Molecular characterization of organic aerosols in urban and forested areas of Paris using high resolution mass spectrometry

Diana L. Pereira[1], Chiara Giorio[2], Aline Gratien[1], Alexander Zherebker[2], Gael Noyalet[1], Servanne Chevaillier[3], Stéphanie Alage[3], Elie Almarj[1], Antonin Bergé[1,a], Thomas Bertin[3], Mathieu Cazaunau[3], Patrice Coll[1], Ludovico Di Antonio[3], Sergio Harb[3,7], Johannes Heuser[3], Cécile Gaimoz[3], Oscar Guillemant[3,4], Brigitte Language[3,b], Olivier Lauret[3], Camilo Macias[1], Franck Maisonneuve[3], Bénédicte Picquet-Varrault[3], Raquel Torres[3,c], Sylvain Triquet[1], Pascal Zapf[3], Lelia Hawkins[5], Drew Pronovost[5], Sydney Riley[5], Pierre-Marie Flaud[6], Emilie Perraudin[6], Pauline Pouyes[6], Eric Villenave[6], Alexandre Albinet[7], Olivier Favez[7], Robin Aujay-Plouzeau[7], Vincent Michoud[1], Christopher Cantrell[3], Manuela Cirtog[3], Claudia Di Biagio[1], Jean-François Doussin[3] and Paola Formenti[1]

[1]Université Paris Cité and Univ Paris Est Creteil, CNRS, LISA, Paris, F-75013, France
[2]Yusuf Hamied Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, United Kingdom
[3]Université Paris Est Creteil and Université Paris Cité, CNRS, LISA, Créteil, F-94010, France
[4]Université Paris-Saclay, Ecole Normale Supérieure Paris-Saclay, 4 avenue des sciences, 91190 Gif-sur-Yvette, France
[5]Department of Chemistry, Harvey Mudd College, 301 Platt Blvd, Claremont, California 91711, United States
[6]Univ. Bordeaux, CNRS, EPOC, EPHE, UMR 5805, F-33600 Pessac, France
[7]INERIS, Parc technologique Alata BP2, 60550 Verneuil en Halatte, France

[a]now at Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ, IPSL, Université Paris−Saclay, 91191 Gif-sur-Yvette, France
[b]now at Unit for Environmental Sciences and Management, North-West University, Potchefstroom, South Africa
[c]now at Center for Research in Sustainable Chemistry-CIQSO, University of Huelva, Campus de El Carmen, E-21071, Huelva, Spain

Supplementary material

Figures S1, S2, S3, S4 and S5, Table S1

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> 0.5, and more oxidized compounds can be found at higher O/C> 0.5. Examples for the domains arise from the analysis of the filter 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.

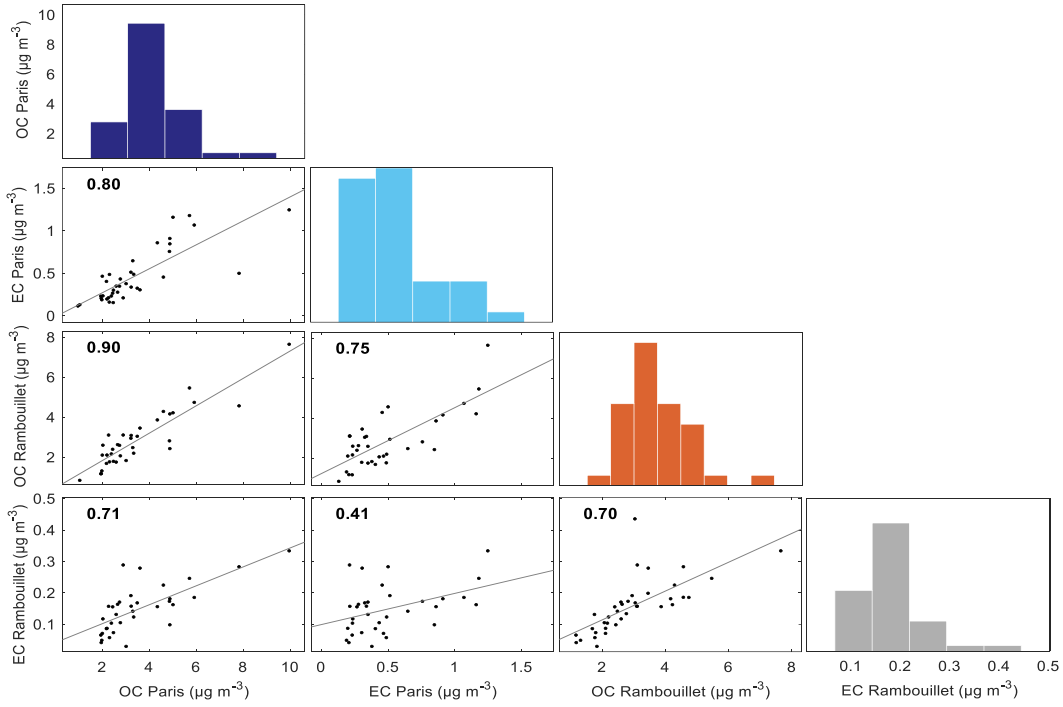

Figure S1: Pearson correlations matrix for OC and EC concentrations for Paris (blue) and Rambouillet (orange and gray). Data from the overlap period (June 27 to July 22) is considered here and r is represented for each correlation. Normal distributions for the values of OC concentrations for Paris and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

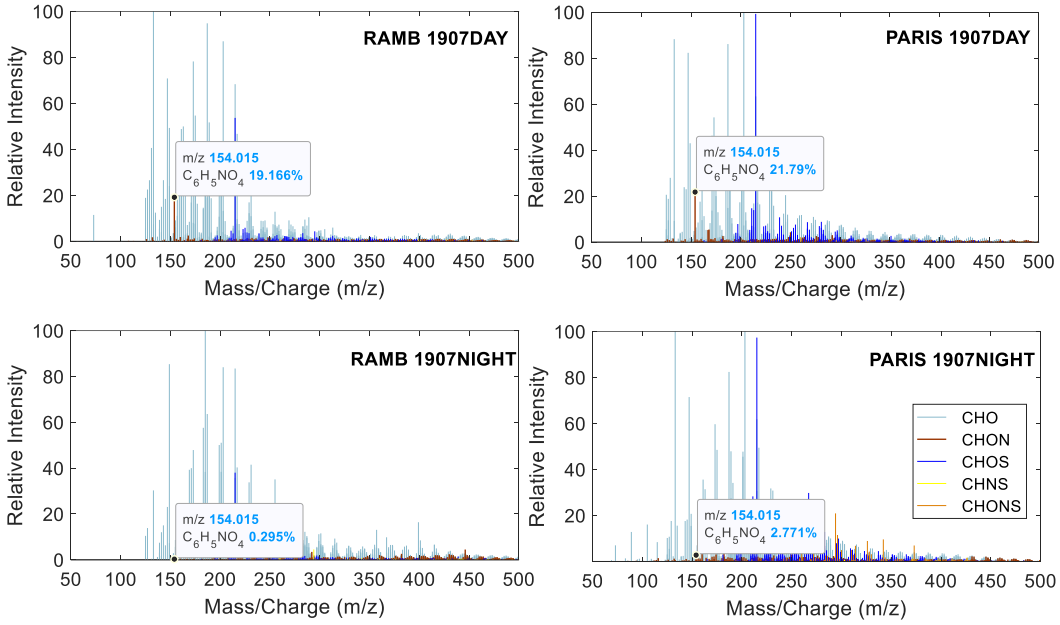

Figure S2: Mass spectra from direct infusion in the negative mode nano-ESI analysis for specific consecutive samples of Rambouillet (RAMB) and Paris samples collected during the day and night periods of July 19 of the summer 2022. Identification of the presence of nitrocathecol as a BB molecular tracer. Molecular formulae are grouped as CHO (clear blue), CHON (brown), CHOS (dark blue), CHNS (yellow) 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 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.

	Number of formulae						Atmospheric conditions				
sample name	CHO	CHON	CHOS	CHNS	CHONS	ALL	T (°C)	RH (%)	O_3 (ppb)	NOx (ppb)	SO_2 (ppb)
RAMB0307 DAY	650	433	379	5	177	1644	19.4 ± 3.9	56.1 ± 18.4	34.7 ± 8.4	0.9 ± 0.3	0.3 ± 0.1
RAMB0307 NIGHT	752	706	382	23	236	2099	11.6 ± 2.8	81.9 ± 8.8	23.5 ± 9.7	1.1 ± 0.9	0.2 ± 0.1
RAMB0407 DAY	1149	995	517	15	350	3026	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	23	419	2371	12.5 ± 3.4	78.9 ± 11.5	29.8 ± 10.9	0.9 ± 0.2	0.4 ± 0.2
RAMB1107 NIGHT	1225	1505	447	36	328	3541	19.4 ± 2.0	64.7 ± 10.0	34.6 ± 5.4	2.7 ± 1.3	0.3 ± 0.1
RAMB1207 DAY	1519	2430	515	113	576	5153	26.3 ± 5.1	41.0 ± 22.3	61.6 ± 22.3	1.4 ± 0.6	0.4 ± 0.1
RAMB1207 NIGHT	1385	1569	548	64	337	3903	18.8 ± 0.9	64.9 ± 3.7	34.4 ± 8.7	1.0 ± 0.7	0.2 ± 0.1
RAMB1307 DAY	1529	2197	334	42	461	4563	29.0 ± 5.9	34.7 ± 17.7	58.3 ± 17.3	1.3 ± 0.9	0.9 ± 0.8
RAMB1707 DAY	1215	1832	468	45	496	4056	25.2 ± 5.2	36.2 ± 17.5	69.1 ± 16.6	1.8 ± 0.8	0.4 ± 0.1
RAMB1707 NIGHT	1547	1789	388	54	287	4065	18.1 ± 1.6	56.6 ± 4.8	46.1 ± 5.8	2.1 ± 0.9	0.3 ± 0.1
RAMB1807 DAY	1571	1901	396	20	322	4210	30.6 ± 6.6	28.2 ± 14.7	77.3 ± 17.9	1.5 ± 0.6	1.0 ± 0.8
RAMB1807 NIGHT	1516	1309	368	11	211	3415	23.7 ± 1.8	40.9 ± 4.4	54.2 ± 6.9	2.3 ± 0.9	0.4 ± 0.3
RAMB1907 DAY	1679	1542	384	20	282	3907	31.6 ± 5.6	33.1 ± 13.5	75.0 ± 14.0	1.4 ± 0.6	1.5 ± 1.2
RAMB1907 NIGHT	1361	1564	222	7	178	3332	21.6 ± 2.7	69.0 ± 13.4	44.1 ± 13.0	1.1 ± 0.4	0.4 ± 0.2
PARIS0307 DAY	1415	2042	534	110	800	4901	20.7 ± 2.6	50.6 ± 10.1	36.0 ± 4.0	3.4 ± 1.4	0.1 ± 0.1
PARIS0307 NIGHT	970	1241	343	41	322	2917	17.4 ± 1.5	61.4 ± 5.0	29.5 ± 2.6	3.3 ± 1.3	0.2 ± 0.2
PARIS0407 DAY	1375	2391	485	115	767	5133	21.9 ± 3.3	45.5 ± 11.9	38.7 ± 11.1	8.0 ± 3.9	0.2 ± 0.2
PARIS0407 NIGHT	1060	1485	410	76	450	3481	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	47	488	3746	21.4 ± 0.0	62.9 ± 0.1	-	-	-
PARIS1207 DAY	807	1271	293	42	292	2705	28.2 ± 4.0	37.8 ± 14.7	49.6 ± 16.7	24.5 ± 17.0	0.1 ± 0.3
PARIS1207 NIGHT	984	1659	257	28	215	3143	26.1 ± 1.9	35.4 ± 6.9	25.7 ± 13.4	22.9 ± 10.8	0.3 ± 0.3
PARIS1307 DAY	1021	1699	286	20	177	3203	31.1 ± 4.1	30.9 ± 9.1	45.5 ± 23.5	25.2 ± 27.4	0.3 ± 0.2
PARIS1707 DAY	1119	1449	517	61	456	3602	26.7 ± 4.2	32.2 ± 10.3	47.3 ± 9.2	6.9 ± 4.0	0.6 ± 0.4
PARIS1707 NIGHT	1396	2161	533	84	609	4783	25.1 ± 1.7	33.2 ± 3.6	27.9 ± 4.8	20.4 ± 5.6	0.7 ± 0.7
PARIS1807 DAY	1268	1509	290	31	181	3279	32.1 ± 5.1	24.8 ± 8.0	45.1 ± 20.3	24.7 ± 14.7	0.7 ± 0.9
PARIS1807 NIGHT	1481	2347	419	67	435	4749	28.4 ± 1.9	31.8 ± 3.4	25.0 ± 6.9	25.1 ± 8.6	0.4 ± 0.3
PARIS1907 DAY	1222	1108	330	7	133	2800	34.0 ± 4.4	28.0 ± 10.2	51.9 ± 15.5	20.1 ± 12.3	0.8 ± 0.8
PARIS1907 NIGHT	1068	1157	516	54	438	3233	25.1 ± 2.1	62.2 ± 12.4	43.7 ± 5.9	4.1 ± 1.4	0.1 ± 0.1

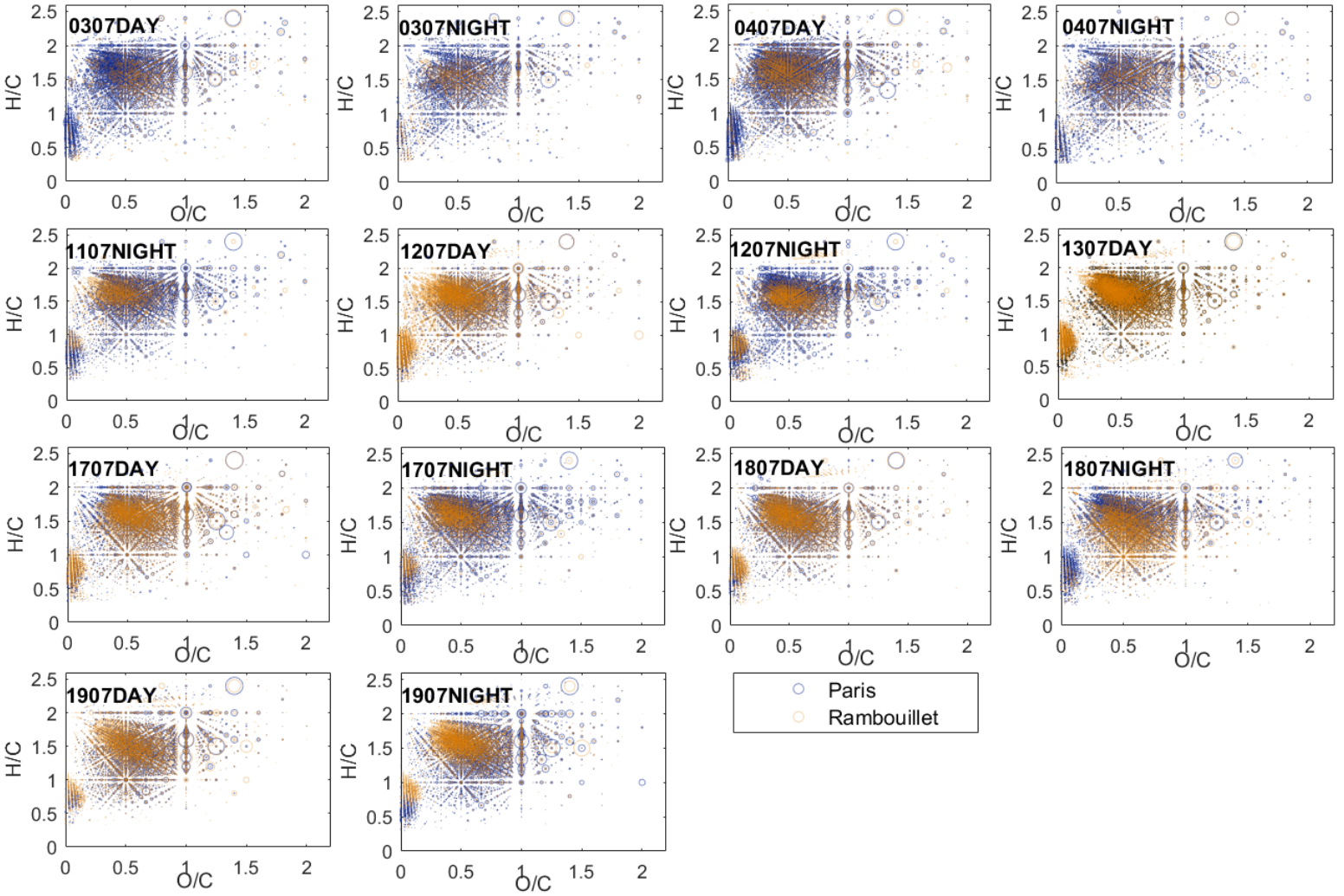

Figure S3: Comparison of Van Krevelen diagrams of specific samples for compounds detected in the aerosol samples collected at Rambouillet (orange) and Paris (blue) in the summer 2022. Data here was obtained from HRMS analysis. The date and day/night sampling condition is indicated in the plot (e.g., 0307DAY means daytime filter for the 3rd of July).

65

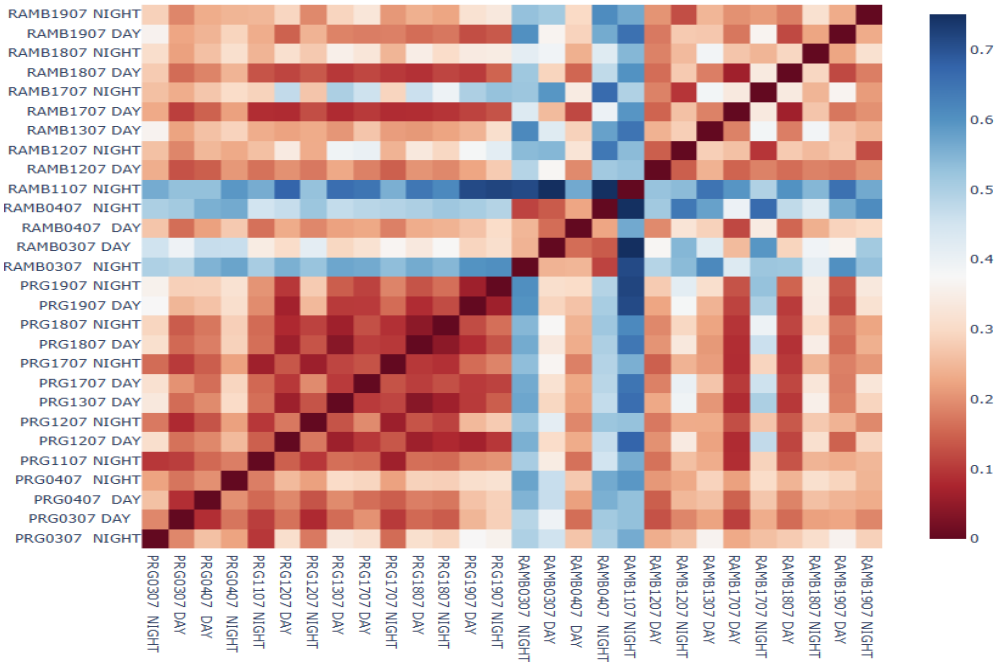

Figure S4 Cosine distances matrix for samples collecting during day and night at Paris and Rambouillet during the summer 2022. Lower values (red) of cosine distances shows similarities between the samples while higher values (blue) show differences between the samples.

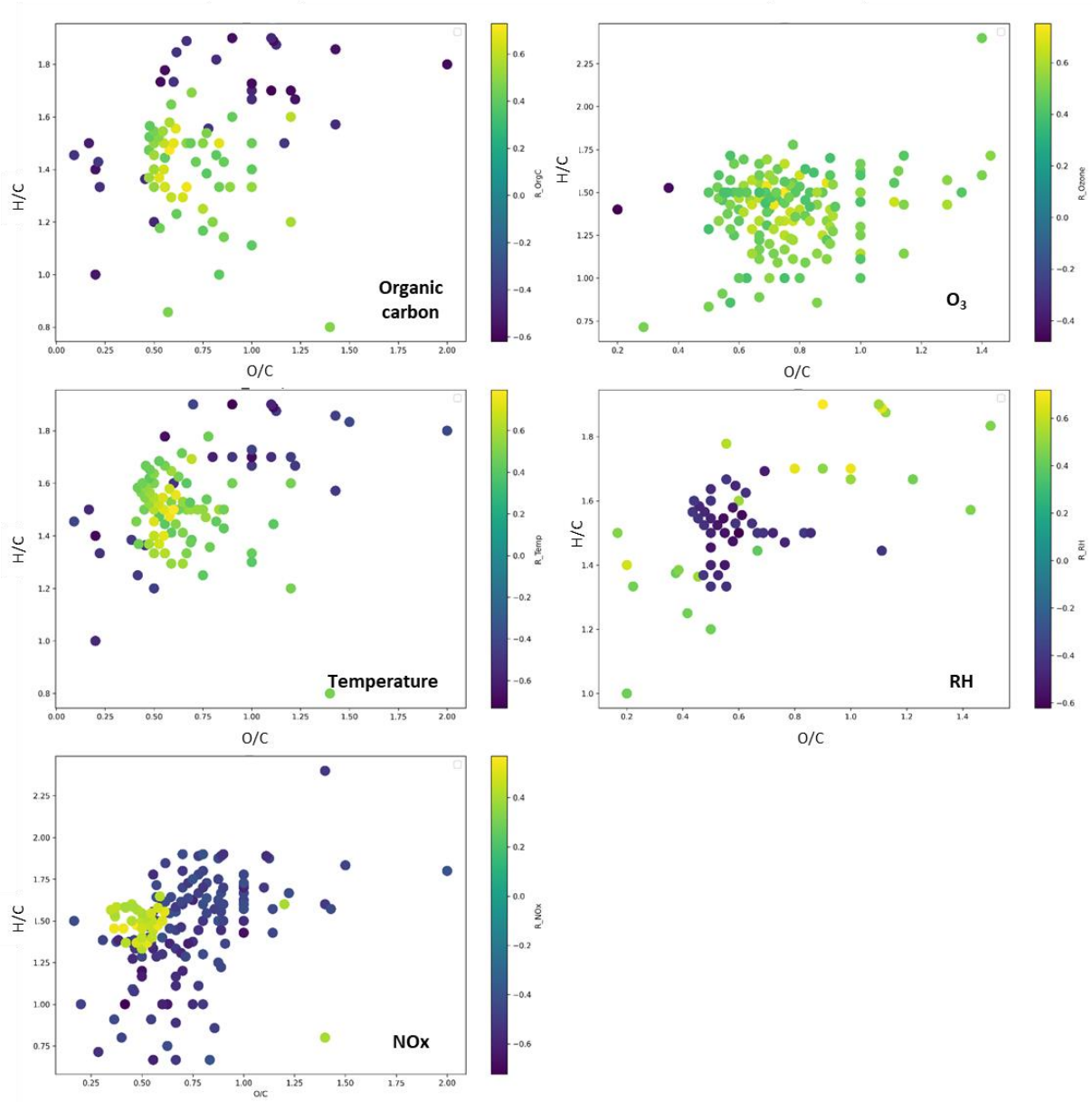

Figure S5: Pearson correlation coefficients for common formulae (577) from different CHO, CHON, CHOS, and CHONS compounds for Paris and Rambouillet samples for p-value<0.05. Negative correlations are shown in blue and positive in yellow colors.

References

Kourtchev, I., Doussin, J.-F., Giorio, C., Mahon, B., Wilson, E. M., Maurin, N., Pangui, E., Venables, D. S., Wenger, J. C., & Kalberer, M. (2015). Molecular composition of fresh and aged secondary organic aerosol from a mixture of biogenic volatile compounds: A high-resolution mass spectrometry study. *Atmospheric Chemistry and Physics*, *15*(10), 5683–5695. https://doi.org/10.5194/acp-15-5683-2015

Kourtchev, I., O'Connor, I. P., Giorio, C., Fuller, S. J., Kristensen, K., Maenhaut, W., Wenger, J. C., Sodeau, J. R., Glasius, M., & Kalberer, M. (2014). Effects of anthropogenic emissions on the molecular composition of urban organic aerosols: An ultrahigh resolution mass spectrometry study. *Atmospheric Environment*, *89*, 525–532. https://doi.org/10.1016/j.atmosenv.2014.02.051

Kristensen, K., Enggrob, K. L., King, S. M., Worton, D. R., Platt, S. M., Mortensen, R., Rosenoern, T., Surratt, J. D., Bilde, M., Goldstein, A. H., & Glasius, M. (2013). Formation and occurrence of dimer esters of pinene oxidation products in atmospheric aerosols. *Atmospheric Chemistry and Physics*, *13*(7), 3763–3776. https://doi.org/10.5194/acp-13-3763-2013

Rincón, A. G., Calvo, A. I., Dietzel, M., & Kalberer, M. (2012). Seasonal differences of urban organic aerosol composition – an ultra-high resolution mass spectrometry study. *Environmental Chemistry*, *9*(3), 298. https://doi.org/10.1071/EN12016

Simoneit, B. R. T. (1985). Application of Molecular Marker Analysis to Vehicular Exhaust for Source Reconciliations. *International Journal of Environmental Analytical Chemistry*, *22*(3–4), 203–232. https://doi.org/10.1080/03067318508076422

Wozniak, A. S., Bauer, J. E., Sleighter, R. L., Dickhut, R. M., & Hatcher, P. G. (2008). Technical Note: Molecular characterization of aerosol-derived water soluble organic carbon using ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Atmospheric Chemistry and Physics*, *8*(17), 5099–5111. https://doi.org/10.5194/acp-8-5099-2008