Orbitrap data interpretation

Different regimes in the assignments of peaks obtained by means of high-resolution mass spectrometry (HRMS) analysis based on oxidation state information in terms of the O/C vs H/C ratios has been performed in order to further understand and assign their compound nature. Using the Van Krevelen diagrams for organic mixtures, regions of condensed hydrocarbons, lipids, secondary organic aerosol (SOA), proteins and carboxylic acids (Wozniak et al., 2008) or more generally as aliphatic, aromatic and SOA domains (Kourtchev et al., 2014) have been described. Considering these definitions, we assigned three domains with aliphatic compounds belonging to the less oxidized domain with O/C≤ 0.5 and high H/C≥ 1.5, low oxygenated aromatic domain is present at O/C≤ 0.5 and H/C≤ 1, and more oxidized compounds can be found at higher O/C> 0.5. Examples for the domains arise from the analysis of filters from Paris and Rambouillet. $C_{10}H_{16}O_3$ (possible pinonic acid) with O/C= 0.3 and H/C= 1.6 in the aliphatic domain, considered as a first oxidation product of α-pinene (Kristensen et al., 2013). $C_8H_6O_4$ with O/C= 0.5 and H/C= 0.62, possible associated to alkylbenzenedioic acids from urban aerosols (Simoneit, 1985) or aromatics with carbonyl and hydroxyl functionalities with formula $C_9H_6O_4$ (Rincón et al., 2012) with O/C= 0.44 and H/C= 0.66, may falls in the aromatic domain. $C_8H_{12}O_6$ (possible 3-methyl-1,2,3-butanetricarboxylic acid, MBTCA) with O/C= 0.75 and H/C= 1.5, as a further oxidation product of cis-pinonic acid (Kourtchev et al., 2015), in the more oxidized domain.

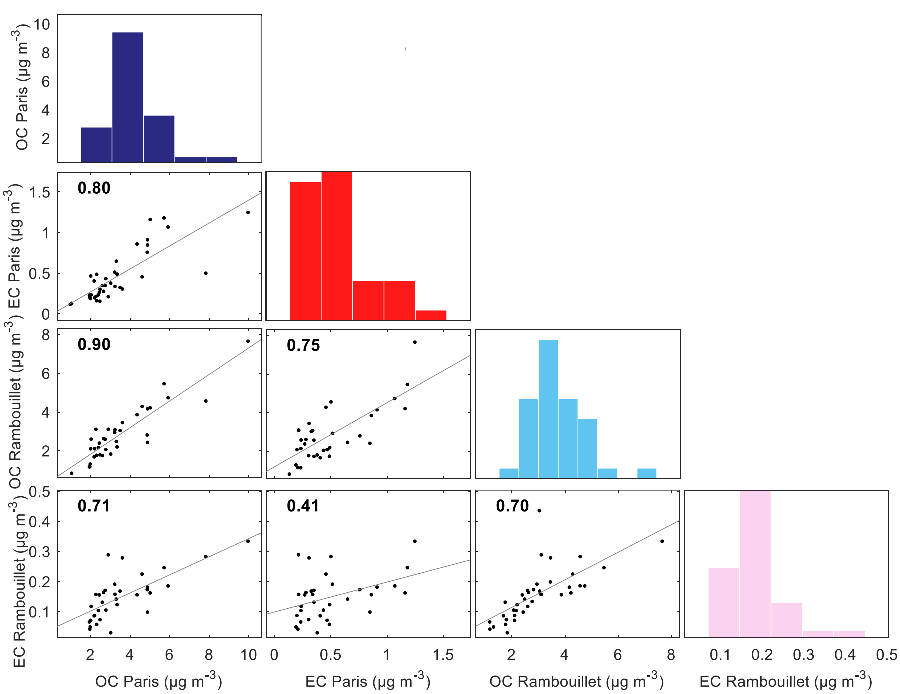

Figure S1: Pearson correlations matrix for OC (blue) and EC (red) concentrations for Paris and Rambouillet. Data from the overlap period (June 27 to July 22) is considered here and r is represented for each correlation. Normal distributions for the values of OC concentrations for Paris and Rambouillet and EC concentrations for Rambouillet are observed here.

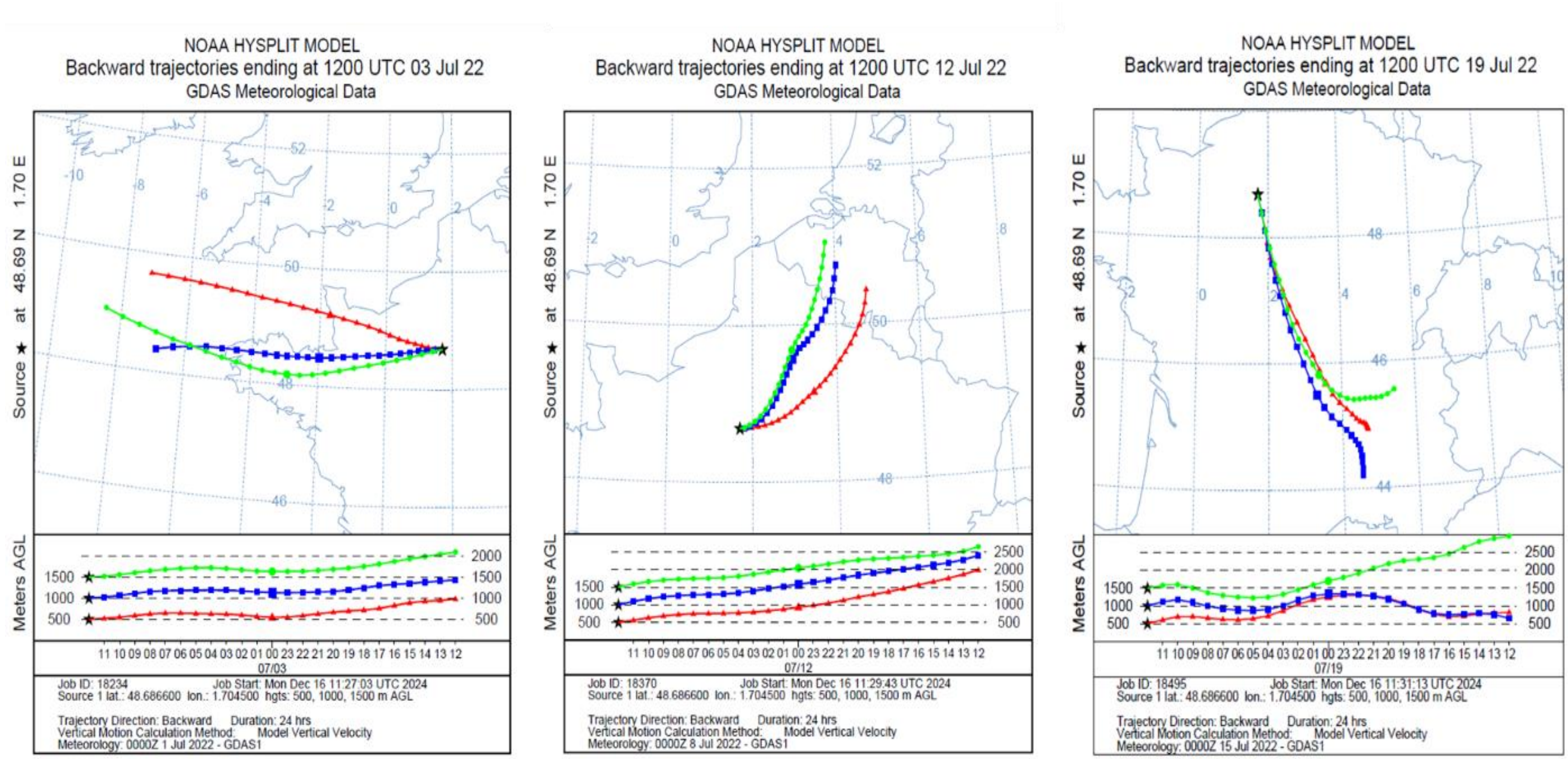

Figure S2. Example of back-trajectories for background and pollution periods calculated with the HYSPLIT model at 1 degree resolution for 24 hours.

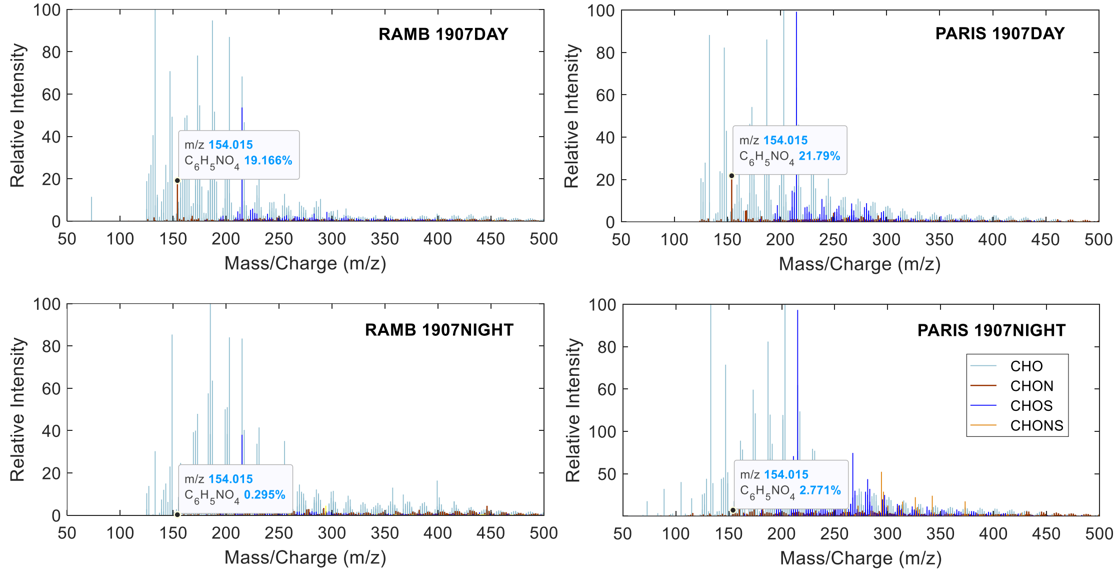

Figure S3: Mass spectra from direct infusion in the negative mode nano-ESI analysis for specific consecutive samples of Rambouillet (RAMB) and Paris samples collected during the day and night periods of July 19 of the summer 2022. Identification of the presence of nitrocathecol as a BB molecular tracer. Molecular formulae are grouped as CHO (clear blue), CHON (brown), CHOS (dark blue) and CHONS (orange) classes.

Table S1. Bulk characteristics and number of formulae detected for each sample of Paris and Rambouillet. Formulae are obtained by HRSM analysis for day and night periods. The values of OC and EC concentrations, T, RH, O_3 concentrations and NOx concentrations presented here represent average values for the period of sampling and are reported with their standard deviations.

	Concentration (µg m^{-3})		**Number of formulae**					**Atmospheric conditions**				
sample name	OC	EC	CHO	CHON	CHOS	CHONS	ALL	T (°C)	RH (%)	O_3 (ppb)	NOx (ppb)	SO_2 (ppb)
RAMB0307 DAY	1.3	0.1	650	433	379	177	1639	19.4 ± 3.9	56.1 ± 18.4	34.7 ± 8.4	0.9 ± 0.3	0.3 ± 0.1
RAMB0307 NIGHT	1.2	0.0	752	706	382	236	2076	11.6 ± 2.8	81.9 ± 8.8	23.5 ± 9.7	1.1 ± 0.9	0.2 ± 0.1
RAMB0407 DAY	1.8	0.1	1149	995	517	350	3011	19.8 ± 5.2	52.1 ± 21.1	38.0 ± 13.9	0.9 ± 0.4	0.4 ± 0.2
RAMB0407 NIGHT	-	-	707	800	422	419	2348	12.5 ± 3.4	78.9 ± 11.5	29.8 ± 10.9	0.9 ± 0.2	0.4 ± 0.2
RAMB1107 NIGHT	3.5	0.2	1225	1505	447	328	3505	19.4 ± 2.0	64.7 ± 10.0	34.6 ± 5.4	2.7 ± 1.3	0.3 ± 0.1
RAMB1207 DAY	3.0	0.2	1519	2430	515	576	5040	26.3 ± 5.1	41.0 ± 22.3	61.6 ± 22.3	1.4 ± 0.6	0.4 ± 0.1
RAMB1207 NIGHT	4.7	0.2	1385	1569	548	337	3839	18.8 ± 0.9	64.9 ± 3.7	34.4 ± 8.7	1.0 ± 0.7	0.2 ± 0.1
RAMB1307 DAY	4.2	0.2	1529	2197	334	461	4521	29.0 ± 5.9	34.7 ± 17.7	58.3 ± 17.3	1.3 ± 0.9	0.9 ± 0.8
RAMB1707 DAY	3.1	0.2	1215	1832	468	496	4011	25.2 ± 5.2	36.2 ± 17.5	69.1 ± 16.6	1.8 ± 0.8	0.4 ± 0.1
RAMB1707 NIGHT	4.2	0.2	1547	1789	388	287	4011	18.1 ± 1.6	56.6 ± 4.8	46.1 ± 5.8	2.1 ± 0.9	0.3 ± 0.1
RAMB1807 DAY	3.9	0.2	1571	1901	396	322	4190	30.6 ± 6.6	28.2 ± 14.7	77.3 ± 17.9	1.5 ± 0.6	1.0 ± 0.8
RAMB1807 NIGHT	5.5	0.3	1516	1309	368	211	3404	23.7 ± 1.8	40.9 ± 4.4	54.2 ± 6.9	2.3 ± 0.9	0.4 ± 0.3
RAMB1907 DAY	7.7	0.3	1679	1542	384	282	3887	31.6 ± 5.6	33.1 ± 13.5	75.0 ± 14.0	1.4 ± 0.6	1.5 ± 1.2
RAMB1907 NIGHT	4.6	0.3	1361	1564	222	178	3325	21.6 ± 2.7	69.0 ± 13.4	44.1 ± 13.0	1.1 ± 0.4	0.4 ± 0.2
PARIS0307 DAY	2.0	0.2	1415	2042	534	800	4791	20.7 ± 2.6	50.6 ± 10.1	36.0 ± 4.0	3.4 ± 1.4	0.1 ± 0.1
PARIS0307 NIGHT	2.0	0.2	970	1241	343	322	2876	17.4 ± 1.5	61.4 ± 5.0	29.5 ± 2.6	3.3 ± 1.3	0.2 ± 0.2
PARIS0407 DAY	2.5	0.3	1375	2391	485	767	5018	21.9 ± 3.3	45.5 ± 11.9	38.7 ± 11.1	8.0 ± 3.9	0.2 ± 0.2
PARIS0407 NIGHT	2.3	0.2	1060	1485	410	450	3405	16.8 ± 2.0	68.1 ± 7.1	29.6 ± 2.7	3.2 ± 1.2	0.2 ± 0.3
PARIS1107 NIGHT	-	-	1038	1818	355	488	3699	21.4 ± 0.0	62.9 ± 0.1	-	-	-
PARIS1207 DAY	3.2	0.5	807	1271	293	292	2663	28.2 ± 4.0	37.8 ± 14.7	49.6 ± 16.7	24.5 ± 17.0	0.1 ± 0.3
PARIS1207 NIGHT	5.9	1.1	984	1659	257	215	3115	26.1 ± 1.9	35.4 ± 6.9	25.7 ± 13.4	22.9 ± 10.8	0.3 ± 0.3
PARIS1307 DAY	5.0	1.2	1021	1699	286	177	3183	31.1 ± 4.1	30.9 ± 9.1	45.5 ± 23.5	25.2 ± 27.4	0.3 ± 0.2
PARIS1707 DAY	3.2	0.3	1119	1449	517	456	3541	26.7 ± 4.2	32.2 ± 10.3	47.3 ± 9.2	6.9 ± 4.0	0.6 ± 0.4
PARIS1707 NIGHT	4.9	0.9	1396	2161	533	609	4699	25.1 ± 1.7	33.2 ± 3.6	27.9 ± 4.8	20.4 ± 5.6	0.7 ± 0.7
PARIS1807 DAY	4.3	0.9	1268	1509	290	181	3248	32.1 ± 5.1	24.8 ± 8.0	45.1 ± 20.3	24.7 ± 14.7	0.7 ± 0.9
PARIS1807 NIGHT	5.7	1.2	1481	2347	419	435	4682	28.4 ± 1.9	31.8 ± 3.4	25.0 ± 6.9	25.1 ± 8.6	0.4 ± 0.3
PARIS1907 DAY	10.0	1.3	1222	1108	330	133	2793	34.0 ± 4.4	28.0 ± 10.2	51.9 ± 15.5	20.1 ± 12.3	0.8 ± 0.8
PARIS1907 NIGHT	7.8	0.5	1068	1157	516	438	3179	25.1 ± 2.1	62.2 ± 12.4	43.7 ± 5.9	4.1 ± 1.4	0.1 ± 0.1

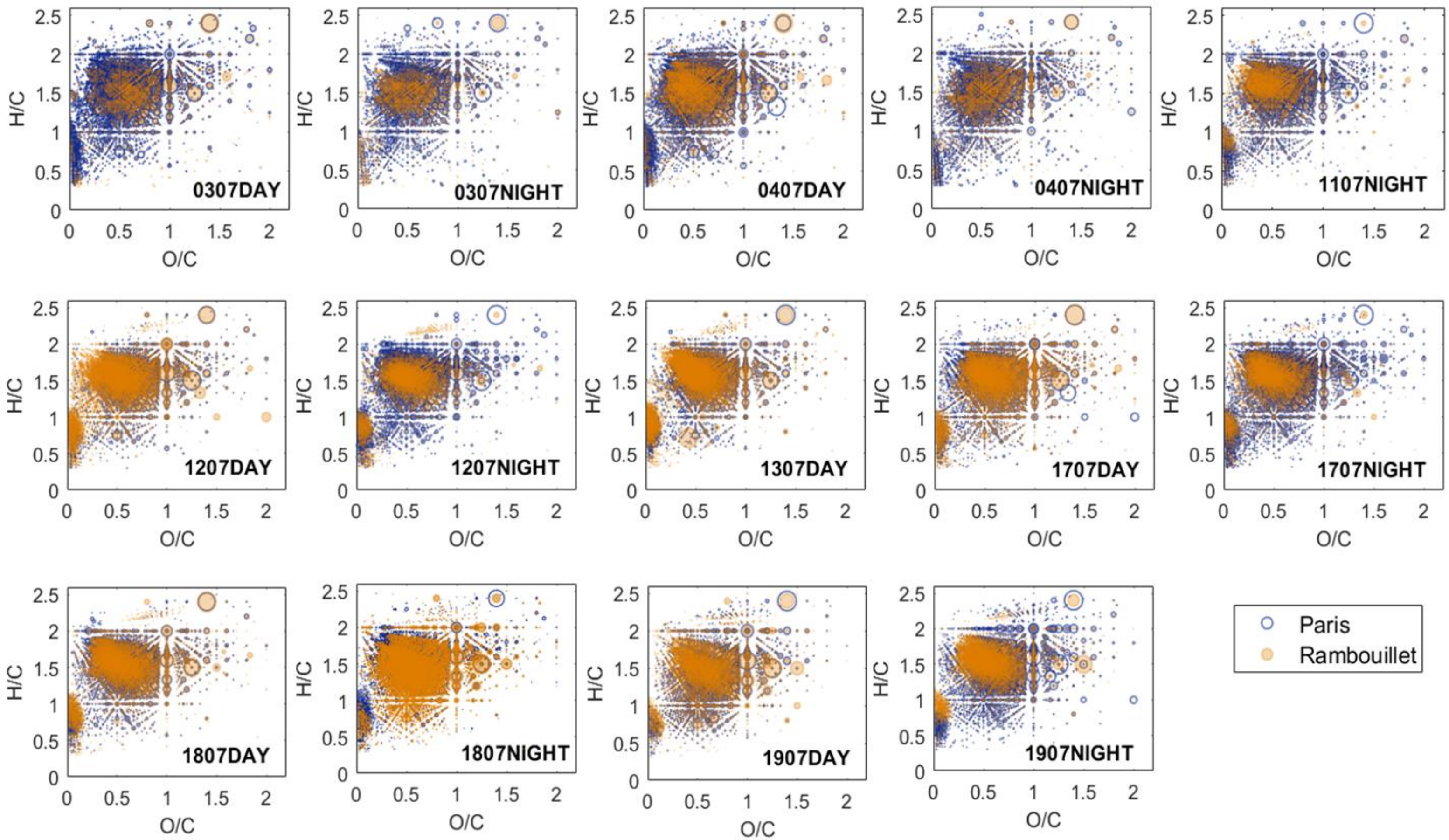

Figure S4: Comparison of Van Krevelen diagrams of specific samples for compounds detected in the aerosol samples collected at Rambouillet (orange) and Paris (blue) in the summer 2022. Data here was obtained from HRMS analysis. The date and day/night sampling condition is indicated in the plot (e.g., 0307DAY means daytime filter for the 3rd of July).

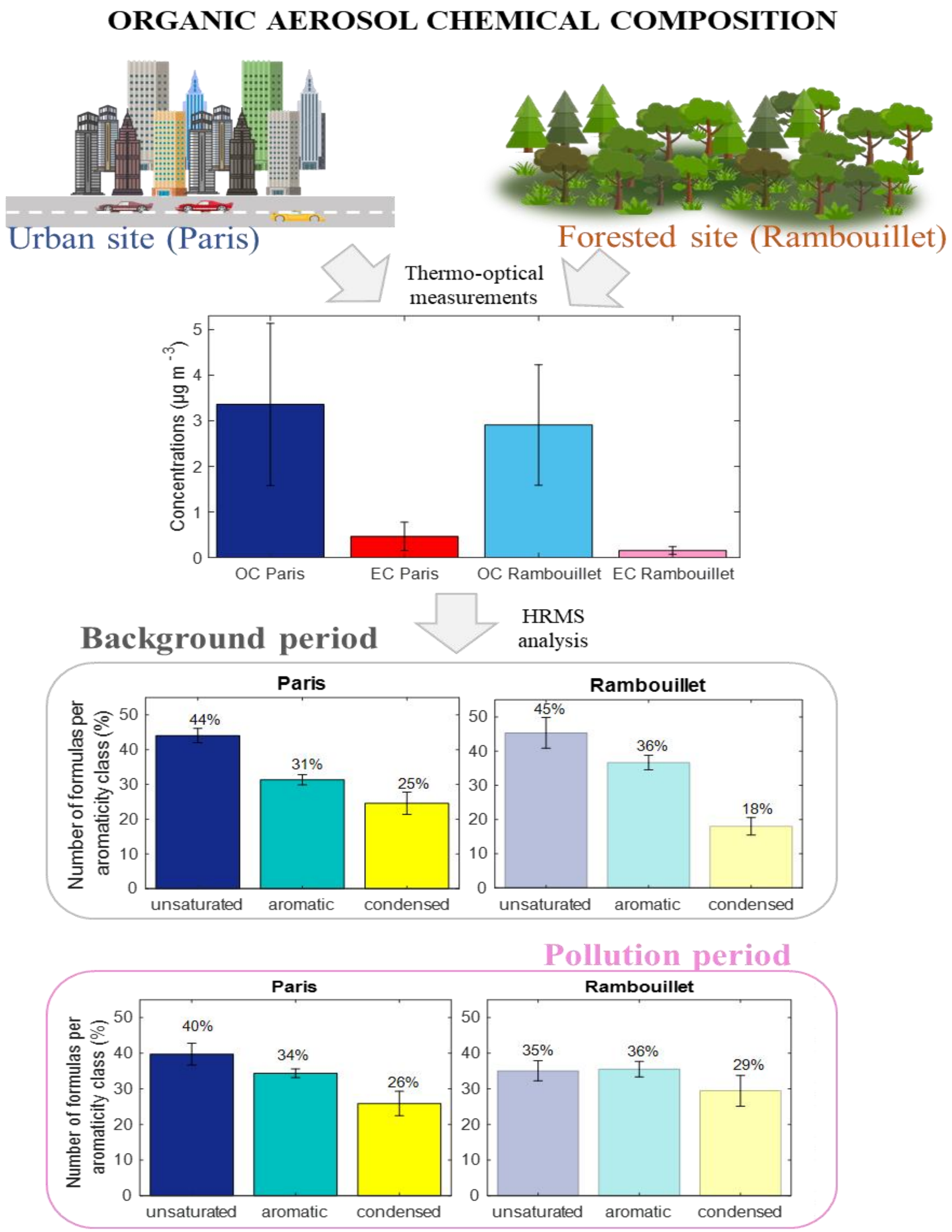

Figure S5: Diagram of the summary of the comparison of the aerosol chemical composition at Paris and Rambouillet for samples collected during the ACROSS campaign and analysis performed by thermo-optical method and HRMS.

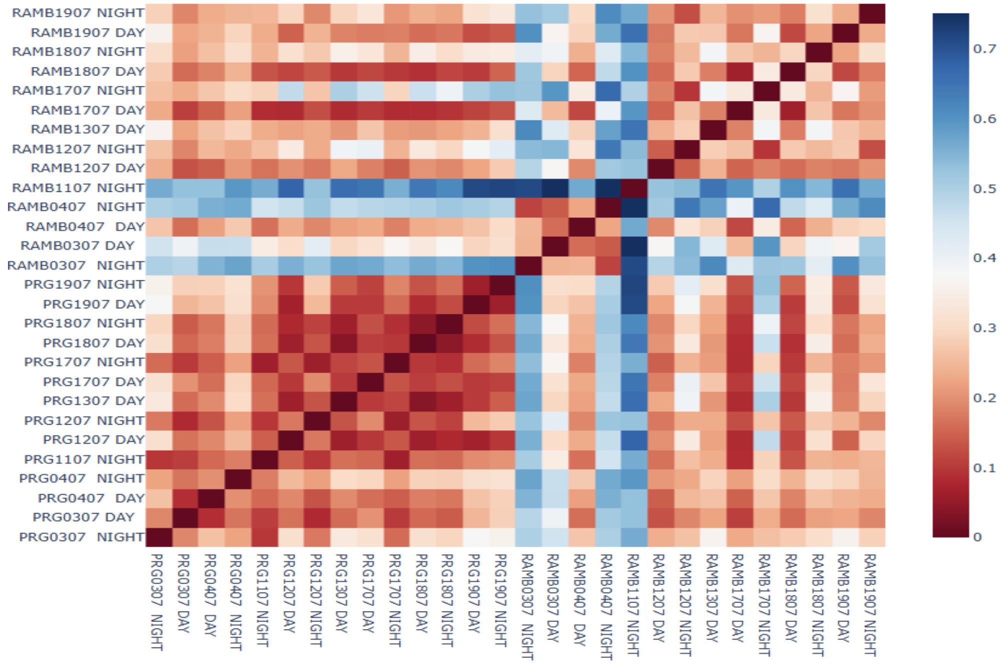

Figure S6: Cosine distances matrix for samples collecting during day and night at Paris and Rambouillet during the summer 2022. Lower values (red) of cosine distances shows similarities between the samples while higher values (blue) show differences between the samples.

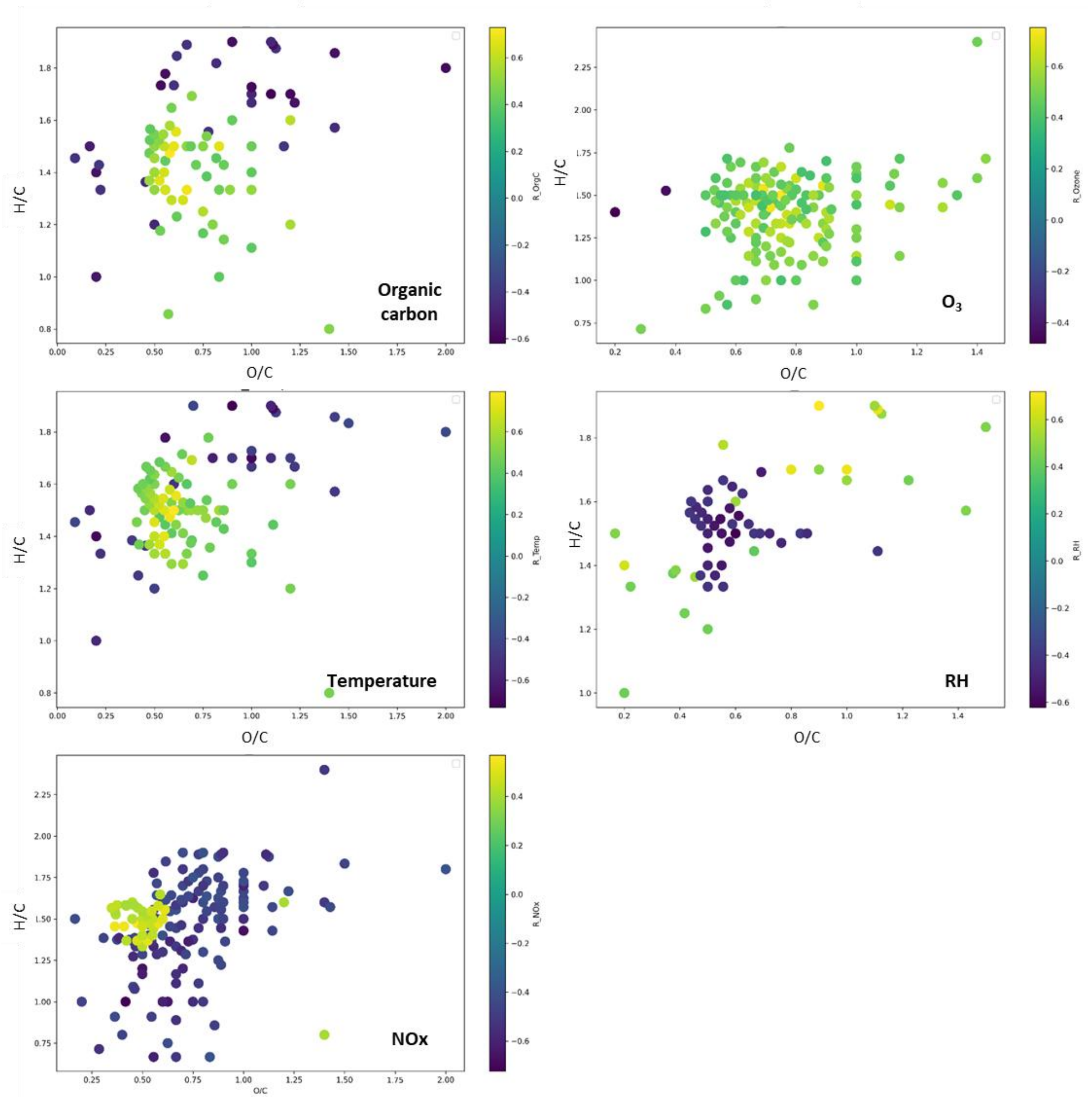

Figure S7: Pearson correlation coefficients for common formulae (577) from different CHO, CHON, CHOS, and CHONS compounds for Paris and Rambouillet samples for p-value<0.05. Negative correlations are shown in blue and positive in yellow colors.

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