Molecular-Level Characterization of Urban Aerosol Analogues in Controlled Atmospheric Simulations

Elie Al Marj[1], Ambre Delater[1], Aline Gratien[1], Marie Line Torrijos[1], Juan Camilo Macias Rodriguez[1], Mathieu Cazaunau[2], Edouard Pangui[2], Antonin Bergé[2], Cécile Gaimoz[2], Thomas Bertin[2], Emmanuelle Mebold[2], Bénédicte Picquet-Varrault[2], Jean-François Doussin[2], Clément Buissot[3], Sophie Lanone[3], Patrice Coll[1]

[1] Université Paris Cité and Univ Paris Est Creteil, CNRS, LISA, F-75013 Paris, France
[2] Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, F-94010 Créteil, France
[3] Univ Paris Est Creteil, INSERM, IMRB, F-94010 Créteil, France

Correspondence to: Patrice Coll (pcoll@lisa.ipsl.fr)

S1 Aerosols Density Estimation

Bulk aerosol density was determined from chemical composition data following the equation provided by (Salcedo et al., 2006):

$$\rho = \frac{[SO_4^{2-}] + [NH_4^+] + [NO_3^-] + [Cl^-] + [\text{Organics}]}{\frac{[SO_4^{2-}] + [NH_4^+] + [NO_3^-]}{1.75} + \frac{[Cl^-]}{1.52} + \frac{[\text{Organics}]}{1.2}}$$

This approach calculated aerosol densities of 1.6 g.cm^{-3} for standard urban scenarios and 1.48 g.cm^{-3} for biomass burning enhanced scenarios, allowing a total PM mass determined using TOF-ACSM in agreement with that given by SMPS.

S2 Identification and Quantification of VOCs Concentrations

The concentrations of compounds identified (based on their *m/z* …) by PTR-TOF-MS are calculated using the equation established by (de Gouw and Warneke, 2007) and (Michoud et al., 2017).

$$[\mathbf{X}] = \frac{\mathbf{i_{X\_net}}}{\mathbf{500 \cdot i_{H_3O^+} + 250 \cdot X_r \cdot i_{H_3O^+ (H_2O)}}} \times \frac{\mathbf{150\,000}}{\mathbf{R_{f,X}}}$$

Where:

[X] is the concentration of the detected mass (ppb).

i_{X_net} is the net signal relative to the detected mass.

$i_{H_3O^+}$ and $i_{H_3O^+ (H_2O)}$ are the relative signals at *m/z* = 21 *and m/z* = 39, respectively, to avoid detector saturation.

X_r is the sensitivity factor of the signal to relative humidity (X_r = 0.5). It is crucial to perform calibrations at different relative humidity values to determine the value of Xr. This ensures that the sensitivity Xr is independent of relative humidity.

$R_{f,X}$ is the response coefficient of the PTR-TOF-MS, experimentally determined for each compound.

Throughout the experiments, we quantified 23 distinct VOCs, as documented in **Table S1**.

Table S1: Identified PTR-TOF-MS peaks, their chemical classification, Log(C*) (determined using "UManSysProp" web platform) and concentrations observed for the simulated atmospheres. Concentration values represent means ± standard deviations over the experimental period.

m/z	Potential identified species	Chemical classification	O:C	Log(C*)	Urban scenario concentration (ppb)	Biomass burning scenario concentration (ppb)
31.011	Formaldehyde - CH_2O	Carbonyl (Aldehyde)	1.00	8.29	14.13 ± 6.69	14.35 ± 2.19
33.033	Methanol - CH_3OH	Alcohol	1.00	8.29	48.88 ± 30.89	50.56 ± 27.80
41.031	Propadiene - C_3H_4	Hydrocarbon (Alkene)	0.00	9.34	6.20 ± 2.01	11.87 ± 2.58
42.029	Acetonitrile - C_2H_3N	Nitrile	0.00	8.01	2.63 ± 0.49	2.36 ± 0.26
45.041	Acetaldehyde - $C_2H_4O_2$	Carbonyl (Aldehyde)	1.00	5.81	1.93 ± 1.12	8.89 ± 2.22
47.013	Formic acid - CH_2O_2	Carboxylic acid	2.00	6.09	13.74 ± 7.47	25.94 ± 5.91
55.059	1,3-butadiene - C_4H_6	Hydrocarbon (Alkene)	0.00	8.86	13.18 ± 6.11	18.18 ± 12.97
57.056	Acrolein - C_3H_4O	Carbonyl (Aldehyde)	0.33	7.49	0.96 ± 0.36	1.07 ± 0.31
59.035	Acetone - C_3H_6O	Carbonyl (Ketone)	0.33	7.49	7.34 ± 4.13	8.20 ± 1.98
61.034	Acetic acid - $C_2H_4O_2$	Carboxylic acid	1.00	5.81	22.14 ± 15.86	76.64 ± 36.64
62.016	Nitromethane - CH_3NO_2	Hydrocarbon (Nitro-compound)	2.00	4.29	9.64 ± 2.58	12.70 ± 2.20
62.992	Ethylene glycol - $C_2H_6O_2$	Alcohol	1.00	5.81	25.00 ± 6.39	17.75 ± 3.44
69.048	Furan - C_4H_4O	Furan	0.25	7.04	3.39 ± 0.73	2.58 ± 1.86
71.056	Methyl-vinyl ketone (MVK) - C_4H_6O	Carbonyl (Ketone)	0.25	7.04	2.53 ± 1.28	3.70 ± 2.19
73.038	Methylglyoxal - $C_3H_4O_2$ (*Precursor*)	Carbonyl (Aldehyde)	0.67	5.46	8.14 ± 3.73	6.58 ± 3.46
75.045	Glyoxylic acid - $C_2H_2O_3$	Carboxylic acid	1.50	3.63	30.21 ± 17.33	48.50 ± 22.46
83.086	2-methylfuran - C_5H_6O	Furan	0.20	6.59	10.24 ± 4.59	16.22 ± 9.36
85.013	Ethyl vinyl ketone (EVK) - C_5H_8O	Carbonyl (Ketone)	0.20	6.59	8.84 ± 4.14	20.91 ± 4.85
89.024	Butanoic acid - $C_4H_8O_2$	Carboxylic acid	0.50	5.06	24.55 ± 13.37	26.66 ± 17.94
93.036	Toluene - C_7H_8 (*Precursor*)	Hydrocarbon (Aromatic)	0.00	7.44	6.14 ± 8.45	7.64 ± 2.08
97.006	Furfural - $C_5H_4O_2$	Carbonyl (Aldehyde) and Furan	0.40	4.65	10.33 ± 4.18	15.64 ± 2.59
107.076	Xylene - C_8H_{10} (*Precursor*)	Hydrocarbon (Aromatic)	0.00	6.96	3.13 ± 3.30	2.77 ± 0.89
127.059	1,2,3-benzenetriol - $C_6H_6O_3$	Hydrocarbon (Aromatic)	0.50	2.21	9.83 ± 3.80	12.82 ± 3.82

S3 Quantitative Analysis of Secondary Organic Aerosols (SOA)

S3.1 Internal Standard and Sample Preparation

To ensure robust quantification and account for potential analyte loss during extraction or matrix effects during ionization, an internal standard (IS) calibration method was used. All filter samples, blanks, and calibration standards were spiked with 5 µL of (1S)-(+)-camphor-10-sulfonic acid (1mg.L^{-1} in 50/50 acetonitrile/ultrapure water) prior to extraction. Filters were extracted in acetonitrile at room temperature under agitation (1000 rpm, 30 min), filtered at 0.2 µm, and evaporated under a nitrogen stream before being redissolved in 200 µL of a 50/50 acetonitrile/ultrapure water mixture.

S3.2 Calibration and Linearity

Quantification was performed for five representative markers detected in both scenarios. Calibration curves were generated using a 5-point range (20 to 160mg.L^{-1}), prepared by spiking pre-pyrolyzed quartz filters to replicate the sample matrix. All analyses were performed in triplicate.

Table S2: Calibration parameters for the quantified SOA markers.

Compound name	Regression equation	R^2
2-nitrophenol	$y=1.35\times10^{-4}x$	0.9735
Cis-pinonic acid	$y=3.41\times10^{-5}x$	0.9959
MBTCA	$y=3.14\times10^{-4}x$	0.9388
Norpinic acid	$y=1.99\times10^{-4}x$	0.9361
Pinic acid	$y=1.33\times10^{-4}x$	0.9287

Note: x represents the mass in ng and y the ratio of compound/IS response area.

S3.3 Atmospheric Concentration Calculation

Atmospheric concentrations (ng.m^{-3}) were determined by dividing the mass quantified on the analysed filter portion by the corresponding volume of air sampled, corrected for the fraction of the total filter surface analysed (typically 1/3 or 1/2 of the filter). Average sampled volumes were 0.54 ± 0.02 m^3 for CESAM and 2.85 ± 0.10 m^3 for the exposure isolator. The concentration drop observed in the isolators is consistent with the 1:10 dilution ratio applied in the PolluRisk platform.

S4 Detected SOAs using UPLC/ESI-IMS-QTOF

Table S3: Summary of identified SOA products detected by UPLC/ESI-IMS-QTOFMS.

No	Tentative Compound name	Molecular formula	Observed RT (min)	Observed *m/z*	O:C	Log(C*)	Volatility	Scenario
1	Levoglucosan isomer	$C_6H_{10}O_5$	0.69	161.0457	0.83	-1.95	LVOC	BB
2	Dihydroxydimethoxyoxane-2-carboxylic acid	$C_8H_{14}O_7$	0.74	221.0663	0.88	-6.90	ELVOC	BB
3	3-Hydroxy-4,4-dimethylglutaric acid (HDMGA)	$C_7H_{12}O_5$	2.85	176.8950	0.71	-2.31	LVOC	BB
4	3-methylbutane-1,2,3-tricarboxylic acid (MBTCA)	$C_8H_{12}O_6$	3.23	203.0558	0.75	-4.78	ELVOC	Both
5	3-acetylhexanedioic acid	$C_8H_{12}O_5$	3.43	187.0610	0.63	-2.69	LVOC	BB
6	5-nitroguaiacol	$C_7H_7NO_4$	3.67	169.0135	0.57	-2.04	LVOC	BB
7	Terpenolic acid	$C_8H_{12}O_4$	3.72	171.0659	0.50	-0.64	LVOC	BB
8	5-propyldihydrofuran-2(3H)-one	$C_7H_{12}O_2$	3.93	127.0710	0.29	3.77	IVOC	BB
9	10-hydroxypinonic acid	$C_{10}H_{16}O_5$	4.57	215.0925	0.50	-3.49	LVOC	BB
10	Norpinic acid	$C_8H_{12}O_4$	4.89	171.0661	0.50	-0.64	LVOC	BB
11	2,3-dihydroxy-4-oxopentanoic acid (DHOPA)	$C_5H_8O_5$	5.35	148.9387	1.00	-1.61	LVOC	BB
12	Vanillylmandelic acid	$C_9H_{10}O_5$	5.36	197.0454	0.56	-3.08	LVOC	BB
13	5-butyldihydrofuran-2(3H)-one	$C_8H_{14}O_2$	6.20	141.0916	0.25	3.32	IVOC	BB
14	Pinic acid	$C_9H_{14}O_4$	6.20	185.0813	0.44	-1.05	LVOC	BB
15	5-nitrosalicylic acid (5NSA)	$C_7H_5NO_5$	6.45	182.0087	0.71	-4.11	ELVOC	BB
16	Norpinonic acid	$C_9H_{14}O_4$	7.04	185.0867	0.44	-1.05	LVOC	BB
17	3-pinalic acid	$C_9H_{13}O_3$	7.06	168.0867	0.33	0.94	SVOC	BB
18	2-nitrophenol	$C_6H_5NO_3$	8.55	138.0192	0.50	0.41	SVOC	BB
19	1-(2,2,3-trimethylcyclobutyl)ethan-1-one	$C_9H_{16}O$	9.10	139.1125	0.11	4.73	IVOC	BB
20	Cis-pinonic acid	$C_{10}H_{16}O_3$	9.10	183.1020	0.30	0.50	SVOC	Both
21	1R-(+)-Nopinone	$C_9H_{14}O$	9.14	183.1023	0.11	4.73	IVOC	BB
22	Sinapaldehyde	$C_{11}H_{12}O_4$	9.42	207.0661	0.36	-1.90	LVOC	BB
23	3-nitrotoluene	$C_7H_7NO_2$	10.51	182.0452	0.29	1.97	SVOC	BB
24	3-methyl-4-nitrocatechol	$C_7H_7NO_4$	11.23	168.0295	0.57	-2.04	LVOC	BB
25	2,6,6-trimethylnorpinan-3-one	$C_{10}H_{16}O$	12.15	151.1122	0.10	4.26	IVOC	BB
26	Benzyl nitrate	$C_7H_7NO_3$	13.01	152.0343	0.43	0.00	SVOC	BB

27	4-nitro-m/o-cresol	$C_7H_7NO_3$	13.09	152.0347	0.43	0.00	SVOC	BB
28	Succinic acid	$C_4H_6O_4$	13.15	117.9279	1.00	0.86	SVOC	BB
29	Norpinonaldehyde	$C_9H_{14}O_2$	13.76	153.0914	0.22	2.87	IVOC	BB
30	Dimethyl-nitrophenol	$C_8H_9NO_3$	15.64	166.0502	0.38	-0.43	SVOC	Both
31	4,6-dinitro-o-cresol	$C_7H_6N_2O_5$	16.10	197.0197	0.71	-4.11	ELVOC	Both
32	3-(2-propan-2-yl)pentanedioic acid	$C_8H_{14}O_4$	26.15	173.8707	0.50	-0.64	LVOC	BB

RT: retention time; C*: saturation mass concentration at 298 K; Log(C*) is determined using "UManSysProp" web platform; VOC: volatile organic compounds, IVOC: intermediate-volatility compound, SVOC: semi-volatile organic compound, LVOC: low-volatility organic compound, ELVOC: extremely low-volatility organic compound, BB: biomass burning scenario.

References

de Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the earths atmosphere using proton-transfer-reaction mass spectrometry, Mass Spectrom Rev, 26, 223, 2007.

Michoud, V., Sciare, J., Sauvage, S., Dusanter, S., Léonardis, T., Gros, V., Kalogridis, C., Zannoni, N., Féron, A., Petit, J.-E., Crenn, V., Baisnée, D., Sarda-Estève, R., Bonnaire, N., Marchand, N., DeWitt, H. L., Pey, J., Colomb, A., Gheusi, F., Szidat, S., Stavroulas, I., Borbon, A., and Locoge, N.: Organic carbon at a remote site of the western Mediterranean Basin: sources and chemistry during the ChArMEx SOP2 field experiment, Atmospheric Chem. Phys., 17, 8837–8865, https://doi.org/10.5194/acp-17-8837-2017, 2017.

Salcedo, D., Onasch, T. B., Dzepina, K., Canagaratna, M. R., Zhang, Q., Huffman, J. A., DeCarlo, P. F., Jayne, J. T., Mortimer, P., Worsnop, D. R., Kolb, C. E., Johnson, K. S., Zuberi, B., Marr, L. C., Volkamer, R., Molina, L. T., Molina, M. J., Cardenas, B., Bernabé, R. M., Márquez, C., Gaffney, J. S., Marley, N. A., Laskin, A., Shutthanandan, V., Xie, Y., Brune, W., Lesher, R., Shirley, T., and Jimenez, J. L.: Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite, Atmospheric Chem. Phys., 6, 925–946, https://doi.org/10.5194/acp-6-925-2006, 2006.