Characterizing the impact of urban emissions on regional aerosol particles; Airborne measurements during the MEGAPOLI experiment.

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Affliations

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Supplementary information

Description MONA :

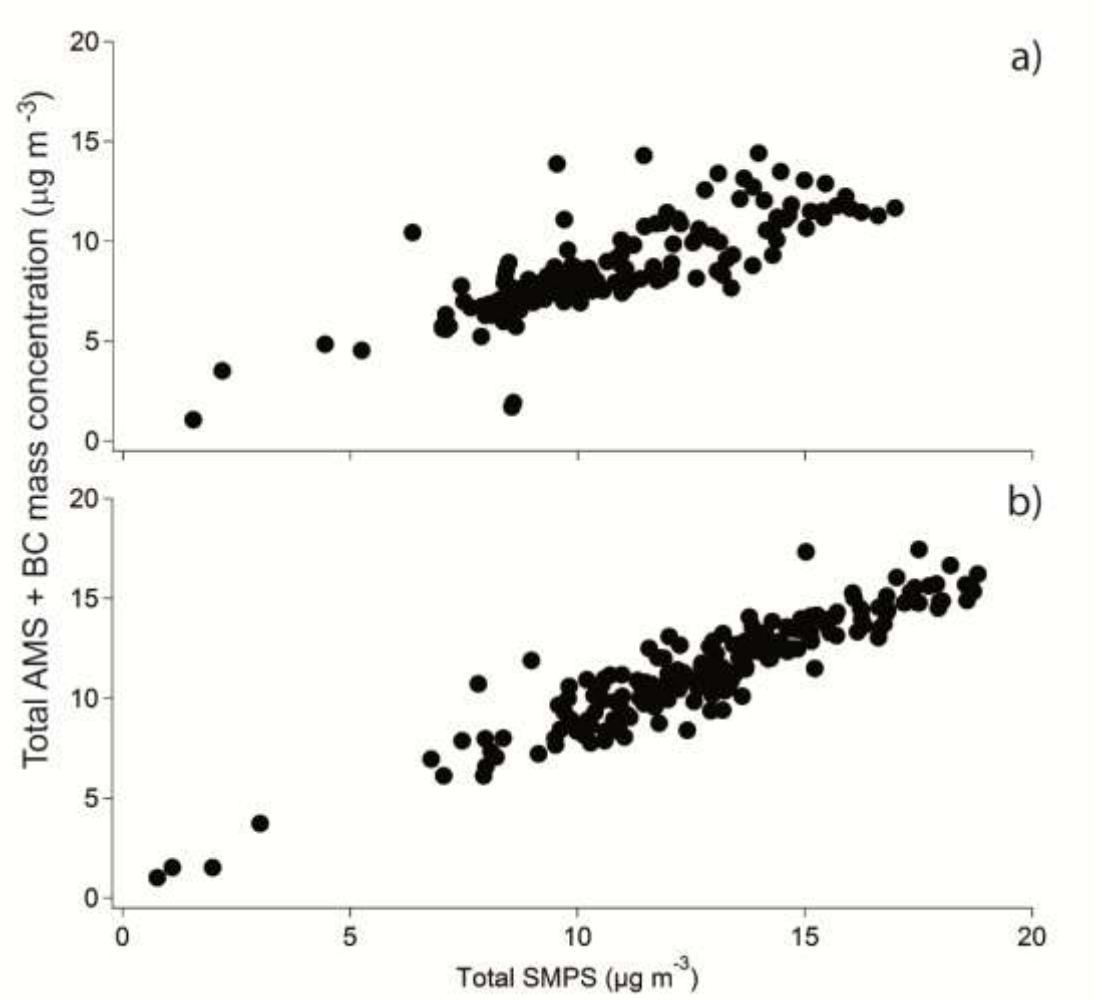
NO, NO_2, and NO_Y were measured, at a 30s time resolution, using the MONA (Measurement Of Nitrogen on Aircraft) instrument developed at LISA. This instrument, composed of two racks, is a unique prototype for airborne measurements and designed to fit into the French ATR-42. It comprises three similar commercial analysers: CLD780TR (ECO-PHYSICS®) which are based on ozone chemiluminescence and thus permit the measurements of NO concentrations at ppt levels (DL = 10ppt). The air is sampled, through backward facing inlets, by a vacuum pump at a flow rate of 9L.min^{-1} (3L.min^{-1} for each analyser). The flow rate of each analyser is controlled by a critical orifice and a system used to control the pressure of the inflow. Furthermore, an O_2 flow of 330mL.min^{-1}, using pure O_2 cylinders (Air liquide, Alphagaz 1), allow the generation of ozone in each analyser. Finally, purified air (air pumped passing trough three cartridges containing drierite®, purafil® and charcoal) is injected into the analytical system before take off and landing to avoid any contamination.

For the measurement of NO_2 concentrations, the air sampled passes through a photolytic converter (Blue light converter- MetAir®) to convert it into NO. NO_y measurements are performed using another sampling line, since this one needs to be heated to avoid any loss of nitric acid (The sampling line was heated at 60°C). Then the air sampled passes through a

gold converter (8mm Inox tube cover of gold) heated at 200°C with H_2 as reagent to convert nitrogen species into NO. H_2 is generated at a flow rate of 0.5mL.min^{-1} thanks to a heated reservoir of hydride to avoid the use of H_2 cylinder.

Calibrations of the three analysers were performed before and after each flight using a standard 8ppm NO/Air mixture (Crystal, Air Liquid (uncertainty: ± 2%)) and a clean air cylinder (Alphagaz 1, zero air at 99,99% Air Liquid) used to dilute NO concentrations (8 ml/min for NO, and 10 L/min for the zero air, which leads to a NO concentration for calibration of 6 ppbv.). Gas-Phase Titration (GPT) was used to calibrate NO_2. The principle of GPT is based on the rapid gas-phase reaction between NO and O_3 that produces stoechiometric quantities of NO_2. If the initial and final NO concentrations for this reaction are known, the resulting NO_2 concentration can be determined. Ozone is added to excess NO in a dynamic calibration system, and the NO channel of the chemiluminescent analyzer detects the changes in NO concentration. After the addition of O_3, the observed decrease in NO concentration is equivalent to the concentration of NO_2 produced. The NO_2 generated is, then, used to calibrate both the NO_2 and the NO_y analysers. Finally, The NO measurement uncertainty was estimated to be 10% and the NO_2 and NO_y measurement uncertainties were estimated to be 20%.

63 **Supplementary figures and tables**



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65 **Figure S1. Comparison between the total mass concentration of the C-ToF-AMS and**
66 **SMPS for a) N13, and b)N29**

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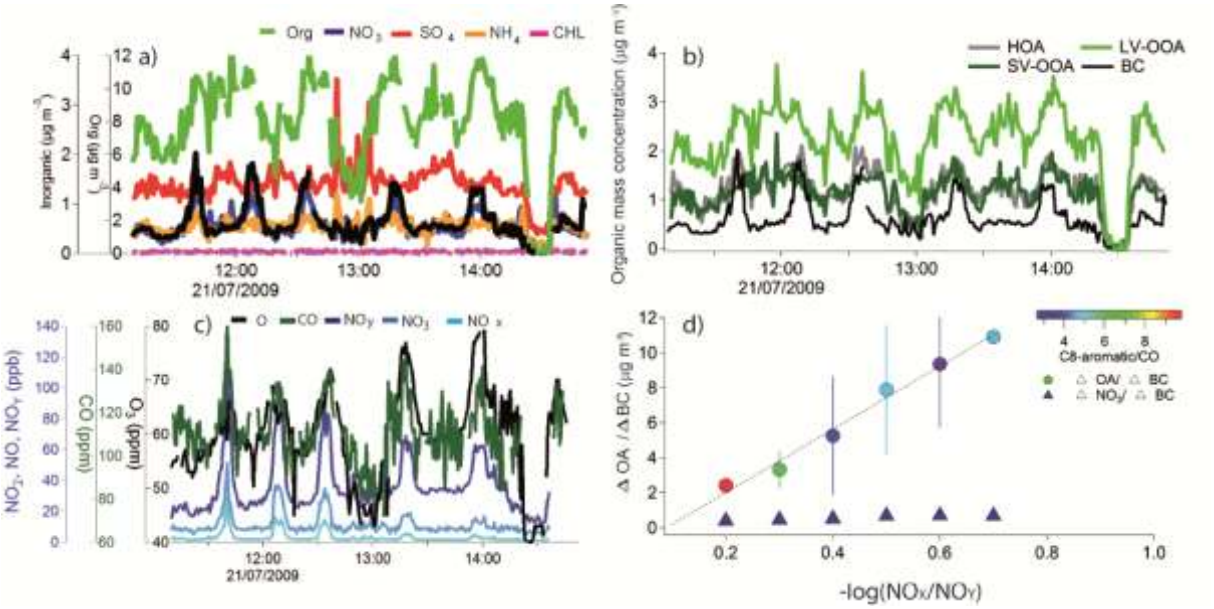

Figure S2. An overview of aerosol gas and particle composition measured during N21. a) Time series of AMS particle composition, and BC (in black). b) PMF analysis of the organic aerosol mass spectra along with BC. d) Temporal evolution of gas-phase species and d) increase in the organic aerosol mass concentration as a function of photochemical age.

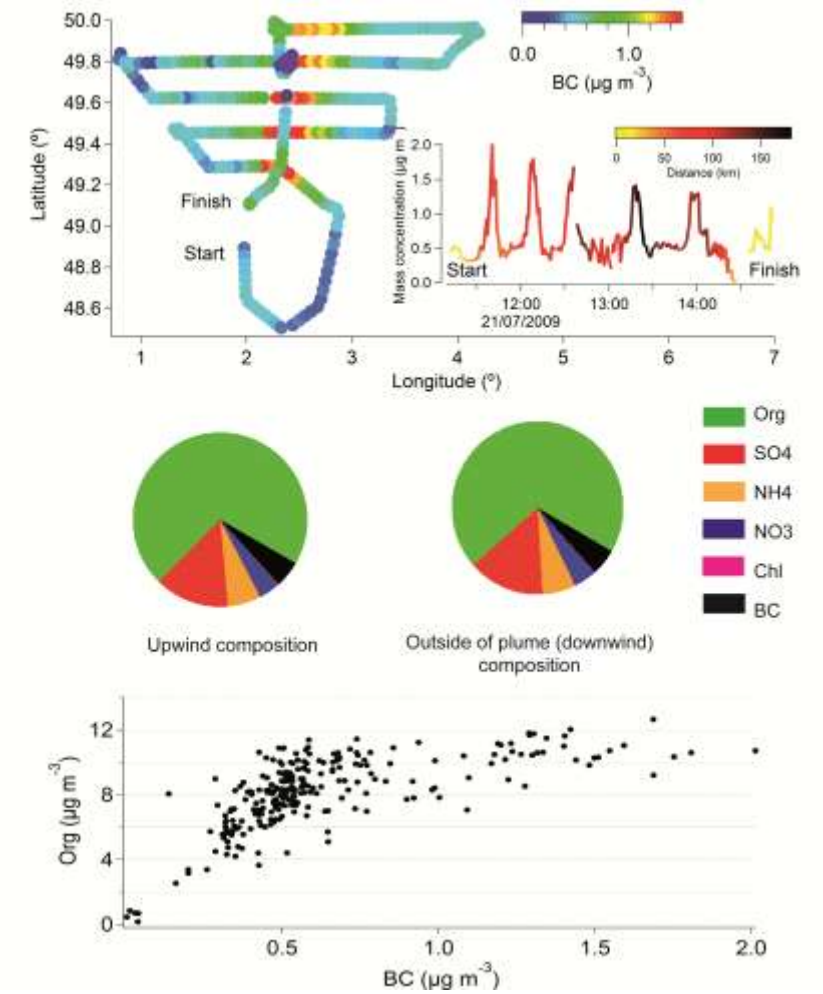

Figure S3: Average aerosol composition measured upwind of the plume area during N21 and on the sides of the plume area. Pie charts illustrate that the composition outside of the plume are representative of upwind aerosol composition.

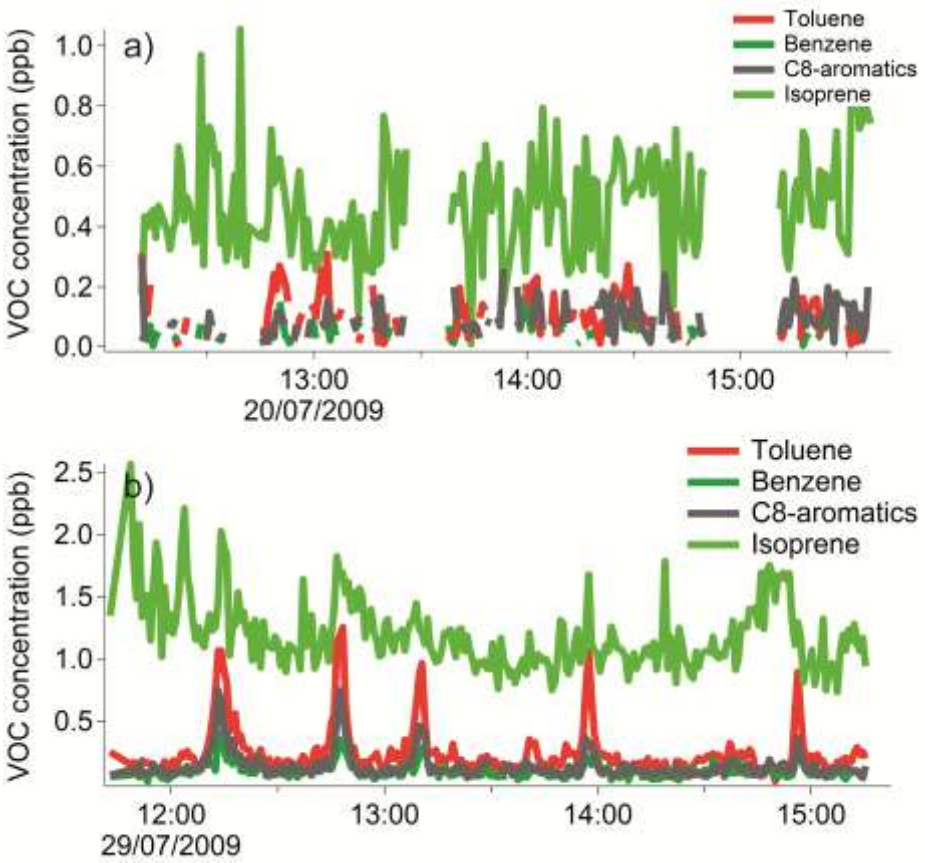

Figure S4. An example of some of the VOC species measured using PTR-MS during E20 and N29.

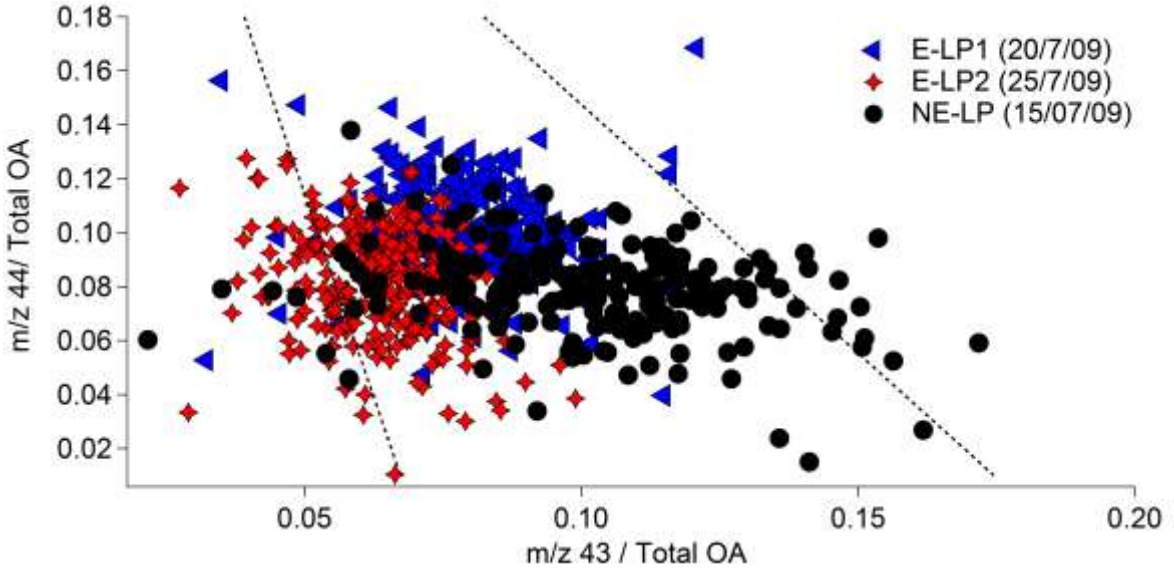

Figure S5: Fraction of Org44 to total Organics (F44) against the fraction of Org 43 to total Organics (F43) for E20, E25, and NE15. The black dotted lines show boundaries set by Ng et al., (2010).

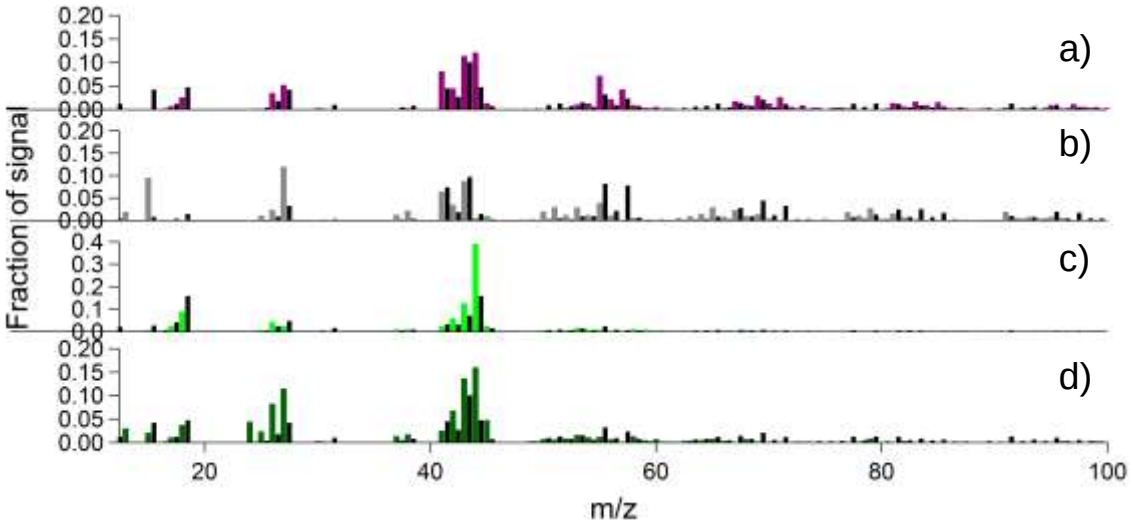

Figure. S6 Four factor PMF solution a) SV-OOA1 b) HOA c) LV-OOA, and d) SV-OOA1. Black mass spectra correspond to reference mass spectra for a) SV-OOA, b) HOA, c) LV-OOA, and d) SV-OOA.

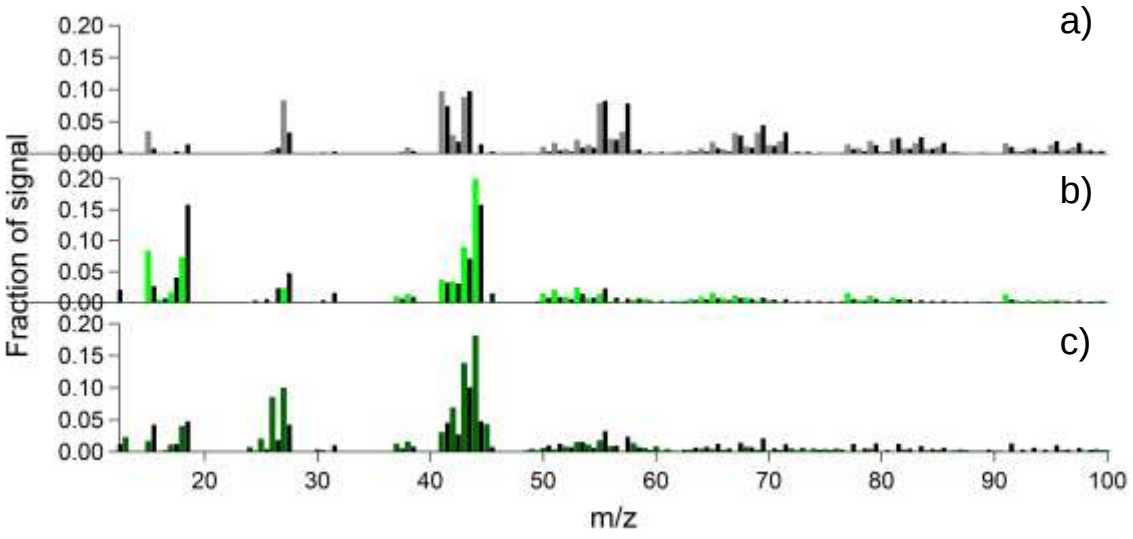

Figure. S7 Three factor PMF solution a) HOA b)LV-OOA, and c)SV-OOA. Black mass spectra correspond to reference mass spectra for a)HOA, b)LV-OOA, and c)SV-OOA.

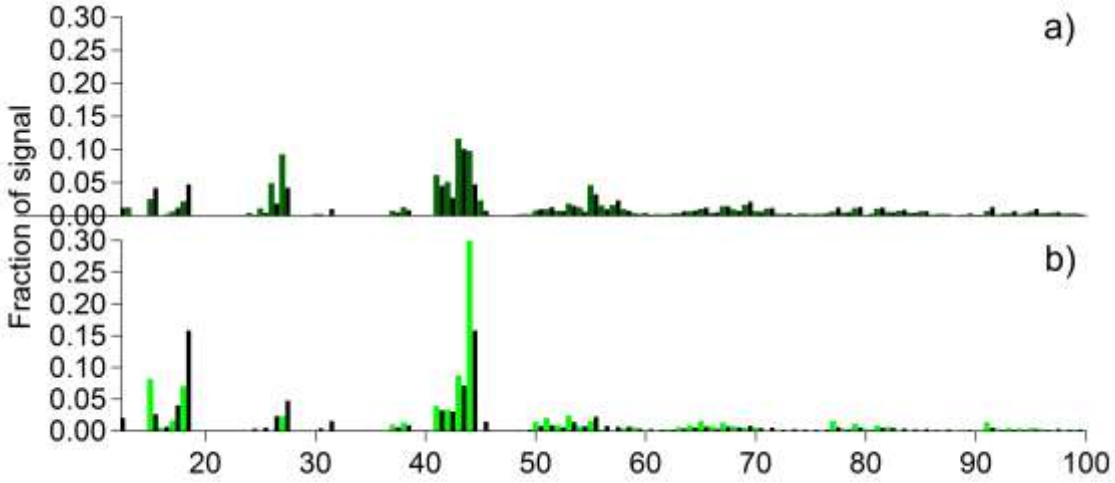

Figure. S8 Two factor PMF solution a) SV-OOA b) LV-OOA. Black mass spectra correspond to reference mass spectra for a) SV-OOA, and b) LV-OOA.

Table S1. Research flight number, date and principal measurements available during each flight. A denotes available and N/A denotes unavailable.

RF	Date	C-ToF-AMS	PTR-MS	MONA	O_3, CO, BC	Classification
28	13/07/09	**A**	A	N/A	A	N13
29	15/07/09	**A**	A	N/A	A	NE15
30	16/07/09	**A**	N/A	A	A	N16
31	20/07/09	**A**	A	A	A	E20
32	21/07/09	**A**	A	A	A	N21
33	25/07/09	**A**	N/A	A	A	E25
35	28/07/09	**A**	N/A	N/A	A	NE28
36	29/07/09	**A**	A	A	A	N29

106 Table S2. Pearsons R (P_R) correlation values a four factor PMF solution using a fpeak =0.

External Data	OOA	SV-OOA	LV-OOA	HOA
CO	-0.077	-0.134	0.262	-0.041
Ozone	-0.106	-0.537	-0.370	-0.511
NO_3	-0.039	0.467	0.304	0.377
SO_4	-0.076	0.172	0.015	0.085
NH_4	-0.049	0.338	0.138	0.235
Chl	-0.072	0.187	-0.003	0.009
RH	0.205	-0.317	-0.116	-0.135
Methanol	0.094	0.894	0.693	0.819
Monoterpenes	0.145	0.476	0.670	0.504
C8-aromatics	0.033	0.421	0.541	0.593
Toluene	-0.090	0.472	0.530	0.619
Benzene	-0.052	0.431	0.596	0.598
Isoprene	-0.160	0.160	0.342	0.127
Methacrolein	0.125	0.642	0.635	0.660
Metheylketone	0.011	0.543	0.341	0.630
NO_2	-0.014	0.073	0.023	0.270
NO	-0.014	0.103	0.062	0.301
NO_Y	-0.016	0.236	0.297	0.437
BC	-0.006	0.522	0.527	0.655
Reference mass spectra				
HOA	0.277	0.476	0.367	**0.876**
OOA	0.439	**0.806**	**0.847**	0.454
LV-OOA	0.419	0.775	**0.844**	0.387
SV-OOA	0.521	0.785	0.745	**0.842**
BBOA	0.476	0.702	0.651	**0.859**

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Table S3. Pearsons R (P_R) correlation values with particle and gas phase species for a three factor PMF solution with an fpeak of 0.2.

External Data	**SV-OOA**	**LV-OOA**	**HOA**
CO	-0.187	0.255	0.031
Ozone	-0.549	-0.374	-0.504
NO_3	**0.455**	0.314	0.380
SO_4	0.184	0.013	0.076
NH_4	0.345	0.142	0.227
Chl	0.177	0.008	0.020
RH	-0.292	-0.127	-0.147
Methanol	0.888	0.698	0.864
Monoterpenes	0.446	0.665	0.571
C8-aromatics	0.404	0.541	0.588
Toluene	0.436	**0.535**	**0.614**
Benzene	0.394	**0.599**	**0.620**
Isoprene	0.085	0.352	0.195
Methacrolein	0.631	0.636	0.673
Metheylketone	0.552	0.349	0.570
NO_2	0.088	0.027	0.187
NO	0.115	0.066	0.221
NO_Y	0.225	0.299	0.392
BC	0.504	0.532	**0.642**
Reference mass spectra			
HOA	0.416	0.262	**0.857**
OOA	**0.803**	**0.842**	0.389
LV-OOA	**0.776**	**0.848**	0.321
SV-OOA	**0.752**	0.662	**0.803**
BBOA	0.667	0.560	0.822

128 Table S4. Pearsons R (P_R) correlation values with particle and gas phase species for a two
129 factor PMF solution with an fpeak of 0.2.

External Data	**SV-OOA**	**LV-OOA**
CO	0.266	-0.004
Ozone	-0.359	-0.525
NO_3	0.307	0.409
SO_4	0.015	0.102
NH_4	0.139	0.259
Chl	0.009	0.063
RH	-0.121	-0.194
Methanol	0.628	0.896
Monoterpenes	0.673	0.563
C8-aromatics	0.522	0.554
Toluene	0.509	0.588
Benzene	0.575	0.580
Isoprene	0.349	0.193
Methacrolein	0.628	0.675
Metheylketone	0.317	0.563
NO_2	0.011	0.151
NO	0.050	0.185
NO_Y	0.286	0.351
BC	0.514	**0.621**
Reference mass spectra		
HOA	0.624	0.560
OOA	0.731	0.837
LV-OOA	0.686	0.809
SV-OOA	**0.869**	0.862
BBOA	**0.813**	0.786

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131 Table S5. Yields used for the prediction of the formation of secondary organic aerosol.

	Low NOx yield	**High NOx Yield**	
Benzene	0.369*	0.08*	*Ng et al., 2007
Toluene	0.3*	0.281*	*Ng et al., 2008
C8-aromatics	0.36**	0.035**	**yield of m-xylene (Ng et al, 2007)
C9-aromatics	0.36**	0.035**	** yield of m-xylene (Ng et al, 2007)

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