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

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Supplementary information

Description MONA(Measurement Of Nitrogen on Aircraft) :

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 through three cartridges containing drierite®, purafil® and charcoal) is injected into the analytical system before takeoff 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%.

<u>Supplementary figures and tables</u>

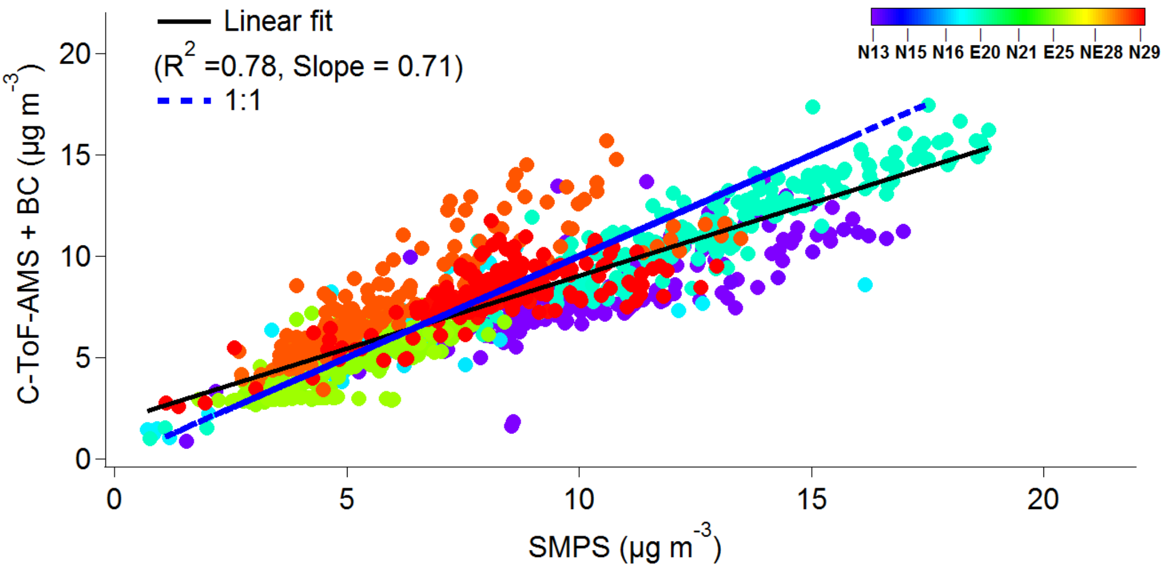


Figure S1. Comparison between the total mass concentration of the C-ToF-AMS and SMPS for all flights. Points are coloured by flight time. The blue line shows a 1:1 fit and the black line shows the linear fit through the data points.

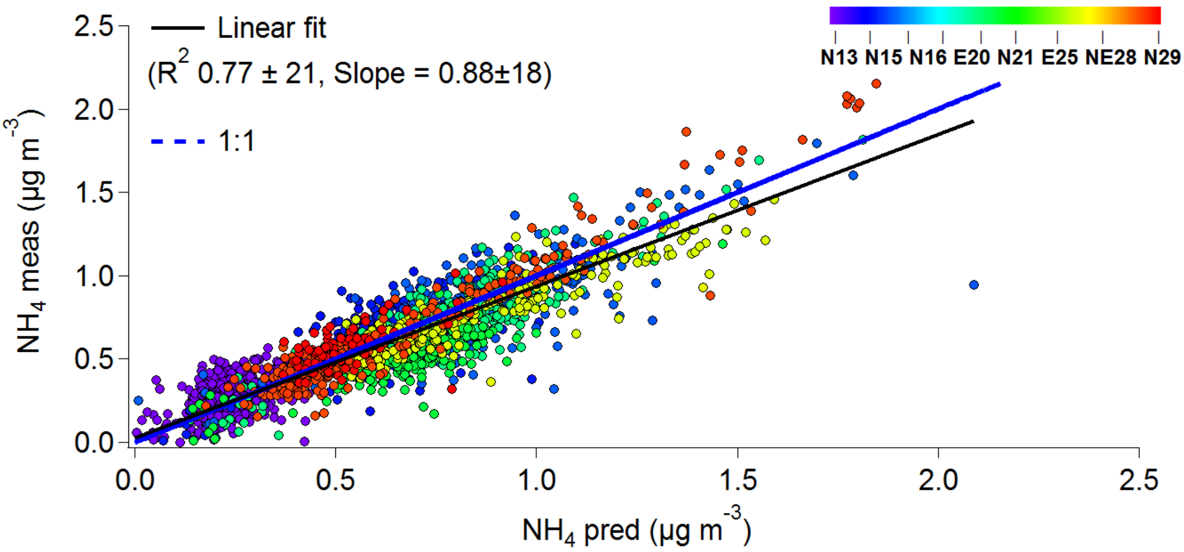


Figure S2: NH_{4MEAS} vs NH_{4PRED} for all flights. Points are coloured by flight time. The blue line shows a 1:1 fit and the black line shows the linear fit through the data points.

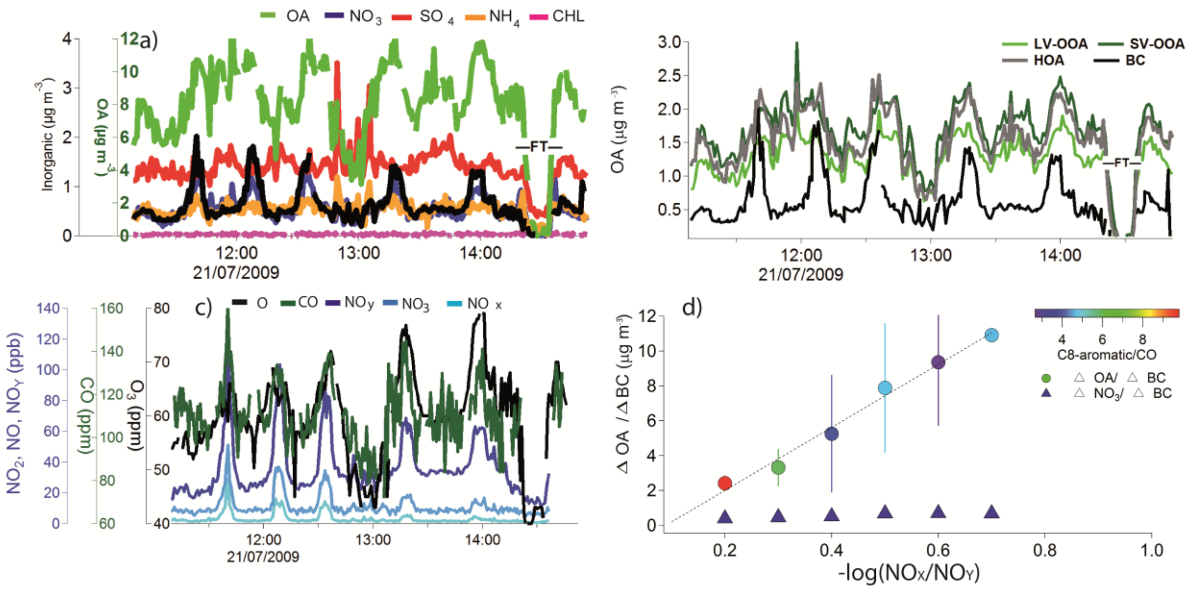
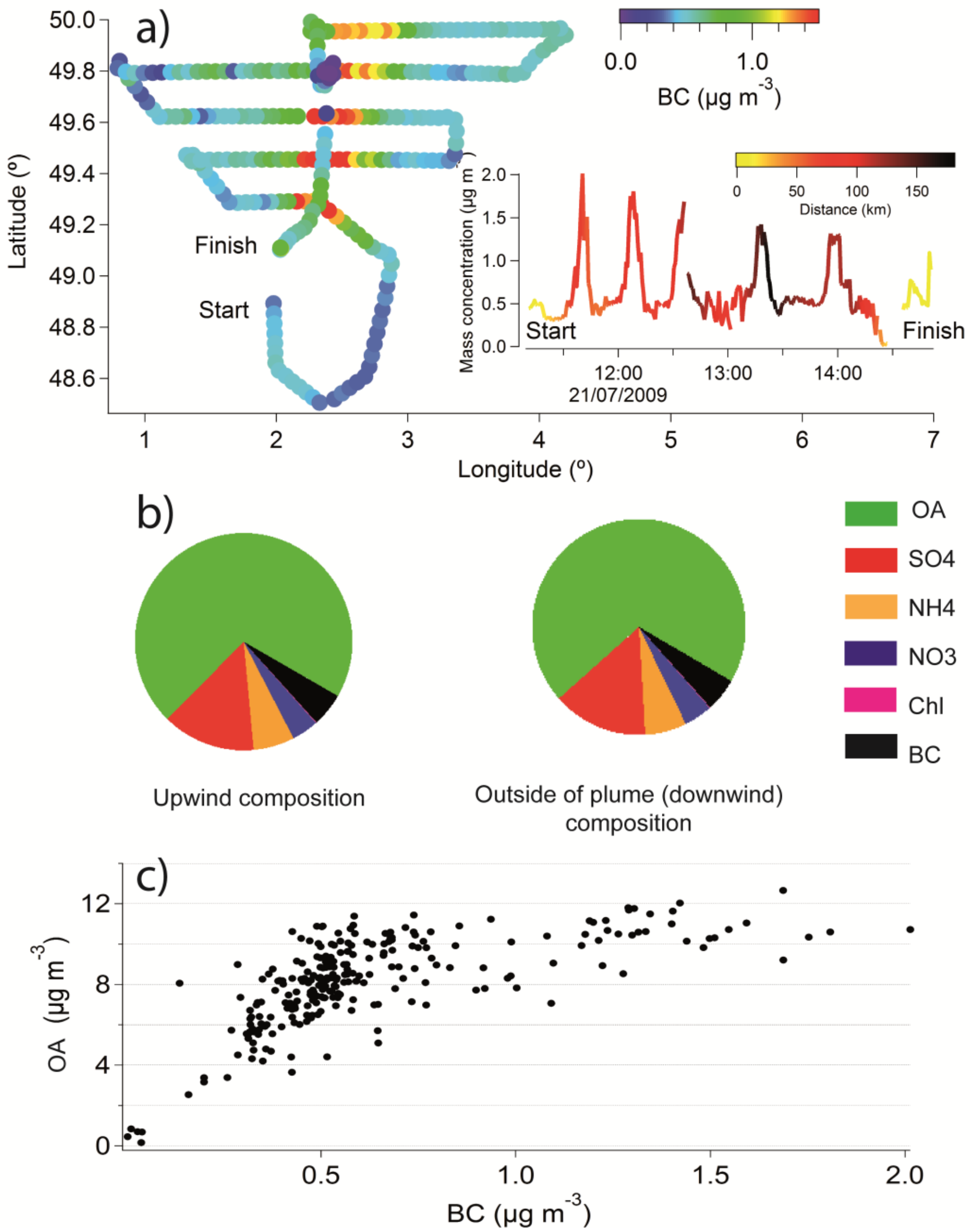


Figure S3. An overview of aerosol gas and particle composition measured during N21. a) Time series of AMS particle composition, and BC (in black). b) PMF analysis of the organic aerosol mass spectra along with BC. d) Temporal evolution of gas-phase species and d) increase in the organic aerosol mass concentration as a function of photochemical age.



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79 Figure S4: Average aerosol composition measured upwind of the plume area during N21 and on the
80 sides of the plume area. Pie charts illustrate that the composition outside of the plume are
81 representative of upwind aerosol composition.

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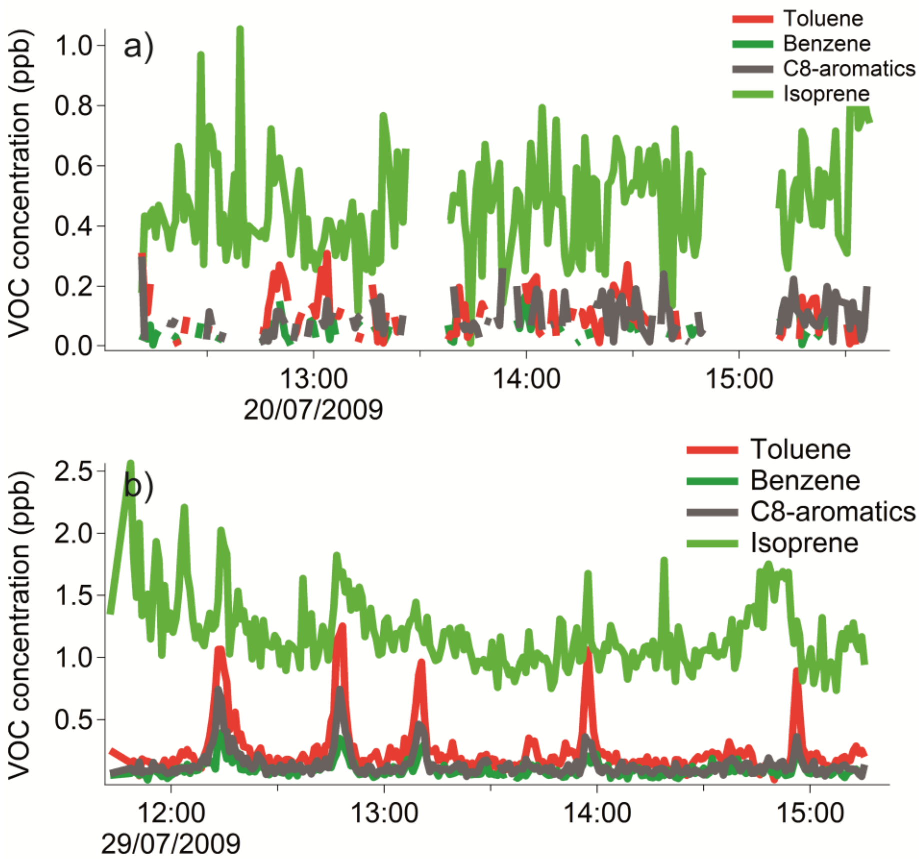

Figure S5. An example of some of the VOC species measured using PTR-MS during E20 and N29.

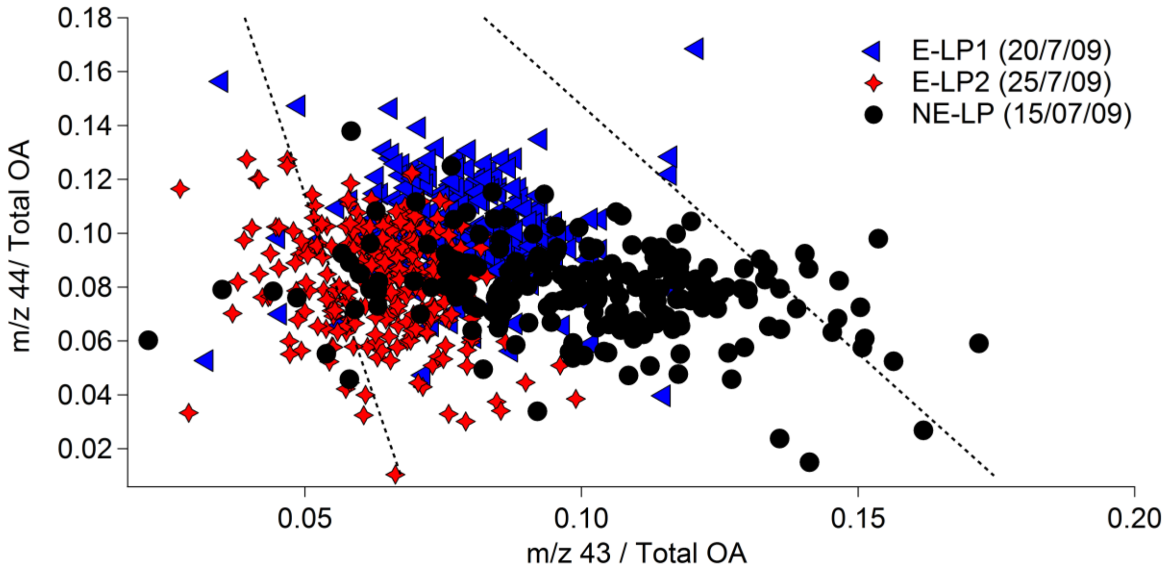

Figure S6: Fraction of Org44 to total Organics (F44) against the fraction of Org 43 to total Organics (F43) for E20, E25, and NE15. The black dotted lines show boundaries set by Ng et al., (2010).

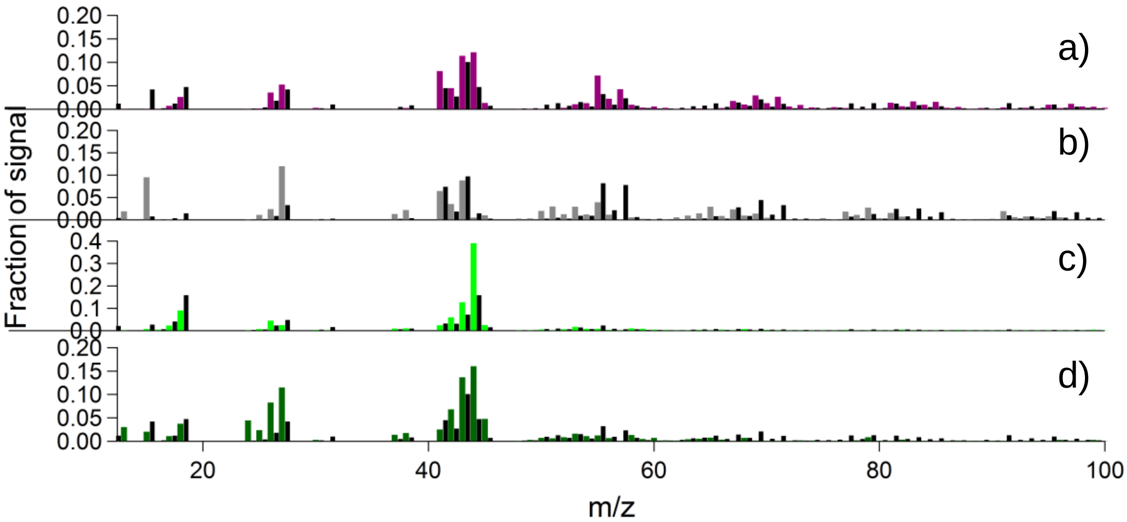

Figure. S7 Four factor PMF solution a) SV-OOA b) HOA c) LV-OOA, and d) SV-OOA1. Black mass spectra correspond to reference mass spectra for a) SV-OOA, b) HOA, c) LV-OOA, and d) SV-OOA. Reference mass spectra were taken from the AMS mass spectral data set (http://cires.colorado.edu/jimenez-group/AMSsd/).

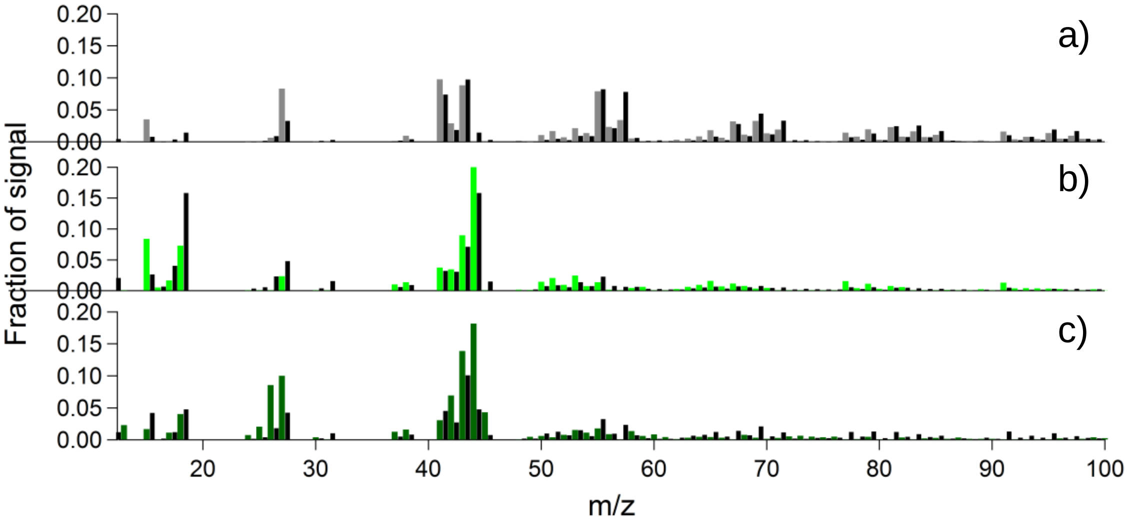

Figure. S8 Three factor PMF solution a) HOA b)LV-OOA, and c)SV-OOA. Black mass spectra correspond to reference mass spectra for a)HOA, b)LV-OOA, and c)SV-OOA. Reference mass spectra were taken from the AMS mass spectral data set (http://cires.colorado.edu/jimenez-group/AMSsd/).

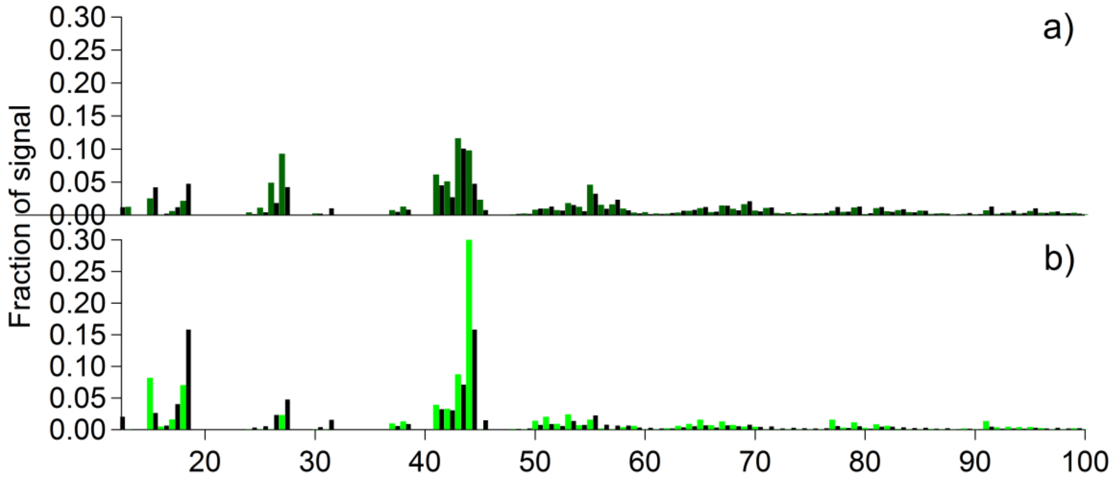

Figure. S9 Two factor PMF solution a) SV-OOA b) LV-OOA. Black mass spectra correspond to reference mass spectra for a) SV-OOA, and b) LV-OOA. Reference mass spectra were taken from the AMS mass spectral data set (http://cires.colorado.edu/jimenez-group/AMSsd/).

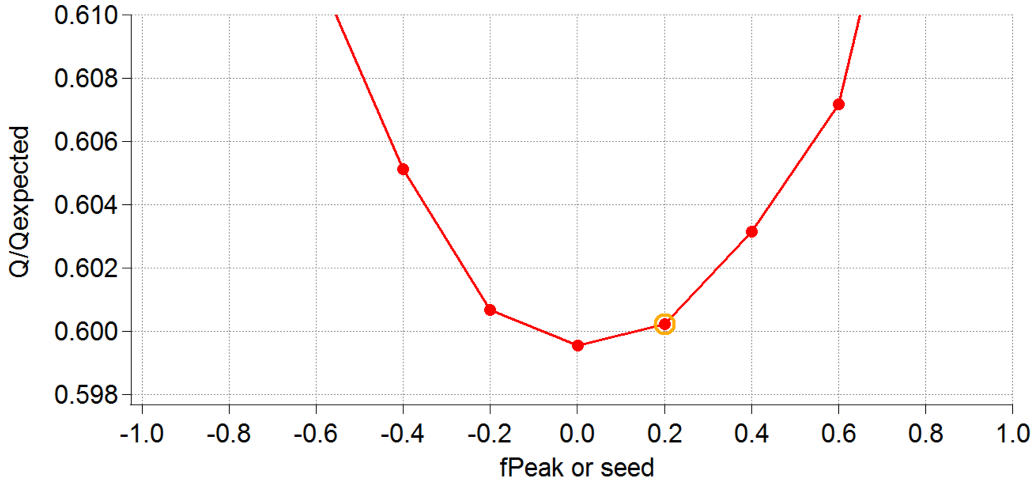

Figure S10: Q/Qexp vs fpeak for a three factor solution.

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

Table S2. Pearsons R (P_R) correlation values a four factor PMF solution using a fpeak =0 for all flights. Reference mass spectra were taken from the AMS mass spectral data set (http://cires.colorado.edu/jimenez-group/AMSsd/).

External Data	SV-OOA	OOA	LV-OOA	HOA
CO	-0.03	-0.37	0.19	0.11
Ozone	-0.46	-0.22	-0.37	-0.42
NO_3	0.34	0.18	0.28	0.28
SO_4	0.05	0.11	0.04	0.07
NH_4	0.02	0.19	0.17	0.19
Chl	0.02	0.1	0.01	-0.06
RH				
Methanol	0.81	0.59	0.77	0.82
Monoterpenes				
C8-aromatics				
Toluene	**0.50**	-0.14	**0.46**	**0.51**
Benzene	**0.48**	-0.1	**0.50**	**0.53**
Isoprene	0.38	0.04	0.43	0.34
Methacrolein				
Metheylketone				
NO_2	0.24	-0.01	0.05	0.16
NO	0.19	0	0.01	0.11
NO_Y	0.39	0.1	0.29	0.38
BC	0.64	0.08	0.52	0.61
Reference mass spectra				
HOA	0.55	0.40	0.23	**0.79**
OOA	0.37	**0.77**	**0.83**	0.75
LV-OOA	0.33	0.74	**0.84**	0.69
SV-OOA	**0.76**	0.76	0.58	**0.85**
BBOA	**0.74**	0.67	0.48	**0.83**

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 for all flights. Reference mass spectra were taken from the AMS mass spectral data set (http://cires.colorado.edu/jimenez-group/AMSsd/).

External Data	**SV-OOA**	**LV-OOA**	**HOA**
CO	-0.05	0.48	0.016
Ozone	-0.48	-0.34	-0.44
NO_3	**0.35**	0.24	0.32
SO_4	0.1	0.01	0.06
NH_4	0.26	0.14	0.06
Chl	0.05	-0.05	-0.02
RH			
Methanol	0.88	0.68	0.82
Monoterpenes			
C8-aromatics			
Toluene	0.43	**0.46**	**0.52**
Benzene	0.42	**0.52**	**0.51**
Isoprene	0.37	0.41	0.35
Methacrolein			
Metheylketone	0.45	0.23	0.49
NO_2	0.12	0.1	0.23
NO	0.08	0.03	0.18
NO_Y	0.30	0.32	0.41
BC	0.58	0.53	**0.65**
Reference mass spectra			
HOA	0.41	0.24	**0.88**
OOA	**0.80**	**0.82**	0.35
LV-OOA	**0.78**	**0.83**	0.28
SV-OOA	**0.77**	0.63	**0.78**
BBOA	0.68	0.53	0.81

Table S4. Pearsons R (P_R) correlation values with particle and gas phase species for a two factor PMF solution with an fpeak of 0.2 for all flights. Reference mass spectra were taken from the AMS mass spectral data set (http://cires.colorado.edu/jimenez-group/AMSsd/).

External Data	**SV-OOA**	**LV-OOA**
CO	0.25	-0.02
Ozone	-0.33	-0.47
NO_3	0.24	0.34
SO_4	0.01	0.08
NH_4	0.14	0.08
Chl	-0.06	0.01
RH		
Methanol	0.70	0.86
Monoterpenes		
C8-aromatics		
Toluene	0.47	0.49
Benzene	0.53	0.48
Isoprene	0.41	0.36
Methacrolein		
Metheylketone		
NO_2	0.08	0.37
NO	0.03	0.18
NO_Y	0.32	0.37
BC	0.54	**0.63**
Reference mass spectra		
HOA	0.68	0.25
OOA	0.74	**0.82**
LV-OOA	0.69	**0.83**
SV-OOA	**0.90**	0.63
BBOA	**0.87**	0.54

Table S5: Pearsons R (P_R) correlation values with particle and gas phase species for a three factor PMF solution at fpeak values of -0.2, 0, and 0.2 for all flights. Reference mass spectra were taken from the AMS mass spectral data set (http://cires.colorado.edu/jimenez-group/AMSsd/).

fpeak	fpeak = 0.2			fpeak = 0			fpeak = -0.2		
	SV-OOA	LV-OOA	HOA	SV-OOA	LV-OOA	HOA	SV-OOA	LV-OOA	HOA
CO	-0.05	0.25	0.02	-0.46	0.20	-0.01	-0.42	0.22	-0.03
Ozone	-0.48	-0.33	-0.45	-0.31	-0.37	-0.45	-0.25	-0.34	-0.40
NO_3	0.35	0.24	0.32	0.27	0.27	0.31	0.21	0.25	0.27
SO_4	0.10	0.01	0.06	0.14	0.04	0.06	0.11	0.05	0.03
NH_4	0.26	0.14	0.21	0.26	0.16	0.21	0.21	0.16	0.17
Chl	0.05	-0.06	-0.03	0.14	-0.02	-0.03	0.12	0.00	-0.07
Methanol	0.88	0.68	0.82	0.77	0.77	0.79	0.69	0.69	0.64
Toluene	**0.43**	**0.46**	**0.52**	-0.04	0.47	**0.51**	-0.11	0.42	**0.52**
Benzene	**0.42**	**0.52**	**0.51**	0.01	0.53	**0.50**	-0.06	0.47	**0.49**
Isoprene	**0.37**	**0.41**	0.35	0.02	0.41	0.32	-0.02	0.41	0.25
NO	0.08	0.03	0.18	0.08	0.03	0.22	0.03	-0.03	0.31
NO_2	0.12	0.07	0.23	0.10	0.07	0.27	0.04	0.02	0.35
NO_Y	0.30	0.32	0.41	0.01	0.31	**0.43**	-0.06	0.26	**0.48**
BC	**0.58**	0.53	**0.65**	0.21	**0.54**	**0.66**	0.12	0.48	**0.65**
	SV-OOA	LV-OOA	HOA	SV-OOA	LV-OOA	HOA	SV-OOA	LV-OOA	HOA
HOA	0.41	0.24	**0.88**	0.43	0.39	**0.87**	0.57	0.47	0.74
OOA	**0.80**	0.82	0.35	**0.80**	**0.86**	0.51	0.78	**0.86**	0.74
LVOOA	0.78	**0.83**	0.28	0.77	**0.85**	0.44	0.74	**0.84**	0.69
SVOOA	0.77	0.63	0.78	**0.79**	0.77	**0.86**	**0.86**	0.81	**0.92**
BBOA	0.68	0.53	**0.81**	0.71	0.67	**0.88**	**0.80**	0.73	**0.89**

Table S6. Yields used for the prediction of the formation of secondary organic aerosol.

	Low NOx yield	High NOx Yield	
Benzene	0.37	0.08	Ng et al., 2007
Toluene	0.3	0.281	Ng et al., 2007
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)