1.5e+11	2.2	0.089	0.1	2.1	0.088	0.11
20.07.2010 18:23:00	21.07.2010 07:48:00	1.5e+11	1.7	0.094	0.11	1.7	0.093	0.12
21.07.2010 07:49:00	21.07.2010 16:52:00	1.1e+12	2.2	0.094	0.11	1.9	0.085	0.15
21.07.2010 16:53:00	21.07.2010 22:20:00	1.5e+12	1.9	0.09	0.11	1.6	0.08	0.16
21.07.2010 17:10:00	21.07.2010 22:43:00	1.5e+12	1.9	0.089	0.11	1.6	0.08	0.16
23.07.2010 18:54:00	24.07.2010 07:38:01	5.8e+11	1	0.086	0.11	0.87	0.07	0.17
21.07.2010 22:21:00	22.07.2010 04:44:00	1.5e+12	1.4	0.09	0.11	1.2	0.079	0.17
25.07.2010 19:54:00	26.07.2010 05:13:00	7.5e+11	1.8	0.086	0.11	1.6	0.074	0.15
26.07.2010 05:14:00	26.07.2010 08:21:00	7.5e+11	2	0.085	0.11	1.8	0.074	0.15
26.07.2010 08:24:01	26.07.2010 12:13:00	1.6e+11	7.4	0.067	0.11	7.8	0.067	0.11
26.07.2010 12:14:01	26.07.2010 19:40:00	1.6e+11	3.8	0.073	0.12	4	0.073	0.12

Table S2. Sampling times, OH exposures (molec cm^{-3} s), organic mass loadings (µg m^{-3}),

f_{43}, and f_{44} for the AmbUV and AmbUVOH conditions. Note that these conditions alternate every 12 minutes throughout the sampling period.

References

Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Zhang, Q., Ulbrich, I. M., and Worsnop, D. R.: Real-time methods for estimating organic component mass concentrations from aerosol mass spectrometer data, Environ. Sci. Technol., 45, 910-916, 2011.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from positive matrix factorization of aerosol mass spectrometric data, Atmos. Chem. Phys., 9, 2891-2918, 2009.