Supplementary material

Section 1. Off-line measurements methodology

PM_1 samples were collected on 150 mm-diameter quartz fiber filters using Digitel automatic high volume (30 m^3/h) samplers one every four days.

A complete chemical analysis of the collected PM_1 samples was carried out. A quarter of the filter was used for an acid digestion (HNO_3:HF:$HClO_4$), and the resulting solution was analyzed by means of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for the major and trace elements concentration determination, respectively. A quarter of the filter was water extracted and the concentrations of NO_3^- , SO_4^{2-}, Cl^- were determined by Ion Chromatography, and concentration of NH_4^+ by selective electrode. Organic (OC) and elemental carbon (EC) concentrations were determined by thermal-optical methods. SO_4^{2-} concentrations in the present study were those calculated from S concentrations determined by ICP-AES, in agreement with all previous works by the research group.

PM_1 mass was reconstructed (PM_1 reconstructed) by the addition of all components and an estimation of 25% to account for water.

Section 2 Supplementary tables and figures

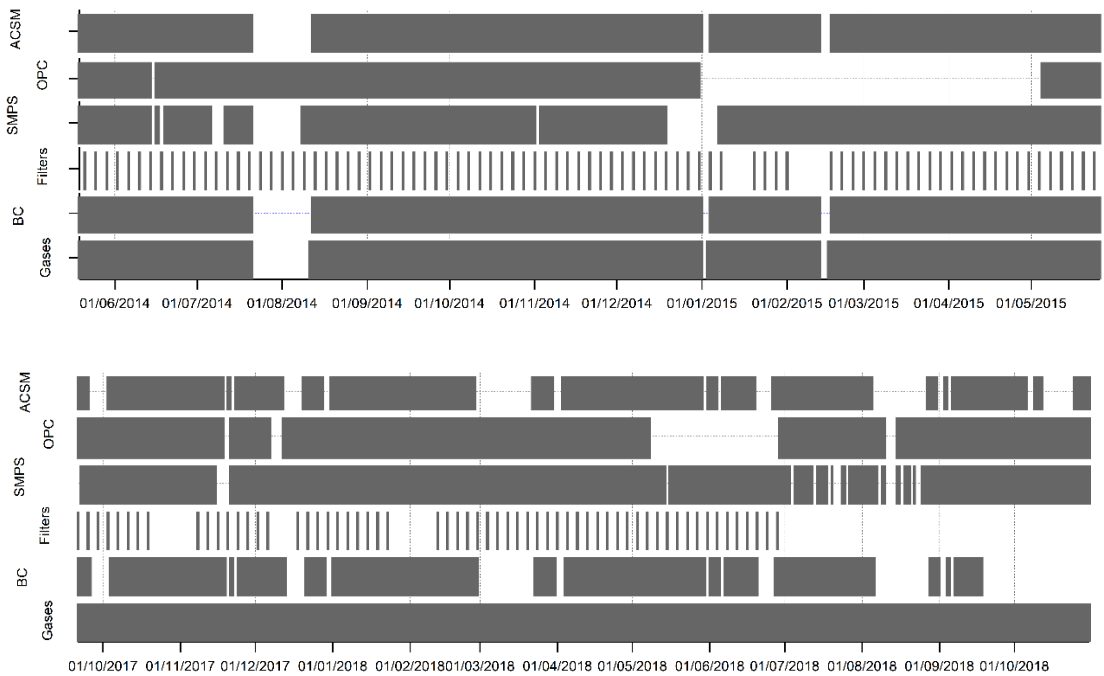


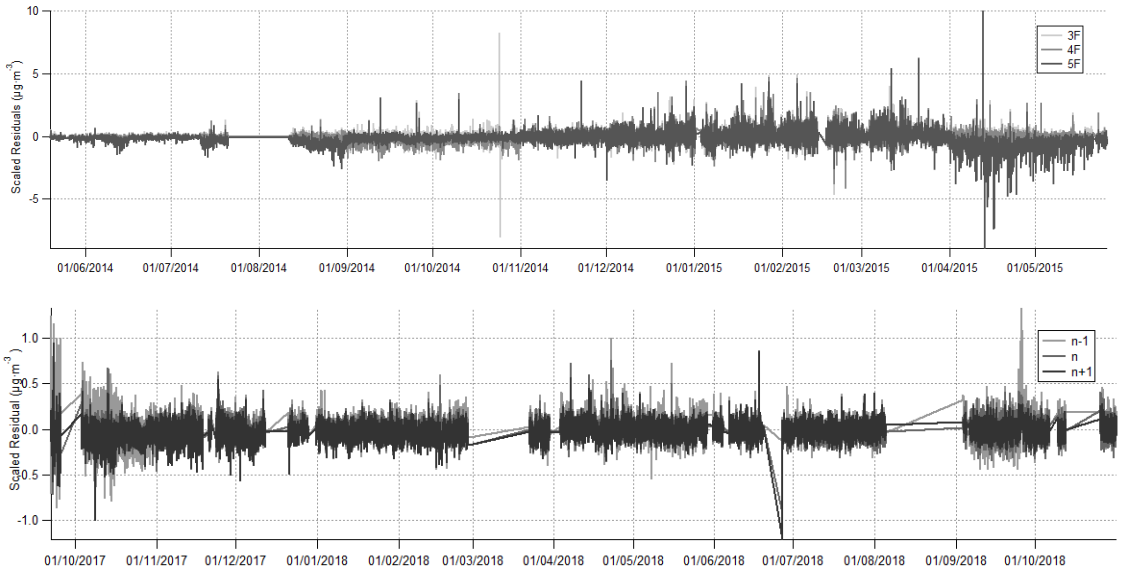
Figure S 1.Data availability for periods A and B.

Table S 1. Output correlations of runs of different number of factors (n) per each season in periods A and B. Bold rows correspond to those selected output runs.

A	n	Q/Qexp	Anchor COA	Anchor HOA	Anchor BBOA	COA vs. m/z55	HOA vs. BC	BBOA vs. m/z60	LO-OOA vs. NO_3^-	MO-OOA vs. SO_4^{2-}	OA meas. Vs OA model	
											R^2	Slope
May 2014	3	0.789 ± 0.009	03	03	-	0.56	0.63	-	0.44	0.04	0.943	1.023±0.011
	4	**0.706 ± 0.008**	**05**	**01**	**-**	**0.60**	**0.67**	**-**	0.37	**0.21**	0.962	0.996±0.008
	5	0.678 ± 0.011	02	05	01	0.61	0.65	0.28	0.47	0.10	0.965	1.029±0.008

Jun-Aug 2014	3	1.858±0.017	0.1	0.5	-	0.77	0.41	-	0.27	0.12	0.954	1.039±0.004
	4	1.712±0.004	0.1	0.5	-	0.76	0.37	-	0.25	0.18	0.959	1.035±0.004
	5	1.572±0.017	0.2	0.5	-	0.74	0.34	-	0.23	0.16	0.964	1.025±0.003
Sep-Oct 2014	3	3.188±0.017	0.1	0.5	-	0.66	0.68	-	035	0.07	0.951	0.9545±0.0041
	4	**2.929±0.008**	**0.1**	**0.3**	**-**	**0.35**	**0.68**	**-**	**0.35**	**0.08**	**0.963**	**0.968**±0.003
	5	2.763±0.031	0.1	0.5	0.5	0.64	0.68	0.4	0.32	0.09	0.967	0.991±0.004
Nov-Mar 2014-2015	3	9.435±0.054	03	05	-	0.68	0.68	-	0.65	0.3	0.972	1.019±0.002
	4	**9.207 ± 0.034**	**0.1**	**0.5**	**0.2**	**0.59**	**0.68**	**0.60**	0.31	0.35	0.976	1.021±0.002
	5	8.677 ± 0.074	0.3	0.5	0.1	0.73	0.67	0.60	020	0.37	0.976	1.020±0.002
Apr-May 2015	3	4.329±0.087	0.5	0.5	-	0.74	0.45	-	0.40	0.26	0.952	1.023±0.004
	4	**4.101±0.045**	**0.3**	**0.5**	**-**	**0.70**	**0.43**		**0.39**	**0.17**	0.956	1.025±0.004
	5	3.703±0.054	0.1	0.5	0.3	0.88	0.5	0.4	0.26	0.26	0.959	1.032±0.004
B	**Nb. Factors**	**Q/Qexp**	**Anchor COA**	**Anchor HOA**	**Anchor BBOA**	**COA vs. m/z55**	**HOA vs. BC**	**BBOA vs. m/z60**	**LO-OOA vs. NO_3^-**	**MO-OOA vs. SO_4^{2-}**	**OA meas. Vs. OA app.**	
											R^2	**Slope**
Sep-Oct 2017	3	1.81±0.001	0.1	0.5	-	0.83	0.51	-	0.60	0.15	0.96	0.999x +0.14
	4	**1.053 ± 0.012**	**0.1**	**0.5**	**-**	**0.80**	**0.52**	**-**	**0.59**	**0.33**	0.96	1.007x+0.09
	5	0.977 ± 0.006	0.1	0.3	0.5	0.61	0.65	0.28	0.53	0.18	0.96	0.96x+0.098
Nov-Mar 2017-2018	4	0.873±0.003	0.3	0.5	0.2	0.68	0.78	0.87	0.80	0.46	0.97	1.013x+0.07
	5	0.808±0.004	0.2	0.5	0.1	0.72	0.61	0.91	0.32	0.47	0.97	1.010x+0.032
	6	0.765±0.002	0.3	0.5	0.3	0.70	0.78	0.91	0.41	0.47	0.97	1.011x+0.125
Apr-May 2018	3	1.076±0.000	0.1	0.5	-	0.78	0.65	-	0.51	0.18	0.97	0.983x+0.20
	4	**0.893±0.006**	**0.4**	**0.5**	**-**	**0.76**	**0.57**	**-**	**0.42**	**0.32**	**0.97**	**0.898x+0.13**
	5	0.778±0.006	0.3	0.2	0.3	0.69	0.56	0.57	0.42	0.31	0.97	1.002x+0.08
Jun-Aug 2018	3	0.957±0.013	0.5	0.5	-	0.69	0.31	-	0.04	0.05	0.97	0.996x+0.15
	4	**0.869 ± 0.008**	**0.5**	**0.5**	**-**	**0.76**	**0.44**	**-**	0.1	0.08	0.96	0.997x+0.14
	5	0.809 ± 0.00	0.5	0.4	-	0.76	0.47	-	0.14	0.07	0.96	1.122x+0.15
Sep-Oct 2018	3	1.273±0.000	0.5	0.5	-	0.73	0.74	-	0.25	0.27	0.95	11.024x+0.03
	4	**1.493±0.008**	**0.3**	**0.5**	**-**	**0.74**	**0.74**	**-**	**0.23**	**0.21**	0.97	1.024x-0.02
	5	0.923±0.003	0.3	0.2	0.1	0.73	0.73	0.55	0.17	0.16	0.97	1.030x-0.04

(a)



(b)

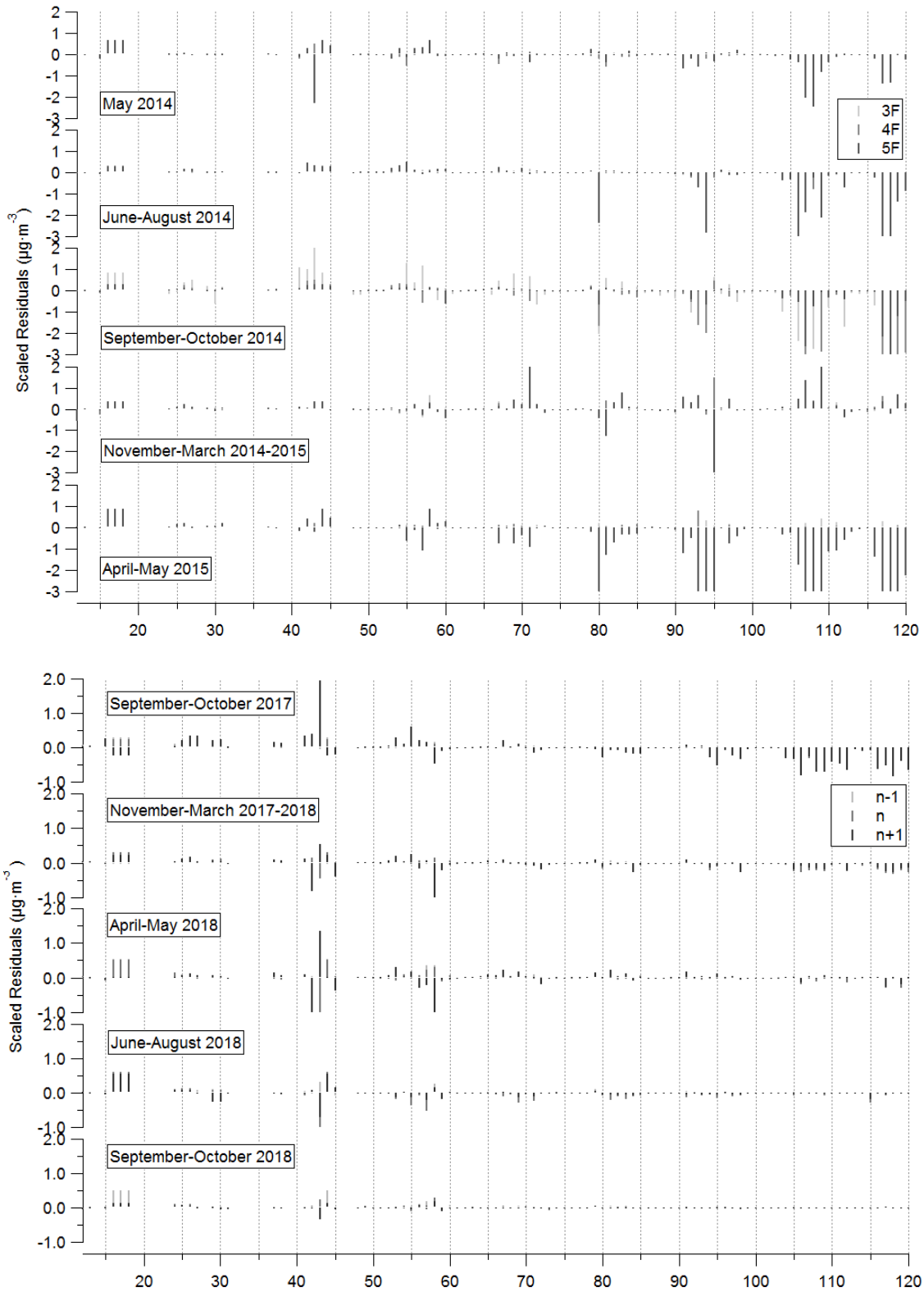
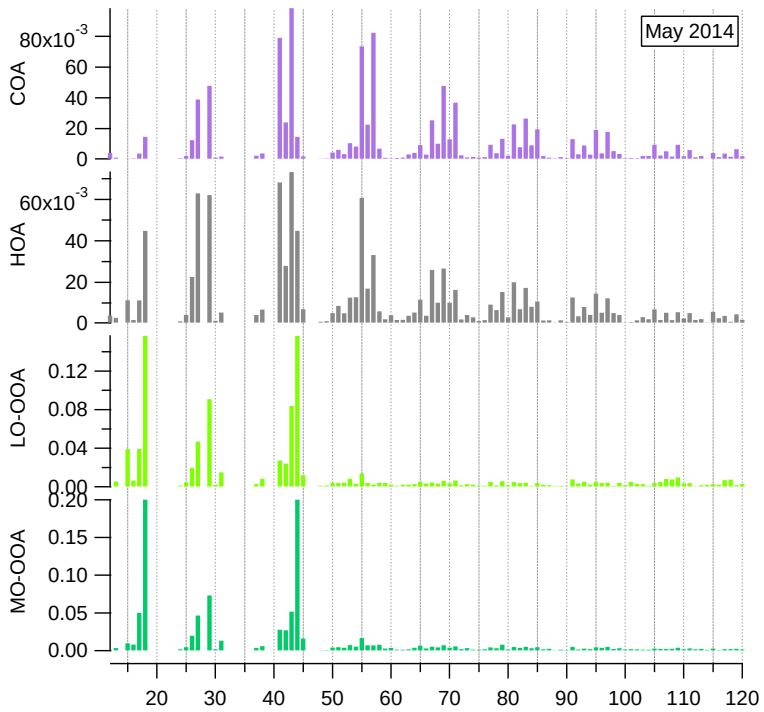
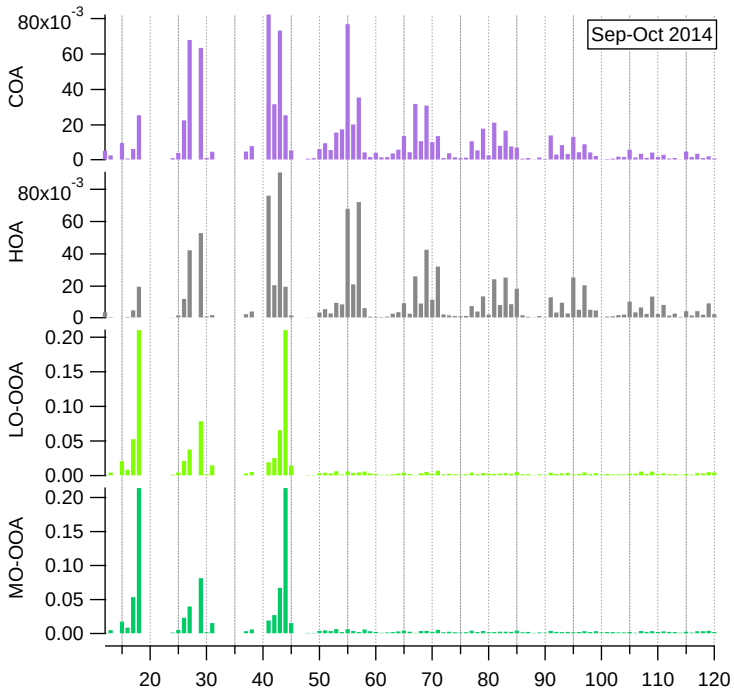
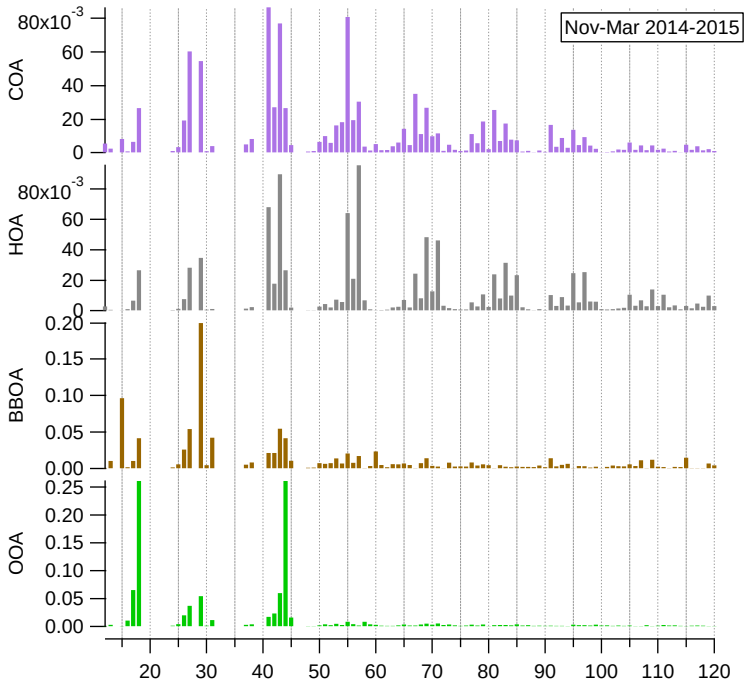


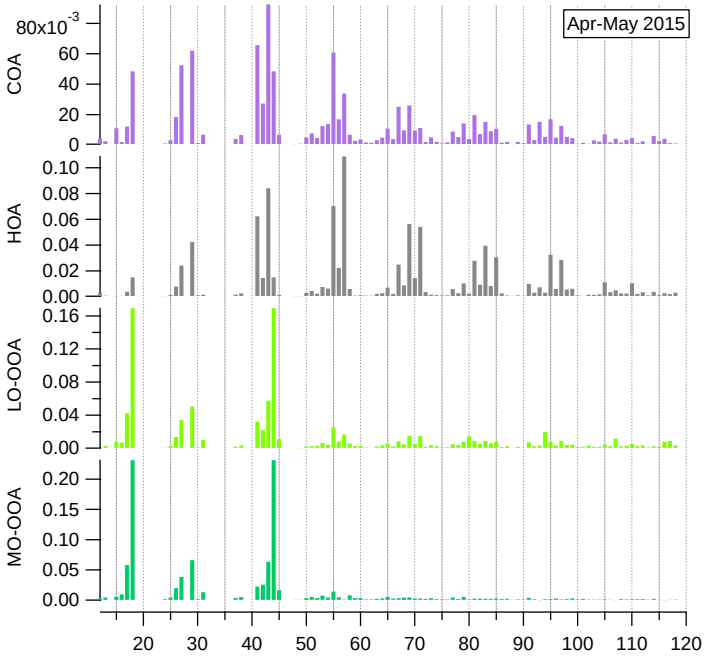
Figure S 2. Scaled residuals (a) time series (b) mass spectra for 3, 4, 5 factors in period A and for n-1, n and n+1 factors in Period B being n the number of factors of the chosen solution.

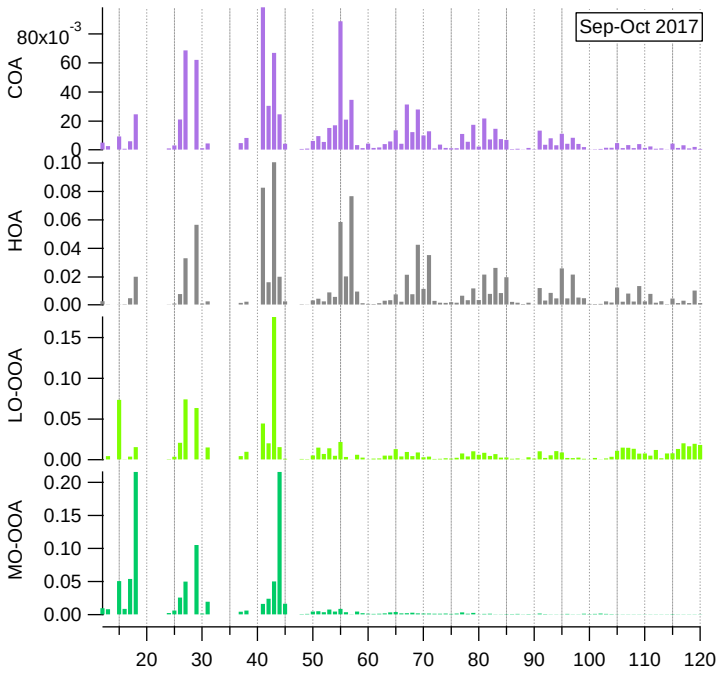

May 2014
COA
HOA
LO-OOA
MO-OOA
80x10-3
60x10-3
0.12
0.08
0.04
0.20
0.15
0.10
0.05
0.00
20
30
40
50
60
70
80
90
100
110
120


Sep-Oct 2014
COA
HOA
LO-OOA
MO-OOA
80x10-3
0.20
0.15
0.10
0.05
0.00
20
30
40
50
60
70
80
90
100
110
120

35


Nov-Mar 2014-2015
COA
HOA
BBOA
OOA
80x10-3
60
40
20
0
0.20
0.15
0.10
0.05
0.00
0.25
20
30
40
50
60
70
80
90
100
110
120


Apr-May 2015
COA
HOA
LO-OOA
MO-OOA
80x10-3
60
40
20
0
0.10
0.08
0.06
0.04
0.02
0.00
0.16
0.12
0.20
0.15
20
30
40
50
60
70
80
90
100
110
120


Sep-Oct 2017
COA
HOA
LO-OOA
MO-OOA
80x10-3
60
40
20
0
0.10
0.08
0.06
0.04
0.02
0.00
0.15
0.10
0.05
0.00
0.20
0.15
0.10
0.05
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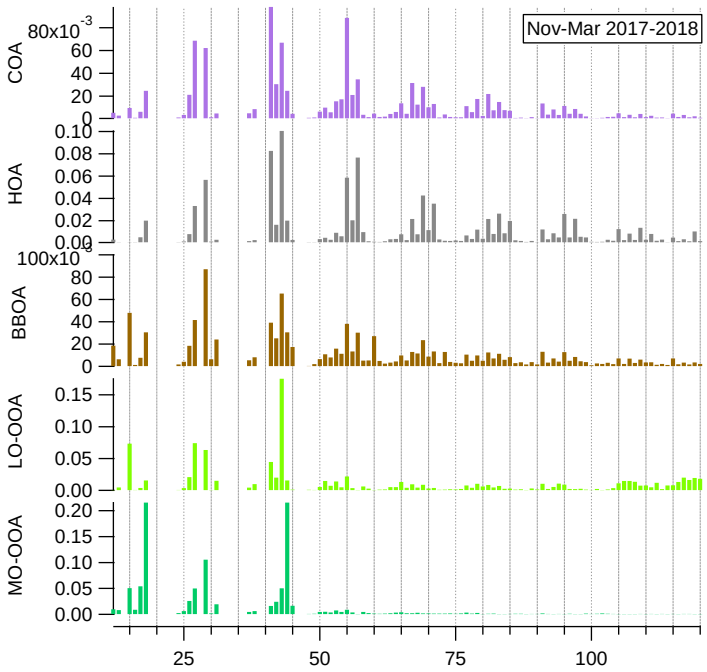
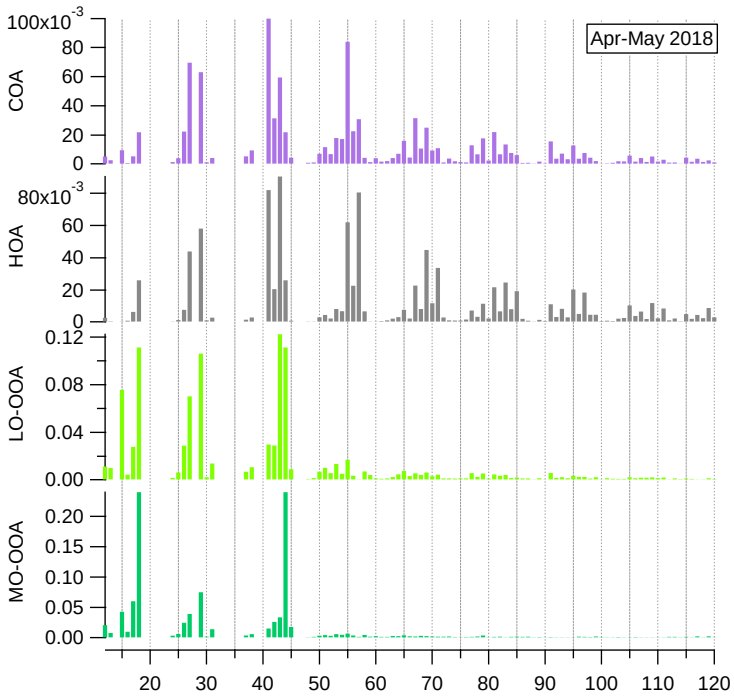

Nov-Mar 2017-2018
COA
HOA
BBOA
LO-OOA
MO-OOA
80x10-3
100x10-3
25
50
75
100


Apr-May 2018
COA
HOA
LO-OOA
MO-OOA
100x10-3
80x10-3
20
30
40
50
60
70
80
90
100
110
120

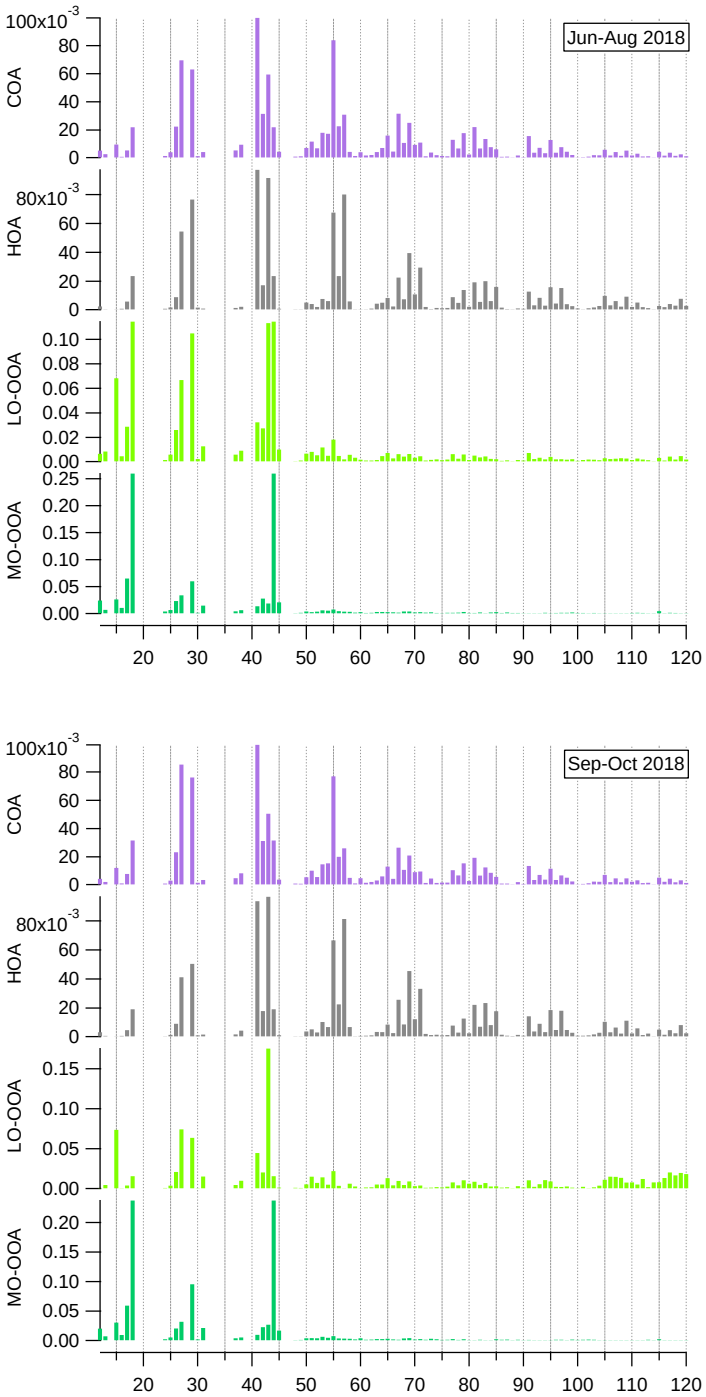


Figure S 3. Seasonal profiles of subperiods of periods A and B by chronological order.

Table S2. Correlations of factors mass spectra with external anchor mass spectra (a), and factors time series with external markers (b).

(a)		Crippa et al., 2013, *Ng et al., 2010				Mohr et al., 2012				
		COA	HOA	BBOA*	OOA	COA	HOA	BBOA	SV-OOA	LV-OOA
A	COA	0.96	0.87	0.74	0.35	0.92	0.76	0.76	0.71	0.19

	HOA	0.77	0.96	0.62	0.34	0.71	0.93	0.62	0.61	0.14
	BBOA	0.25	0.13	0.67	0.36	0.38	0.08	0.35	0.34	0.27
	LO-OOA	0.13	0.06	0.31	0.95	0.27	0.03	0.28	0.66	0.97
	MO-OOA	0.10	0.05	0.25	0.93	0.22	0.02	0.24	‘.65	0.95
B	COA	0.98	0.71	0.66	0.27	0.86	0.58	0.66	0.65	0.16
	HOA	0.79	0.99	0.61	0.19	0.73	0.94	0.65	0.55	0.10
	BBOA	0.62	0.50	0.99	0.40	0.77	0.40	0.72	0.65	0.33
	LO-OOA	0.39	0.25	0.70	0.79	0.64	0.16	0.66	0.75	0.72
	MO-OOA	0.07	0.02	0.03	0.89	0.17	0.05	0.16	0.56	0.94

(b)	Period A	Apr-May 2015	Jun-Aug 2014	Sep - Oct 2014	Nov-Mar 2014-2015	Period B	Ap-May 2018	Jun-Aug 2018	Sep-Oct 2018	Nov-Mar 2017-2018
COA vs. m/z 55	0.58	0.69	0.76	0.35	0.63	0.71	0.76	0.76	0.74	0.72
COA vs. HOA	0.20	0.32	0.24	0.02	0.26	0.31	0.32	0.32	0.28	0.33
HOA vs. BC	0.62	0.42	0.40	0.70	0.63	0.68	0.57	0.57	0.74	0.68
HOA vs. NO	0.44	0.36	0.16	0.53	0.42	0.63	0.41	0.41	0.68	0.76
HOA vs. NO_2	0.49	0.33	0.39	0.51	0.49	0.55	0.51	0.51	0.70	0.75
HOA vs. NO_x	0.44	0.40	0.29	0.45	0.44	0.65	0.51	0.51	0.70	0.75
LO-OOA vs. m/z 43	0.51	0.48	0.25	0.60	-	0.41	0.86	0.86	0.84	0.66
LO-OOA vs. NO_3^-	0.29	0.39	0.74	0.34	-	0.60	0.40	0.68	0.75	0.58
MO-OOA vs. m/z 44	0.60	0.40	0.68	0.75	0.58	0.69	0.84	0.84	0.96	0.96

MO-OOA vs. SO_4^{2-}	**0.02**	**0.09**	**0.13**	**0.03**	**0.03**	**0.10**	**0.32**	**0.32**	**0.31**	**0.47**
BBOA vs. m/z 60	**0.60**	**-**	**-**	**-**	**0.60**	**0.91**	**-**	**-**	**-**	**0.91**
BBOA vs. m/z 73	**0.55**	**-**	**-**	**-**	**0.55**	**0.61**	**-**	**-**	**-**	**0.61**

Table S 3. Comparison between i. total PM_1 from the sum of ACSM components (NR-PM_1) and BC concentrations and co-located measurements of PM_1 from OPC, SMPS and quartz-fiber filters and ii. ACSM species concentration vs. 24-h samples concentrations. Fit parameters correspond to least orthogonal distance regression method.

(i)		A			B		
y	x	R^2	Slope	Intercept	R^2	Slope	Intercept
NR-PM_1+BC	OPC	0.71	0.989 ± 0.007	0.98 ± 0.07	0.76	1.285 ± 0.006	-2.31 ± 0.07
NR-PM_1+BC	SMPS (Mass)	0.61	1.001 ± 0.006	0.37 ± 0.07	0.72	1.177 ± 0.006	-0.47± 0.05
NR-PM_1+BC	PM_1 reconstructed	0.75	1.40 ± 0.09	-1.1 ± 0.8	0.63	1.70 ± 0.17	-3.4 ± 1.3

(ii)		A			B		
y	x	R^2	Slope	Intercept	R^2	Slope	Intercept
SO_4^{2-} ACSM	SO_4^{2-} offline	0.89	1.24±0.05	-0.31±0.10	0.93	1.32±0.06	-0.19±0.09
NO_3^- ACSM	NO_3- offline.	0.84	1.9±0.1	-0.12±0.09	0.86	1.72±0.10	0.35±0.12
NH_4^+ ACSM	NH4 offline	0.86	1.72±0.08	-0.26±0.07	0.85	1.98±0.13	-0.05±0.09
OA ACSM	OC offline	0.73	2.69±0.17	-0.9±0.4	0.86	2.96 ± 0.19	-1.5± 0.4

Table S 4. Mean and standard deviation for variables under study in periods A and B.

			Period A		**Period B**	
	Variables	**Units**	**Average**	**Standard Deviation**	**Average**	**Standard Deviation**

Meteorological parameters	Temperature	°C	18.2	5.7	18.4	6.8
	Relative Humidity	%	70.7	15.3	70.2	14.8
	Pressure	hPa	1006.5	7.3	1005.5	7.32
	Sun Radiation	$W \cdot m^{-2}$	180.0	266.0	178.9	268.5
	Wind Speed	$m \cdot s^{-1}$	2.0	1.4	2.0	1.5
	Wind Direction	°	170.0	102.0	200.4	104.8
Gas-phase pollutants	O_3	$\mu g \cdot m^{-3}$	52.4	28.0	47.6	23.8
	CO	$\mu g \cdot m^{-3}$	0.3	0.2	0.3	0.3
	SO_2	$\mu g \cdot m^{-3}$	2.0	1.7	1.7	1.4
	NO	$\mu g \cdot m^{-3}$	8.3	19.2	8.5	1.2
	NO_2	$\mu g \cdot m^{-3}$	32.3	24.8	30.6	21.3
NR-PM_1 ACSM Species	OA	$\mu g \cdot m^{-3}$	4.2	2.8	4.0	2.8
	SO_4^{2-}	$\mu g \cdot m^{-3}$	1.9	1.5	1.5	1.2
	NO_3^-	$\mu g \cdot m^{-3}$	1.3	1.7	1.4	1.9
	NH_4^+	$\mu g \cdot m^{-3}$	1.1	0.9	1.0	0.8
	Cl^-	$\mu g \cdot m^{-3}$	0.05	0.08	0.06	0.08
MAAP	BC	$\mu g \cdot m^{-3}$	1.7	1.6	1.4	1.4
ACSM + MAAP	PM_1	$\mu g \cdot m^{-3}$	10.1	6.7	9.6	6.6
OPC	PM_1	$\mu g \cdot m^{-3}$	8.3	5.4	9.1	5.0
SMPS	PM_1	$\mu g \cdot m^{-3}$	9.8	7.0	8.5	5.3
Filters	PM_1	$\mu g \cdot m^{-3}$	8.0	4.2	7.1	3.0

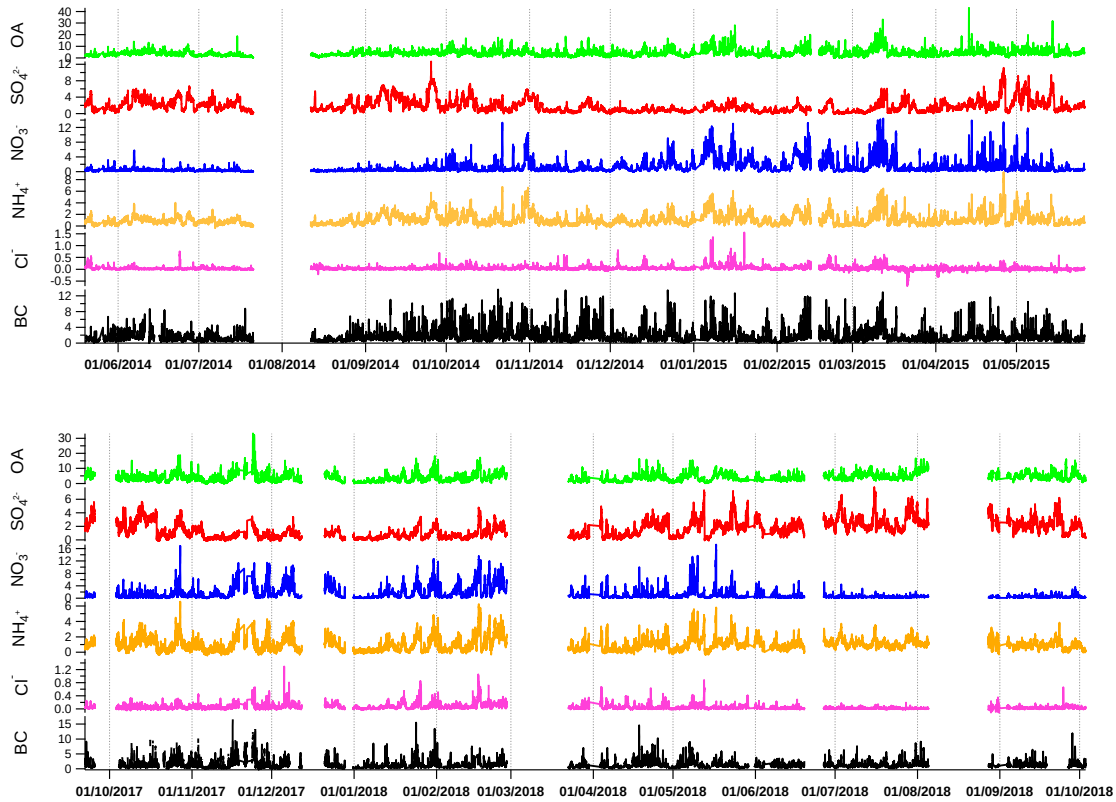
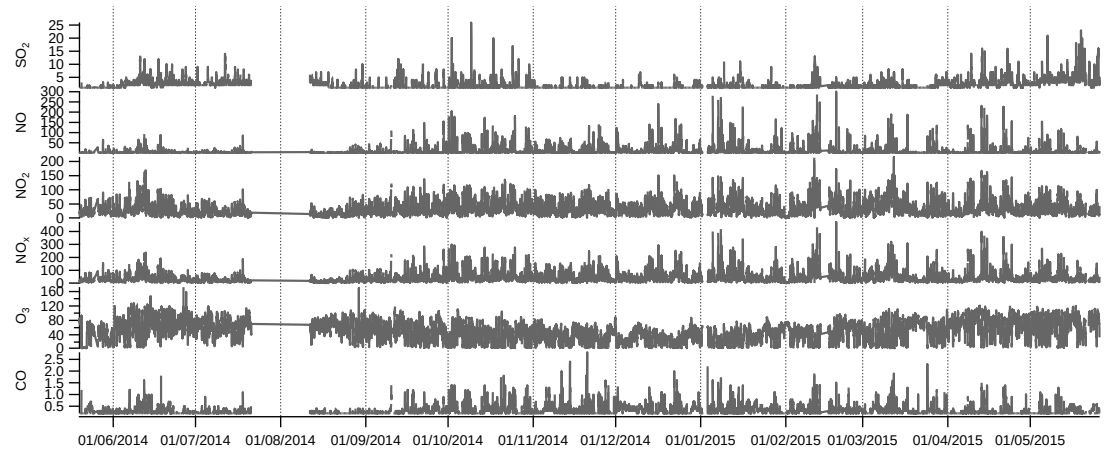


Figure S 4. Time series for NR-PM$_1$ species and BC concentrations in periods A (top) and B (bottom).



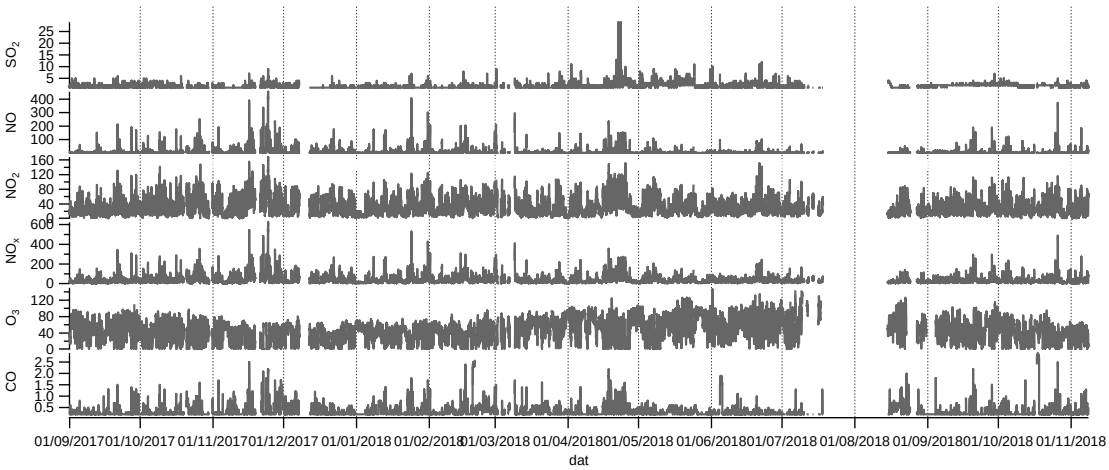


Figure S 5. Time series of co-located gases measurements for period A (top) and B (bottom).

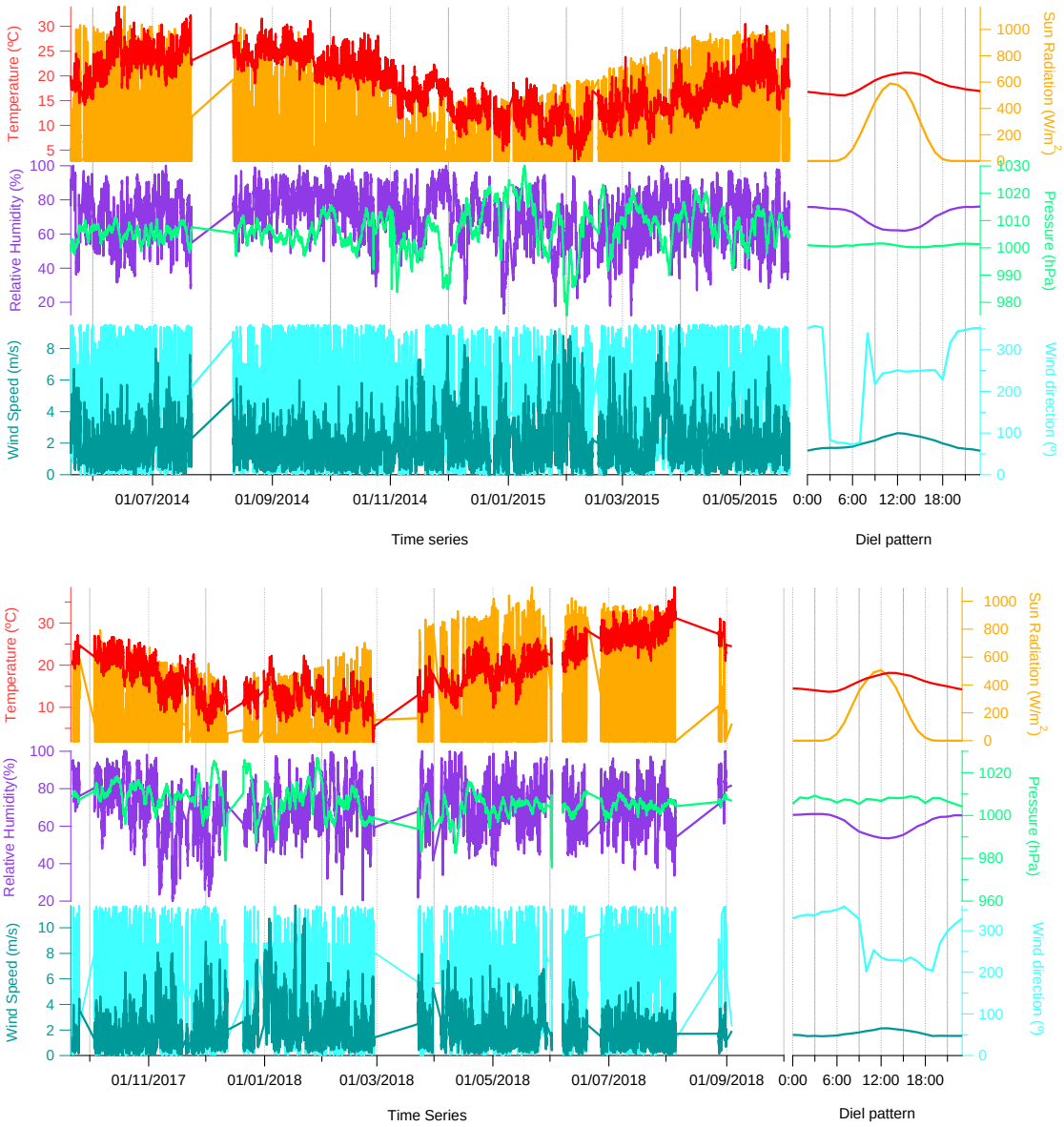


Figure S 6. Time series and diel patterns of meteorological variables for periods A (top) and B (bottom).

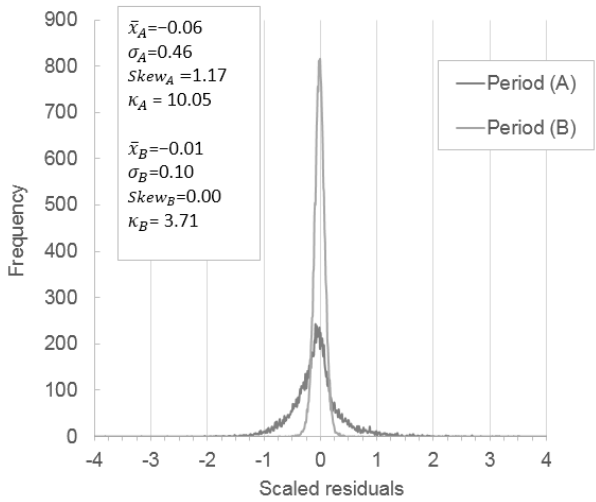
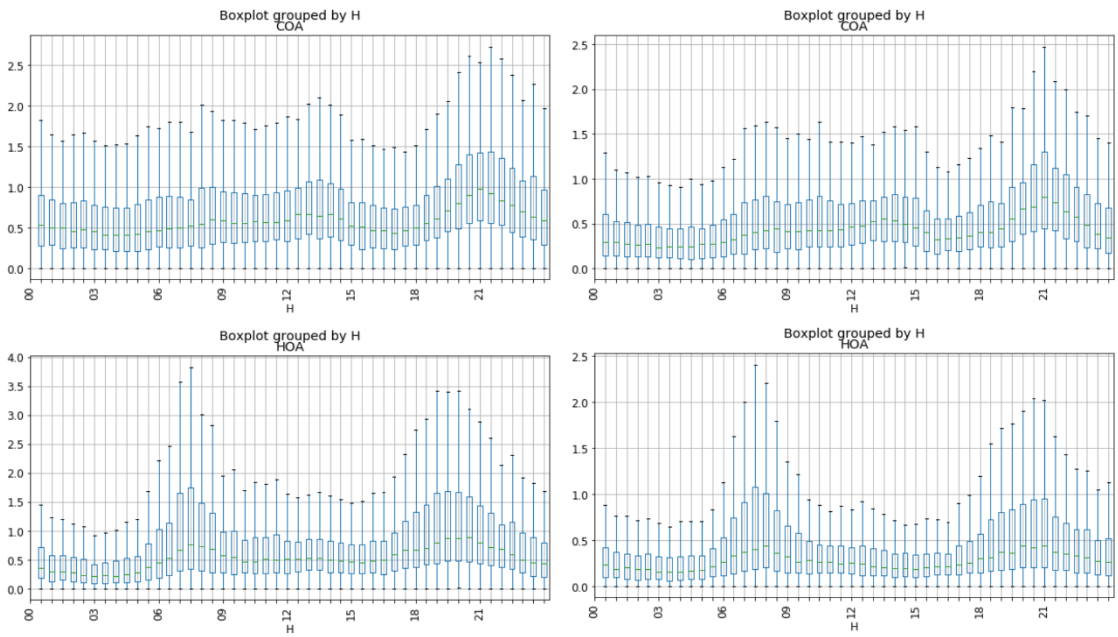


Figure S 7. Residual scaled distributions of PMF OA source distribution using ME-2 approach for periods A and B. Parameters of both distributions (mean, standard deviation, skewness coefficient and kurtosis coefficient) are listed.



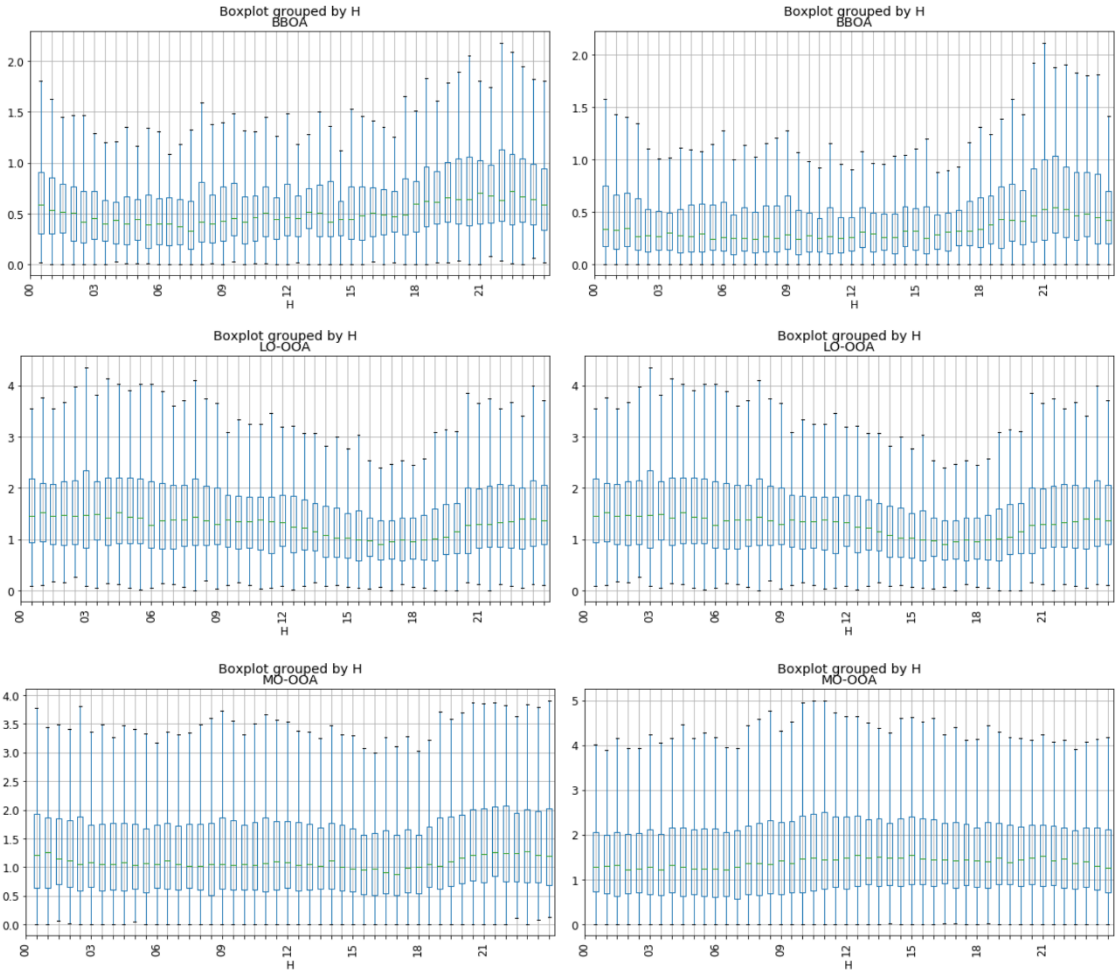


Figure S 8. Diel patterns of apportioned factors. Boxplots represent median and interquartile range and whiskers show maximum and minimum values. Factors are in this order COA, HOA, BBOA, LO-OOA and MO-OOA and left column corresponds to period A and right one to B.

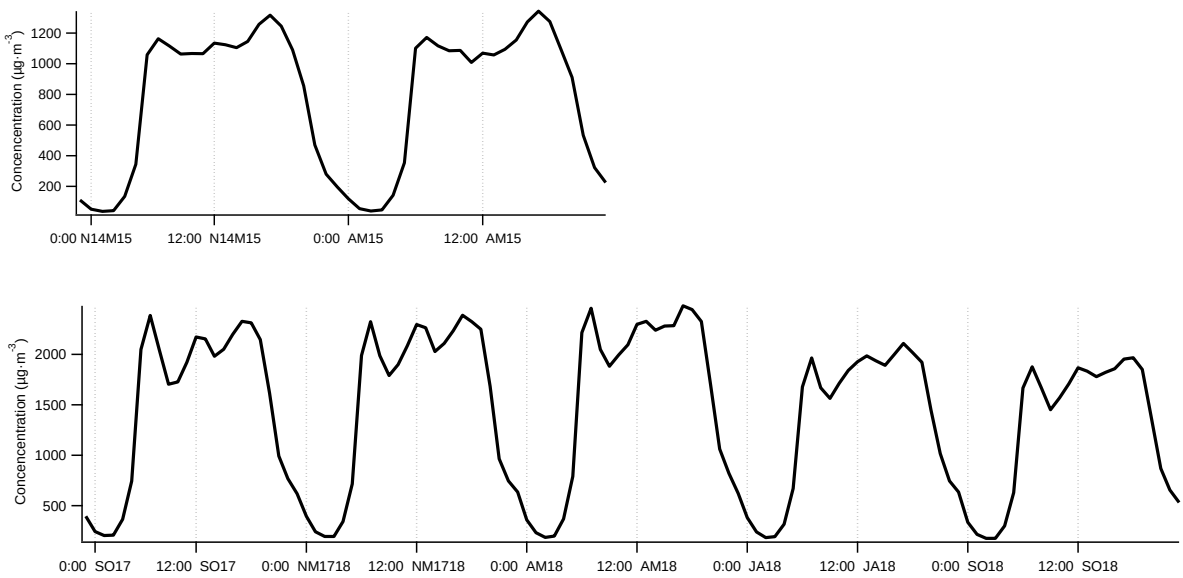


Figure S 9. Mean diel seasonal pattern of available traffic intensity from data from period A and B to 2018 at 400m away from site for period A (a) and B (b).

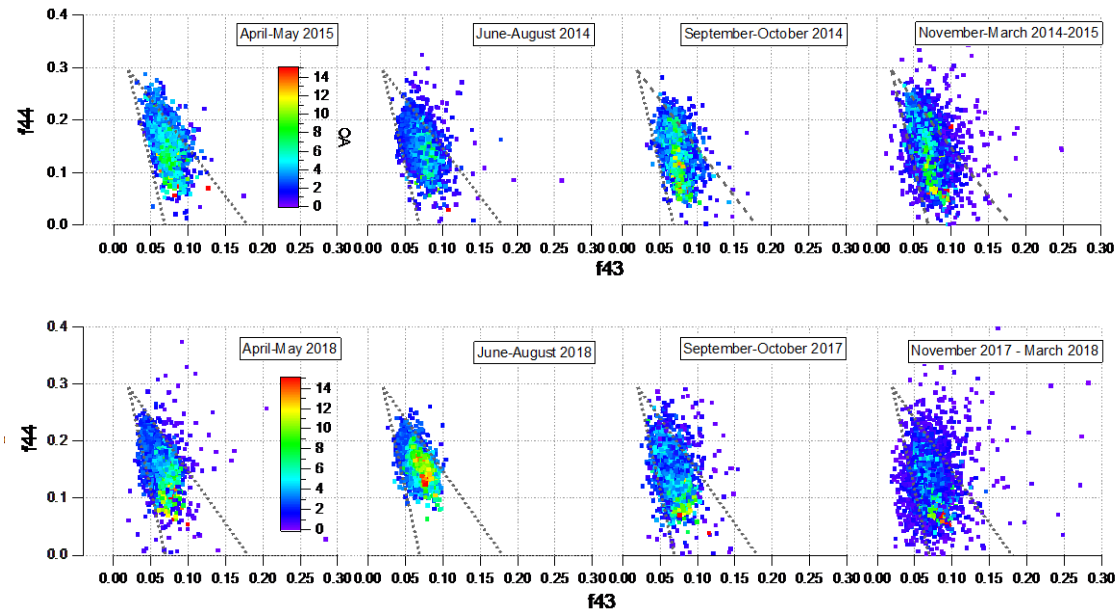
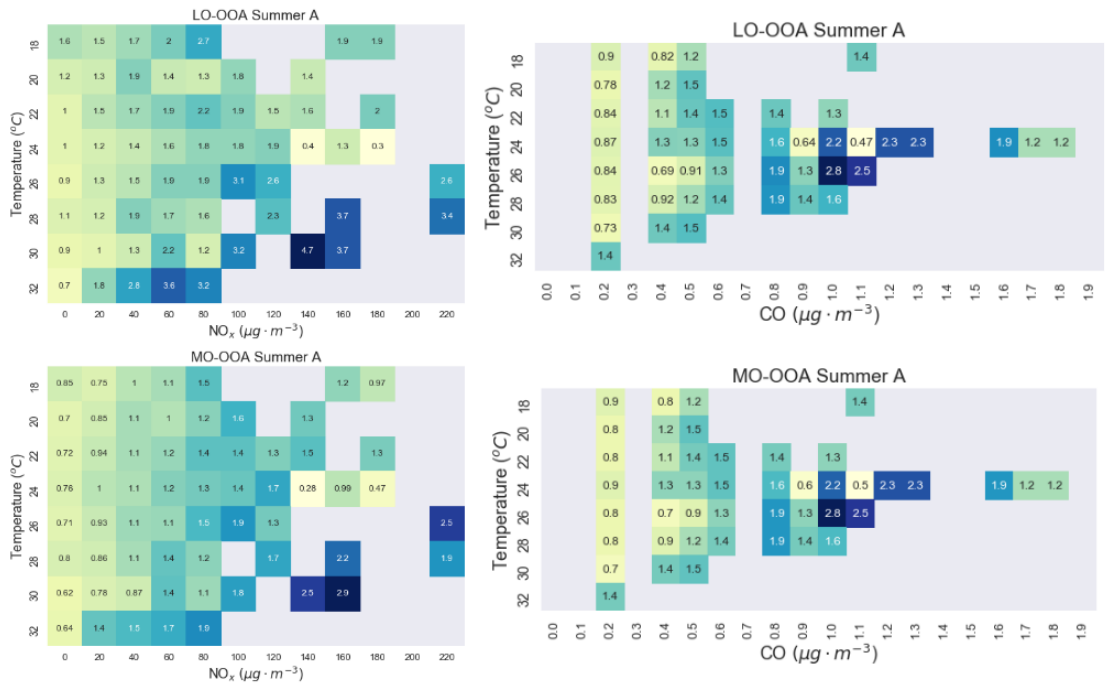
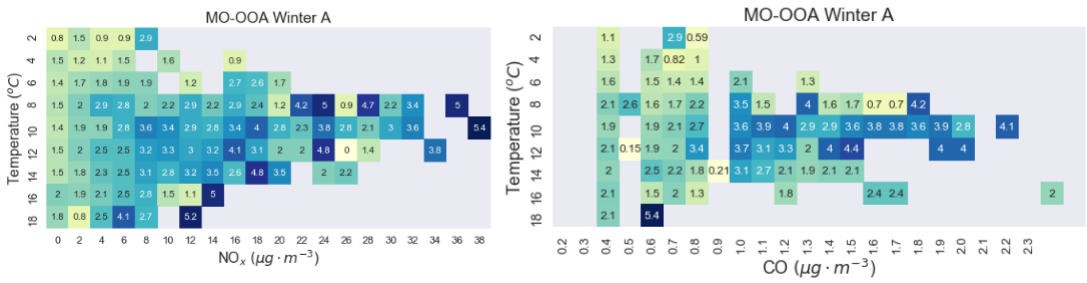


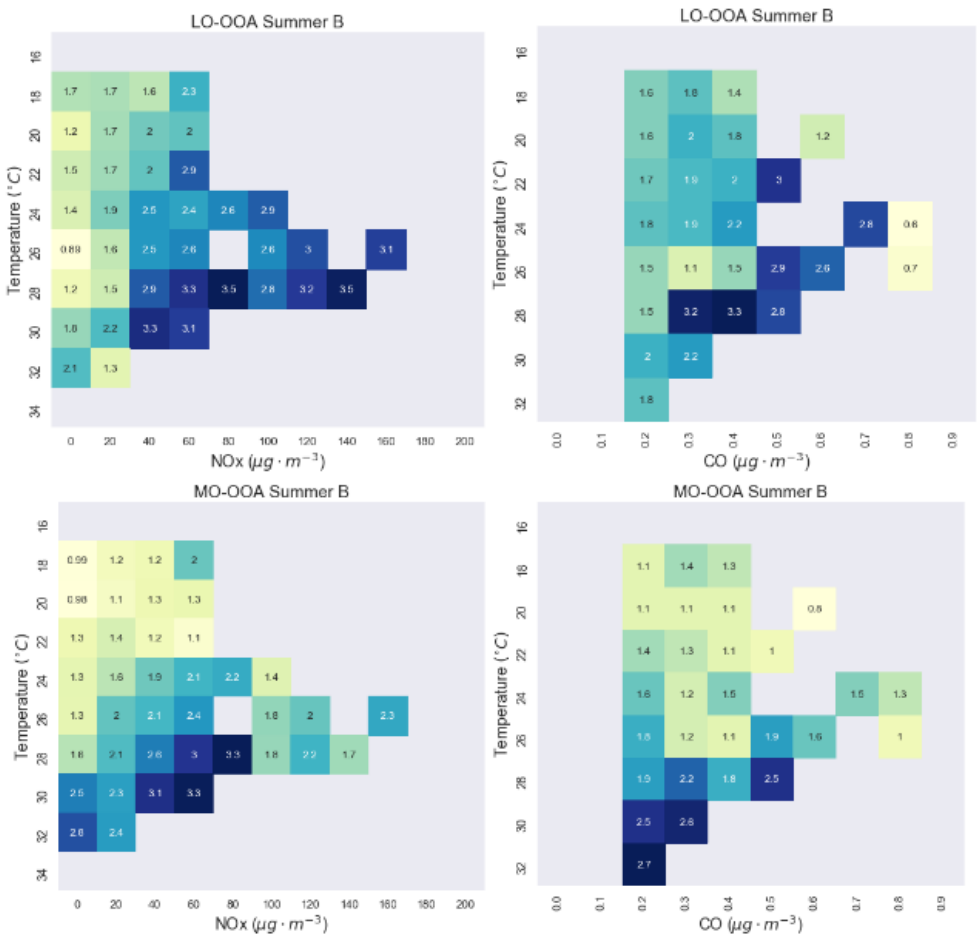
Figure S 10. Seasonal scatterplot of f44 and f43 arranged colored by OA concentrations. Top and bottom graphs correspond to period A and B respectively. Dashed lines correspond to the triangle plot (Ng et al., 2010)**.**

(a)




MO-OOA Winter A
Temperature (°C)
NO_x ($\mu g \cdot m^{-3}$)
MO-OOA Winter A
Temperature (°C)
CO ($\mu g \cdot m^{-3}$)

(b)


LO-OOA Summer B
Temperature (°C)
NOx ($\mu g \cdot m^{-3}$)
LO-OOA Summer B
Temperature (°C)
CO ($\mu g \cdot m^{-3}$)
MO-OOA Summer B
Temperature (°C)
NOx ($\mu g \cdot m^{-3}$)
MO-OOA Summer B
Temperature (°C)
CO ($\mu g \cdot m^{-3}$)

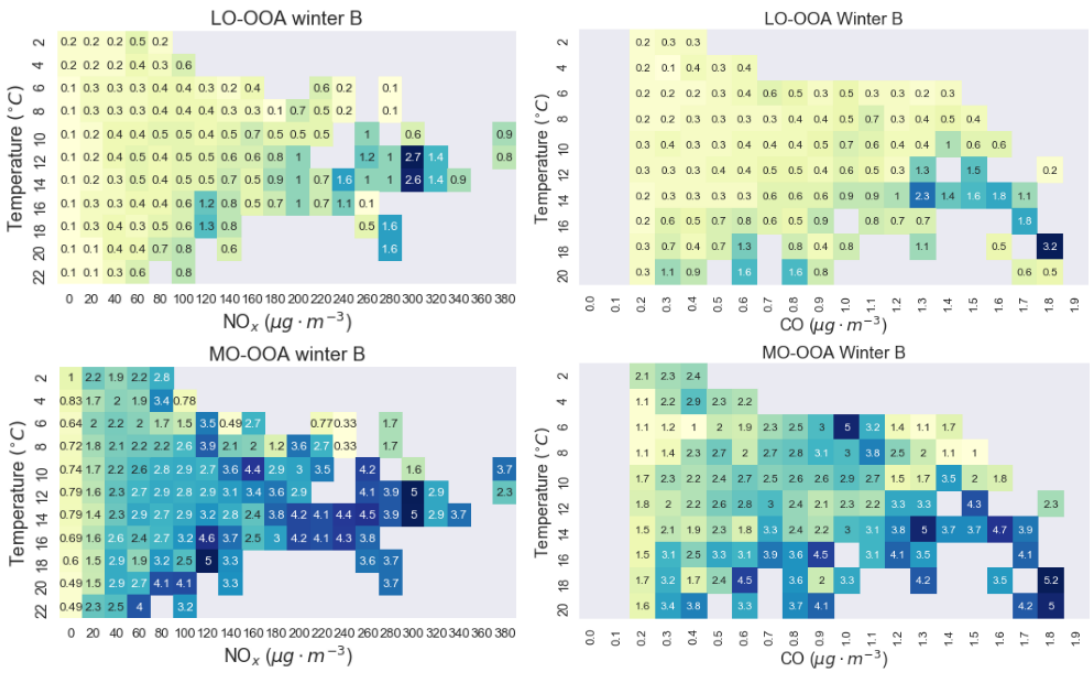


Figure S 11. Heatmap of Temperature vs. NOx for summer (JJA) and winter (DJF) and LO-OOA and MO-OOA respectively for period A (a) and B (b). Figure S 12. Ozone (O_3) diel cycle for seasons in period A (top) and period B (bottom) at Palau Reial (PR) and Montseny (MSY).

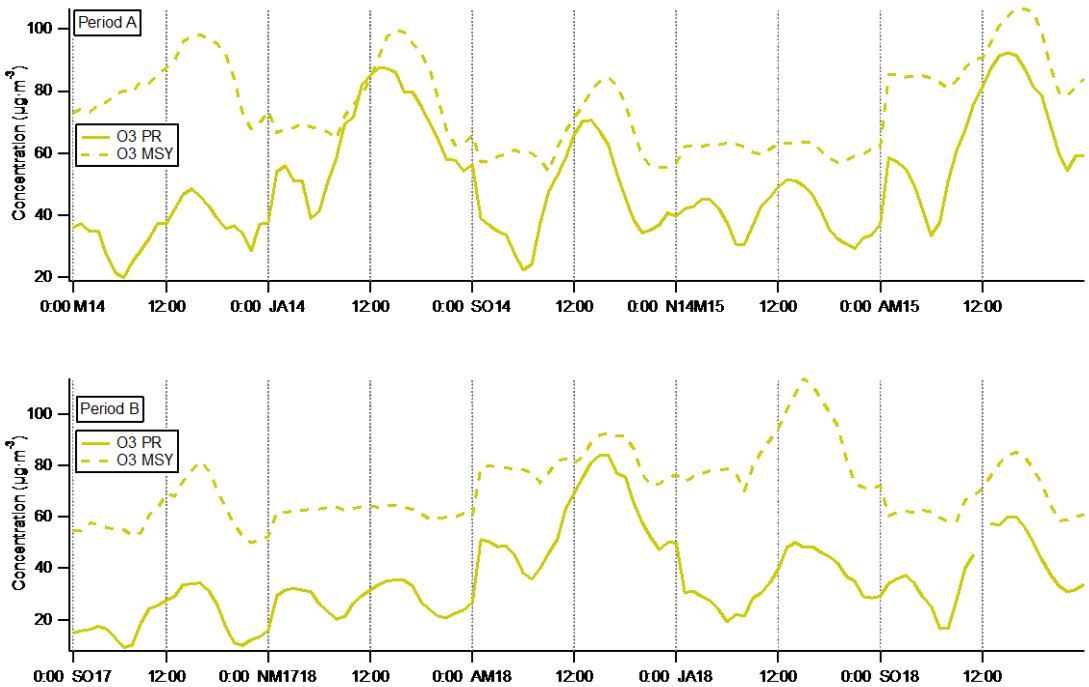


Figure S 12. Ozone diel cycle for seasons in period A (top) and period B (bottom) at Palau Reial (PR) and Montseny (MSY).

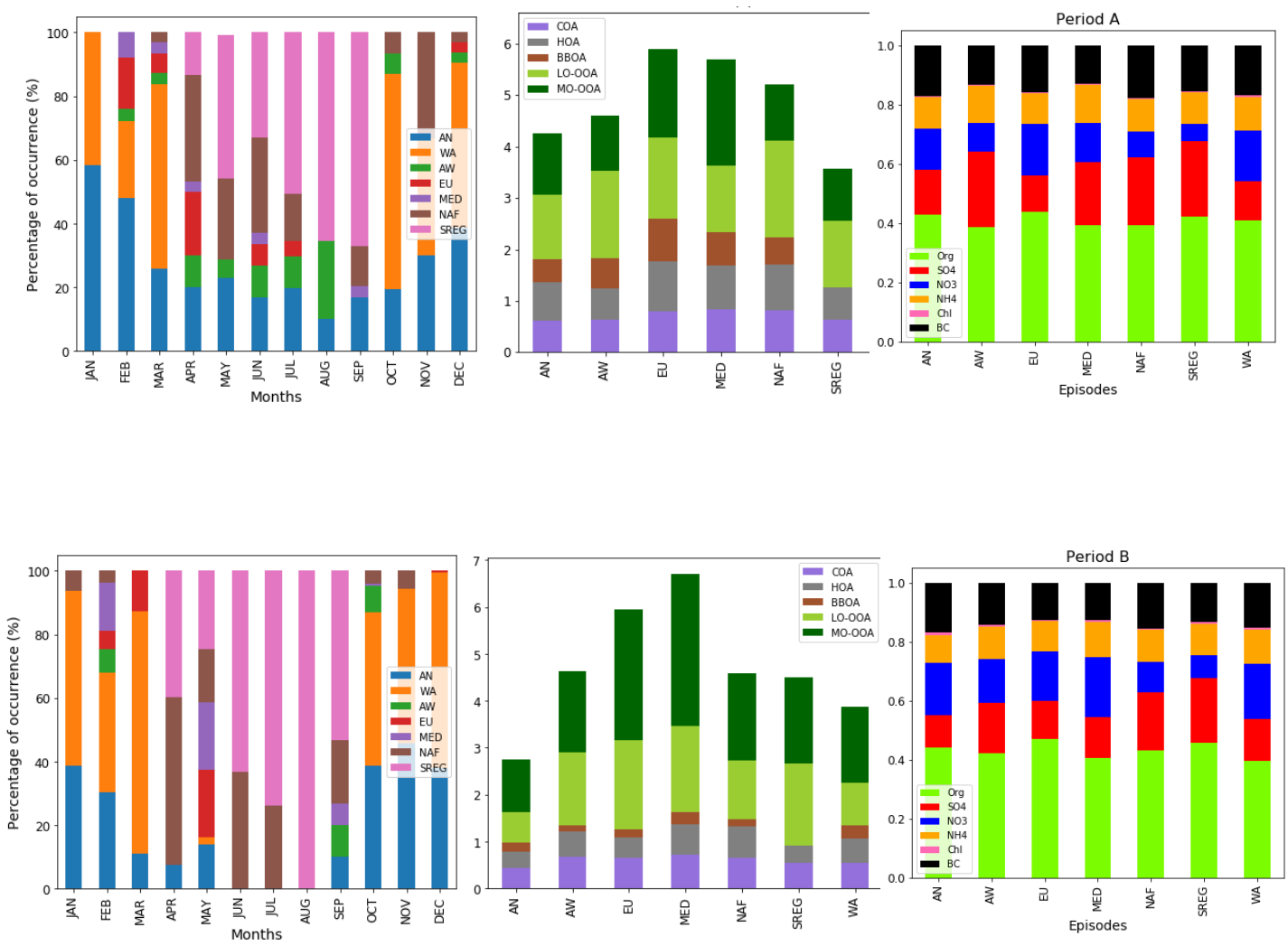


Figure S 13. Relative frequency of occurrence of episodes sorted by month, mean concentrations per each factor grouped by episodes and relative concentrations of NR-PM1 components grouped by episodes from left to right and for period A (top) and B (bottom).