

Transformation of logwood combustion aerosols in a smog chamber – Implications for day and nighttime aging

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SUPPORTING INFORMATION

S1: Emission characterization and particle size distributions

S2: SOA-to-POA ratio analysis of experiment 3A

S3: Positive matrix factorization (PMF), the identification of factors

S4: PMF diagnostics and FPEAK analysis

Supplement S1: Emission characterization and particle size distributions

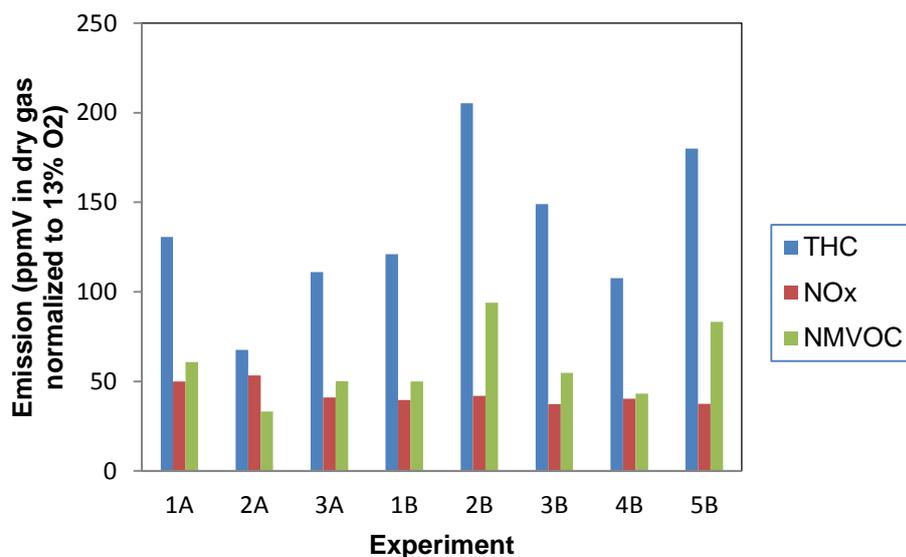


Figure S1: Total hydrocarbon (THC), NO_x and non-methane VOC (NMVOC) emissions (FTIR) from logwood emissions for all experiments.

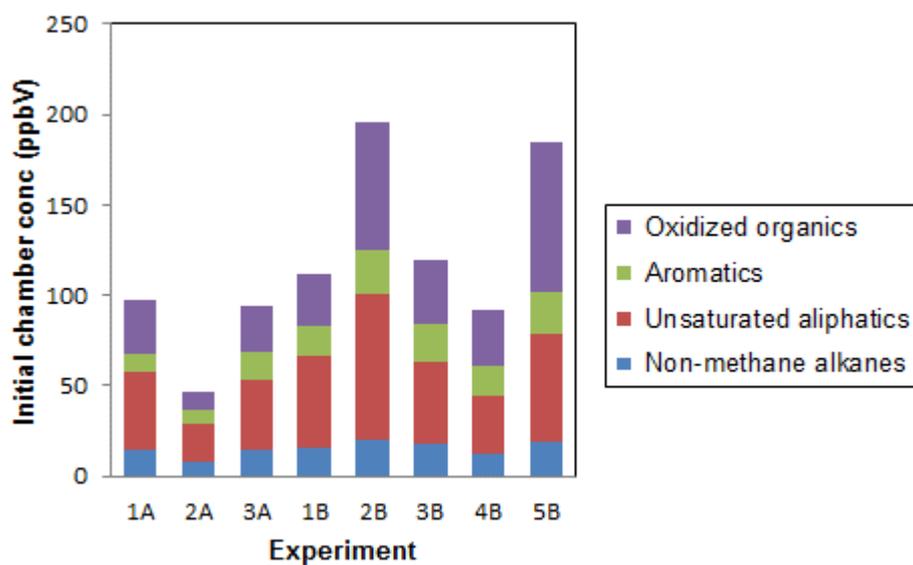


Figure S2: Gas-phase organic emissions (FTIR) from logwood combustion for all experiments. Emissions are calculated for initial chamber concentrations.

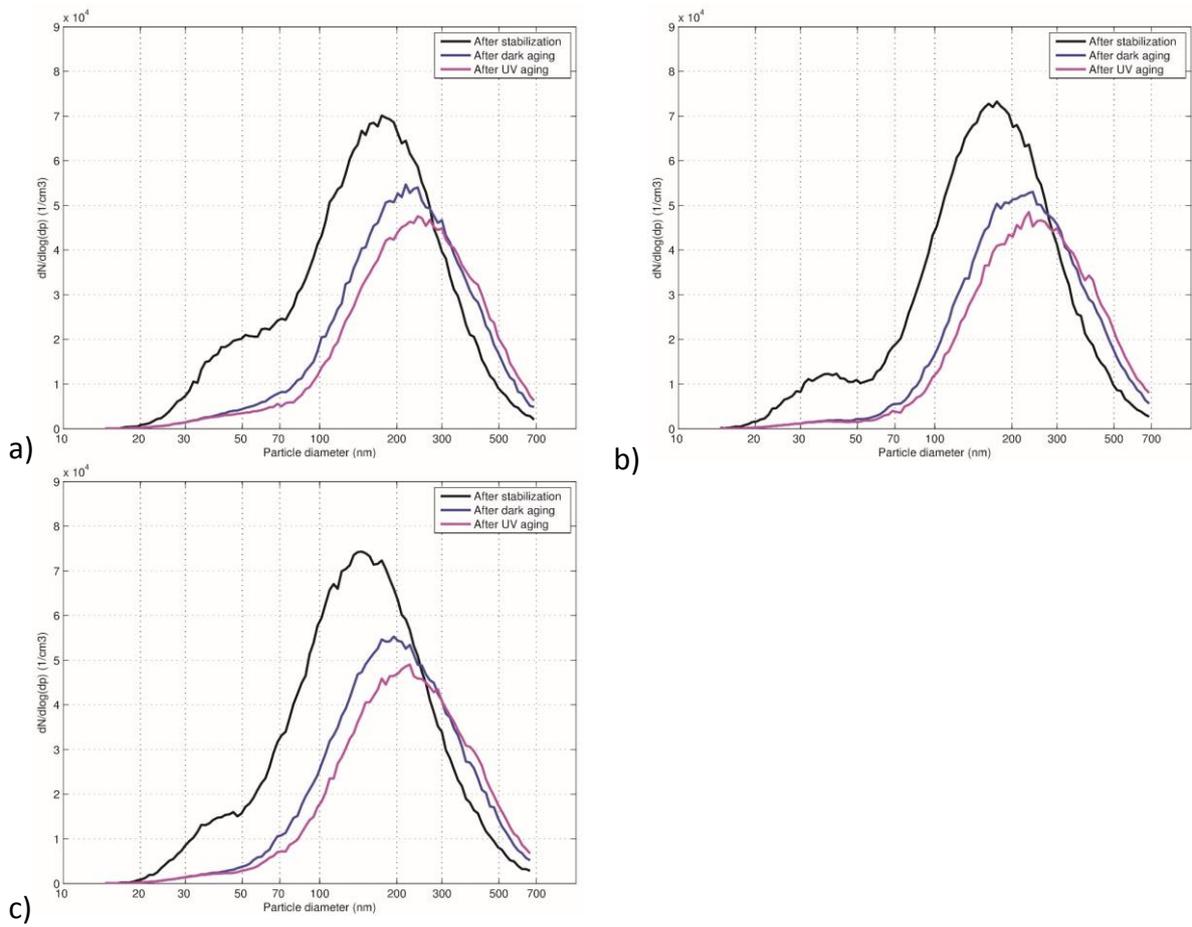


Figure S3: Wall loss corrected size distributions for the first set of experiments (a) 1A, (b) 2A, and (c) 3A.

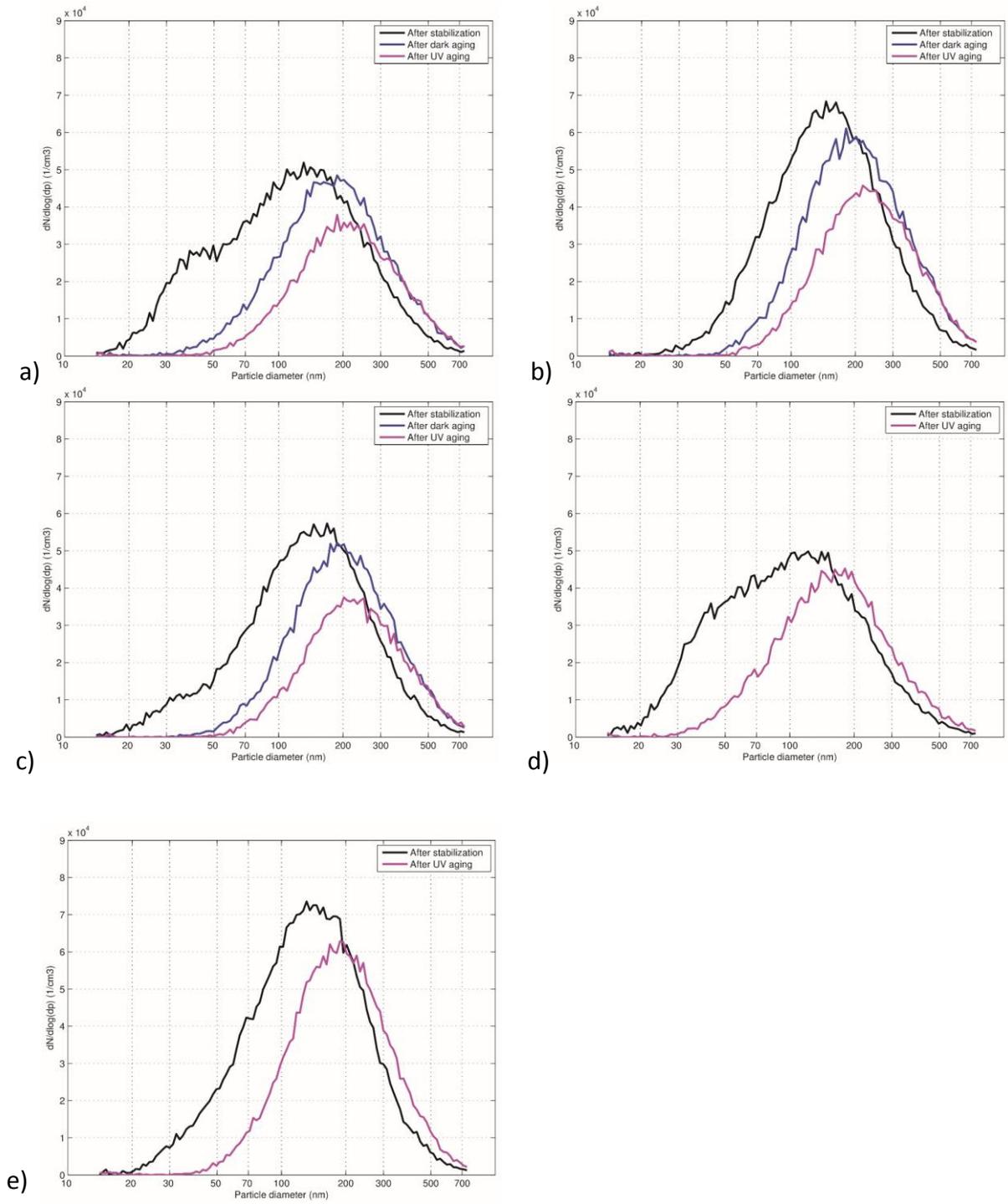


Figure S4: Wall loss corrected size distributions for the second set of experiments (a) 1B, (b) 2B, (c) 3B, (d) 4B, and (e) 5B.

Table S1: Flue gas compounds measured during the experiments using FTIR.

APP-153 Calibrations		1/1/2005		Range 1	Unit	Range 2	Unit
Gas	Formula	CAS					
1 Water vapour	H2O	7732-18-5			30 %		
2 Carbon dioxide	CO2	124-38-9			25 %		
3 Carbon monoxide	CO	630-08-0		5000 ppm		2 %	
4 Nitrous oxide	N2O	10024-97-2		200 ppm			
5 Nitrogen monoxide	NO	10102-43-9		1000 ppm			
6 Nitrogen dioxide	NO2	10102-44-0		200 ppm			
7 Sulphur dioxide	SO2	7446-09-5		1000 ppm			
8 Carbonyl sulfide	COS	463-58-1		100 ppm			
9 Ammonia	NH3	7664-41-7		500 ppm			
10 Hydrogen chloride	HCl	7647-01-0		200 ppm			
11 Hydrogen cyanide	HCN	74-90-8		100 ppm			
12 Hydrogen fluoride	HF	7664-39-3		100 ppm			
13 Methane	CH4	74-82-8		1000 ppm			
14 Ethane	C2H6	74-84-0		200 ppm			
15 Propane	C3H8	74-98-6		200 ppm			
16 Butane	C4H10	106-97-8		200 ppm			
17 Pentane	C5H12	109-66-0		200 ppm			
18 Hexane	C6H14	110-54-3		200 ppm			
19 Heptane	C7H16	142-82-5		200 ppm			
20 Octane	C8H18	111-65-9		200 ppm			
21 Acetylene	C2H2	74-86-2		200 ppm			
22 Ethylene	C2H4	74-85-1		200 ppm			
23 Propene	C3H6	115-07-1		200 ppm			
24 1,3-Butadiene	C4H6	106-99-0		200 ppm			
25 Benzene	C6H6	71-43-2		200 ppm			
26 Toluene	C7H8	108-88-3		200 ppm			
27 m-Xylene	C8H10	108-38-3		200 ppm			
28 o-Xylene	C8H10	95-47-6		200 ppm			
29 p-Xylene	C8H10	106-42-3		200 ppm			
30 1,2,3-Trimethylbenzene	C9H12	526-73-8		200 ppm			
31 1,2,4-Trimethylbenzene	C9H12	95-63-6		200 ppm			
32 1,3,5-Trimethylbenzene (Mesitylene)	C9H12	108-67-8		200 ppm			
33 Formic acid	CH2O	64-18-6		200 ppm			
34 Acetic acid	C2H4O2	64-19-7		200 ppm			
35 Formaldehyde	CH2O	50-00-0		200 ppm			
36 Acetaldehyde	C2H4O	75-07-0		200 ppm			
37 Methanol	CH3OH	67-56-1		500 ppm			
38 Ethanol	C2H5OH	64-17-5		500 ppm			
39 Propanol	C3H7OH	71-23-8		500 ppm			
40 Methyl tertiary butyl ether (MTBE, tert-Butyl methyl ether)	C5H12O	1634-04-4		200 ppm			

Supplement S2: SOA-to-POA ratio analysis of experiment 3A

There were no obvious reason for the high SOA-to-POA ratio in experiment 3A compared to other experiments. It can be e.g. due to slight different unspecified burning condition leading to lower POA and higher SOA / POA ratios. The SOA emissions were almost the same in experiment 3A (175 mg kg^{-1}) than in experiment 2A for beech ($170 \text{ mg kg}^{-1}\text{fuel}$) although SOA-to-POA ratio was much higher.

Supplement S3: Positive matrix factorization, the identification of factors

The identification of factors was conducted as follows. The 2-factor PMF solution separated secondary organic aerosol (SOA) and primary organic aerosol (POA) from the total OA spectra. The 3-factor solution split the POA factor into two separate POA factors, i.e., POA1 and POA2, and the 4-factor solution split the SOA factor into two separate SOA factors, i.e., SOA1 and SOA2. A third SOA factor was identified in the 5-factor solution.

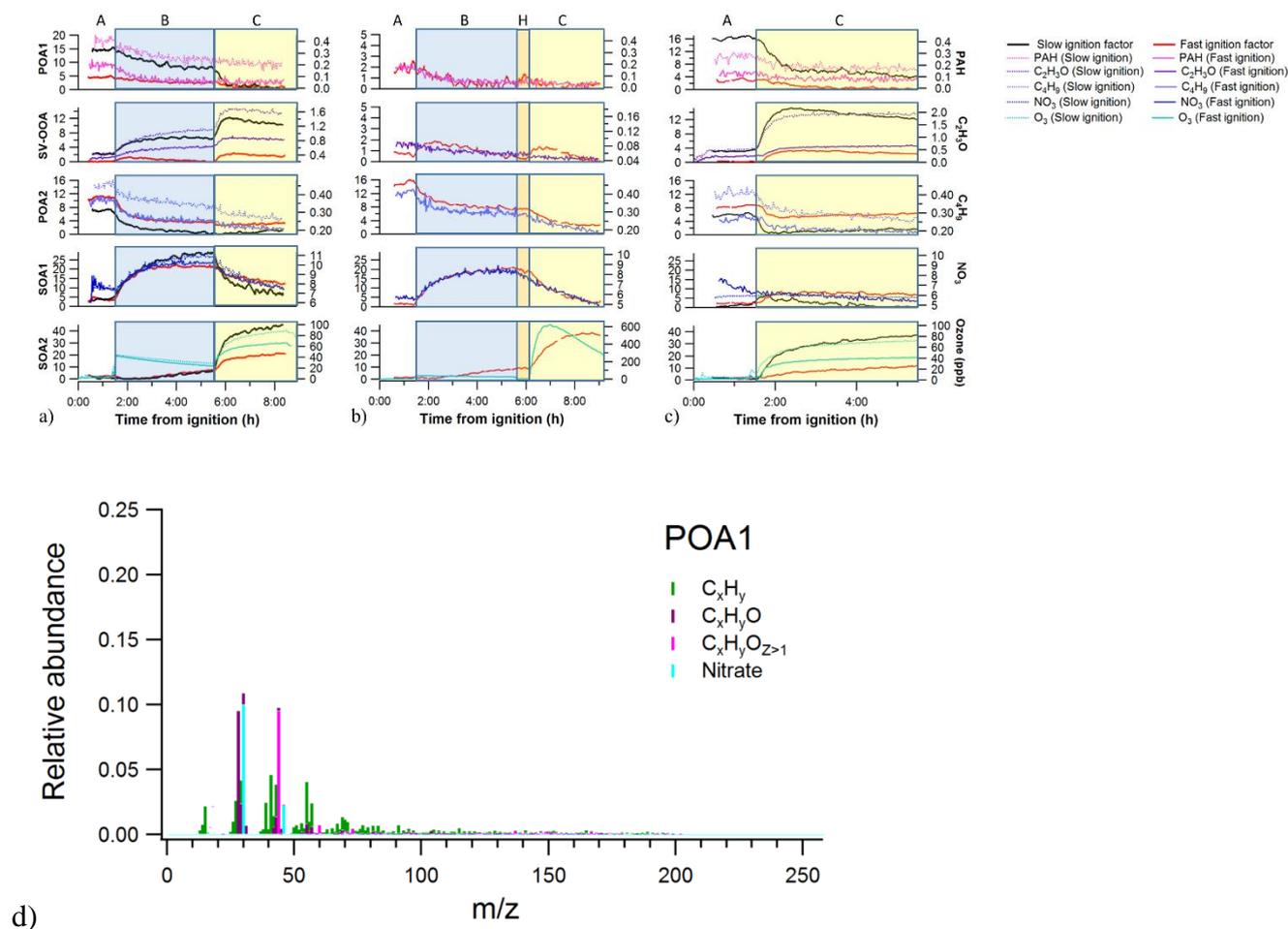
The POA1 spectra (Fig. S5) corresponded with the wood BBOA (Kortelainen et al., 2015) and LV-OOA spectra, and the carbon oxidation state (OS) was higher than in standard BBOA (Ng et al., 2011b). This finding was likely caused by softwood material (see Section 3.3). The time series of POA1 was best correlated with the PAH concentration ($R = 0.8$).

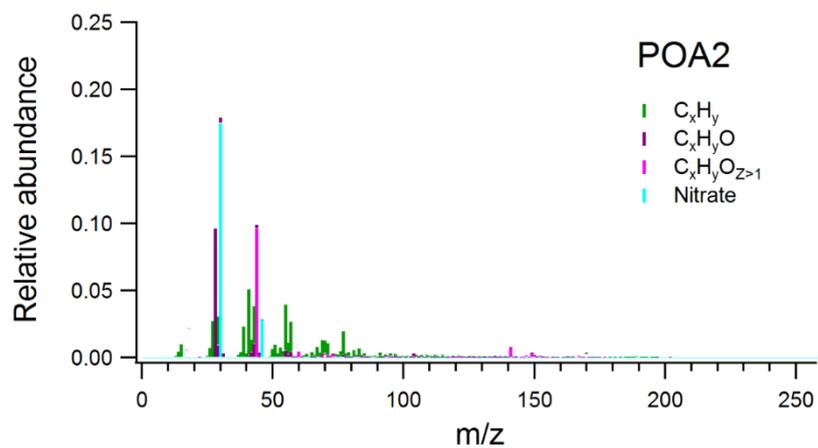
The POA2 time series was best correlated with the HOA tracer ion (C_4H_9), representing the hydrocarbon-like composition of this factor (Fig. S5), and its spectra corresponded with the HOA spectra (Aiken et al., 2009) with a correlation coefficient R of 0.6. The HOA characteristic of this factor was also supported by the slightly lower OS_c of POA2 than in POA1 (Table 7). The POA2 spectra were similar to the wood BBOA spectra (Kortelainen et al., 2015) and the OOA spectra (Aiken et al., 2009). Thus, the commonly identified hydrocarbon-like organic aerosol (HOA) factor could not be isolated in this work and was probably part of the POA factors. This conclusion is as expected because the aliphatic compounds in wood pyrolysis products contain oxygen functional groups.

The SOA1 spectra identified in this work corresponded best with SV-OOA (Aiken et al., 2009; Kortelainen et al., 2015), having a higher oxidation state than the POA factors, but a clearly lower oxidation state than the other SOA factors, i.e., SOA2 and SOA3 (Table 6). In contrast to the POA factors, SOA1 appeared only after ozone addition and was well correlated with the $C_2H_3O^+$ ion ($R=0.9$), a commonly used less oxidized OA tracer, which indicates the condensed less oxidized OA fraction and the semi-volatile characteristic of this factor.

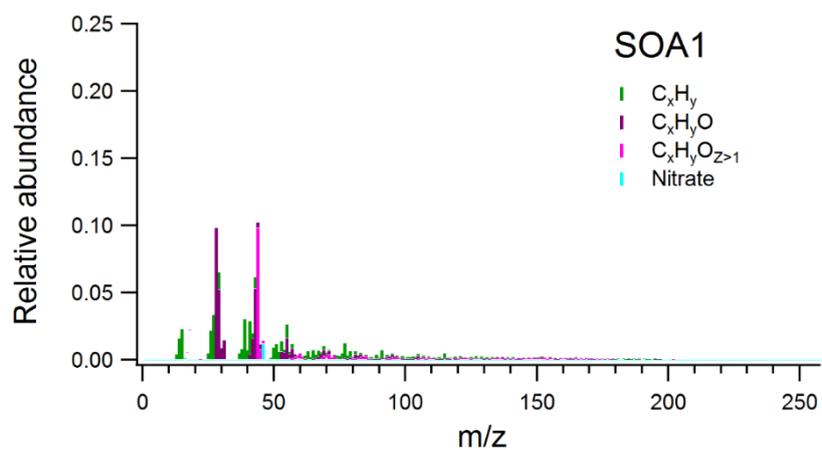
The SOA2 spectra corresponded well with the ambient LV-OOA (Aiken et al., 2009) and wood combustion LV-OOA spectra (Kortelainen et al., 2015), containing highly oxidized OOA. The mass spectra of LV-OOA are typically associated with a high peak at m/z 44 due to the presence of CO_2^+ . In addition, the SOA2 time series was well correlated with the particle-phase NO_3^- time series, especially in the dark aging experiments (Fig. S5), indicating the presence of organonitrates (Farmer et al., 2010), such as those formed during dark aging (Rollins et al., 2012). The SOA3 spectra were in agreement with the standard LV-OOA and wood combustion

LV-OOA spectra. These factors appeared when the UV lights were switched on. In addition to ozone, the SOA3 time series was well correlated with SO_4 ($R \geq 0.9$), NH_4^+ , and CO_2^+ -ion, which are important LV-OOA tracers in ambient air (Ng et al., 2011b). Supplement S4 represents details of the FPEAK analyses from which an FPEAK value of -0.9 was selected for further analyses.

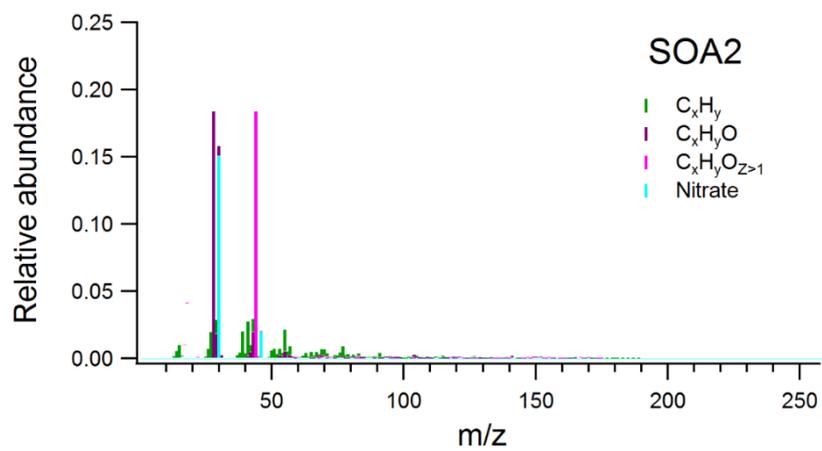




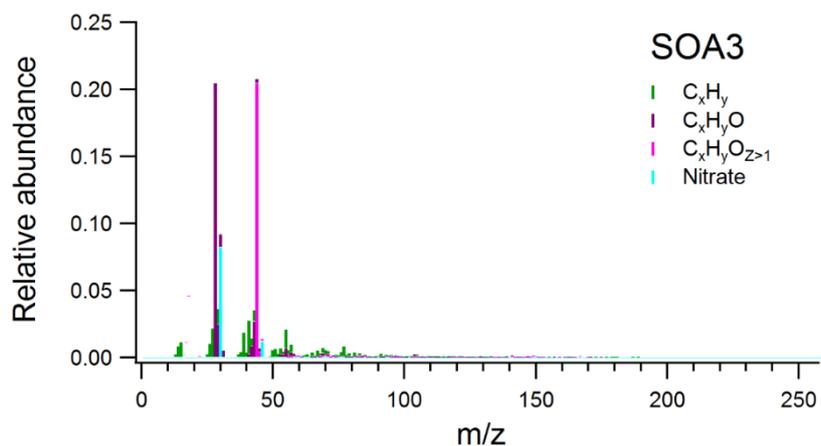
e)



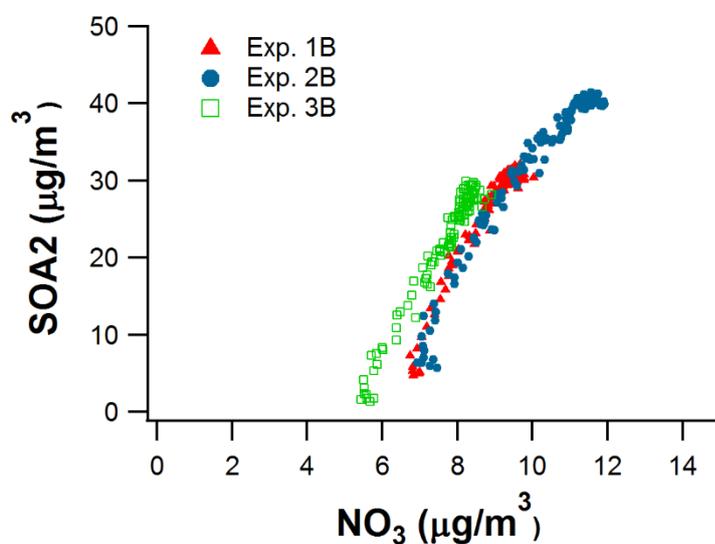
f)



g)



h)



i)

Figure S5: Mass concentrations of PMF factors (CE=1 and RIE=1) together with tracers (PAH, C_2H_3O , C_4H_9 , particle-phase NO_3 and O_3 for experiments (a) 1B and 2B, (b) 3B, and (c) 4B and 5B. Also corresponding normalized mass spectra (d-h) and SOA2 vs. particulate nitrate (i) during dark aging is presented.

Supplement S4: PMF diagnostics and FPEAK analysis.

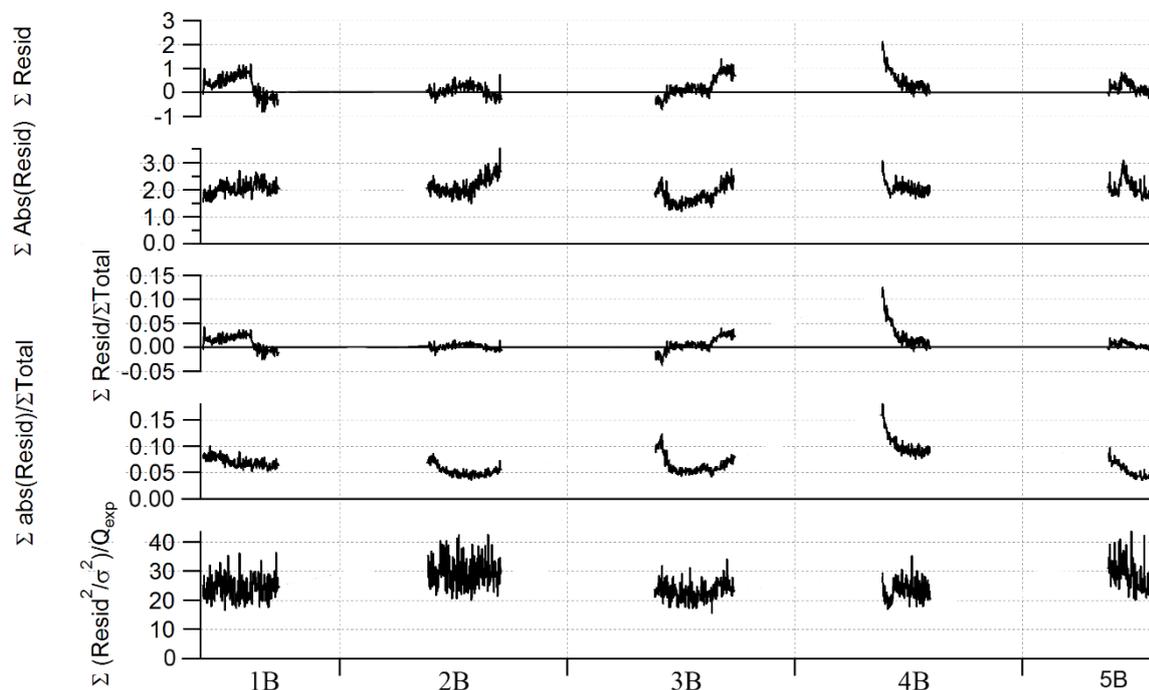


Figure S6: PMF diagnostic plot based on time series of the residuals for each experiments.

Table S2: FPEAK analysis for 5-factor PMF analyses. Mass spectra from Aiken et al. 2009 was used as a reference (LV-OOA, HOA, SV-OOA and BBOA).

Factor	Tracer	fpeak=0.2	fpeak=0	fpeak=-0.2	fpeak=-0.4	fpeak=-0.6	fpeak=-0.8	fpeak=-0.9	fpeak=-1.0	fpeak=-0.7	fpeak=-0.5	fpeak=0.4	fpeak=1.0
		R	R	R	R	R	R	R	R	R	R	R	R
SOA3	SO4/CO2	0.57	0.57	0.69	0.56/0.76	0.73/0.77	0.73/0.77	0.76/0.74	0.76/0.74	0.76/0.74	0.71/0.76	0.71/0.77	0.69/0.79
SOA2	NO3	0.92	0.92	0.92	0.92	0.93	0.92	0.92	0.92	0.92	0.92	0.92	0.93
POA2	C4H9	0.31	0.32	0.31	0.32	0.33	0.33	0.33	0.33	0.33	0.33	0.32	0.32
SOA1	C2H3O	0.89	0.89	0.89	0.89	0.9	0.9	0.91	0.91	0.91	0.89	0.89	0.897
POA1	PAH	0.8	0.8	0.8	0.8	0.8	0.8	0.79	0.79	0.79	0.798	0.798	0.81
Spectra													
SOA3	LV-OOA	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
SOA2	LV-OOA	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.98	0.98	0.99	0.99	0.99
POA2	HOA	0.57	0.58	0.57	0.56	0.56	0.56	0.56	0.24	0.55	0.55	0.64	0.64
SOA1	SV-OOA	0.92	0.78	0.86	0.91	0.91	0.97	0.96	0.81	0.93	0.93	0.88	0.88
POA1	BBOA	0.63	0.63	0.63	0.635	0.64	0.66	0.68	0.67	0.64	0.64	0.62	0.62

An fpeak value of -0.9 was selected for further analyses.