Organic aerosol from an urban and suburban area of Paris during the summer 2022

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Secondary Organic Aerosol (SOA) formation can be formed from the oxidation of VOC from both natural or anthropogenic origin

Volatile Organic Compounds (VOC)

Biogenic

Anthropogenic

Oxidation (OH, O_3, NO_3)

VOC

OH

$O_2 \rightarrow HO_2$

R

$NO \rightarrow NO_2$

HO_2

O_2

RO_2

$NO \rightarrow NO_2$

RO

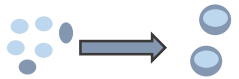
O_2

Secondary organic compounds

Semi-VOC non-VOC

Homogeneous nucleation

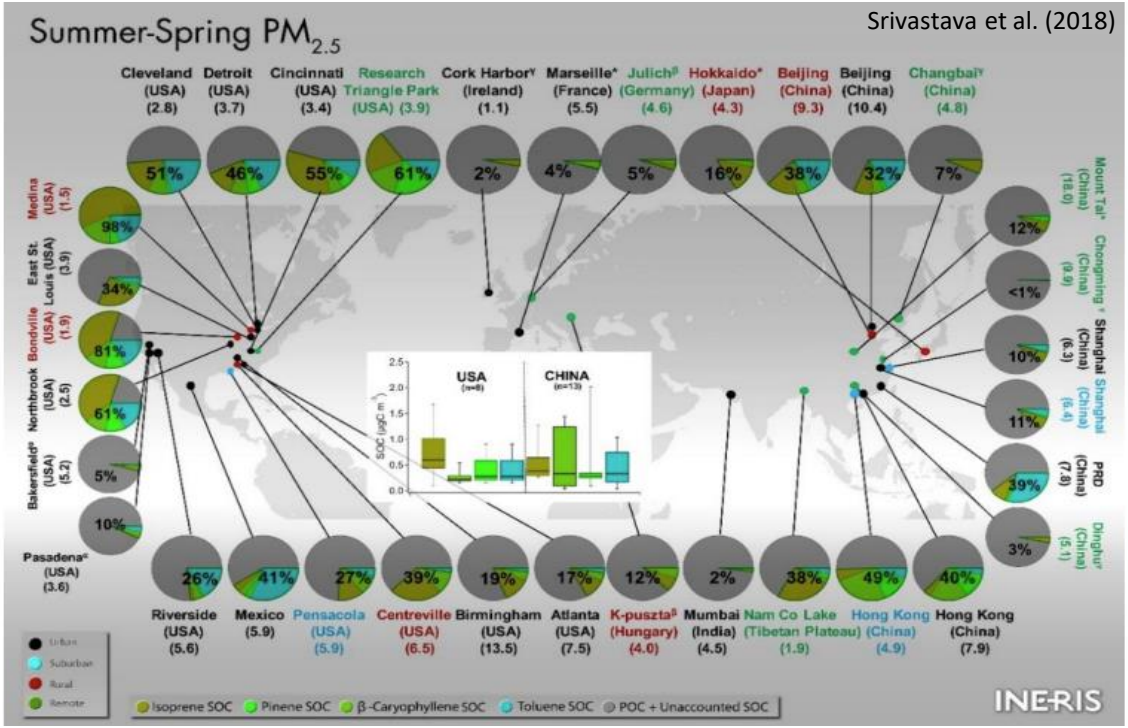
Heterogeneous nucleation or condensation



Preexisting particles

(SOA)

SOA composition derived for different locations around the world



Secondary organic carbon (SOC) contributions to $PM_{2.5}$ OC over the world for all the selected sites from 2006 to 2016.
* Toluene SOC was not reported at these locations. α/β-caryophyllene SOC was not reported at these locations.

The impact of anthropogenic contributions is limited and gaps remind in its understanding.

Determine the contribution of different VOCs precursors to the SOA formation in the urban and suburban area of Paris

CHAMBER SIMULATIONS

Identify tracers for specific anthropogenic VOC in realistic conditions and determine **SOC mass fractions (f_{SOC})**

$$f_{SOC,voc} = \frac{\sum_i [tracer_i]}{[SOC]}$$

[tracer$_i$]=concentration of the tracer
[SOC]= total SOC concentration

FIELD MEASUREMENTS

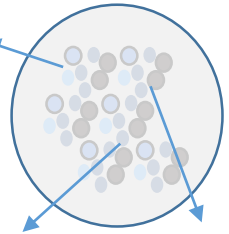
Quantify the tracers in the real atmosphere.

ACROSS campaign (Cantrell and Michoud, 2022)

MOLECULAR SCALE ANALYSIS ON FILTER SAMPLES

(UPLC-QTOF-MS) (ORBITRAP)

Low volatility compounds



(SFE-GC-MS)

High volatility compounds

(Sunset analyzer)

Organic and elemental carbon

PRAMMICS

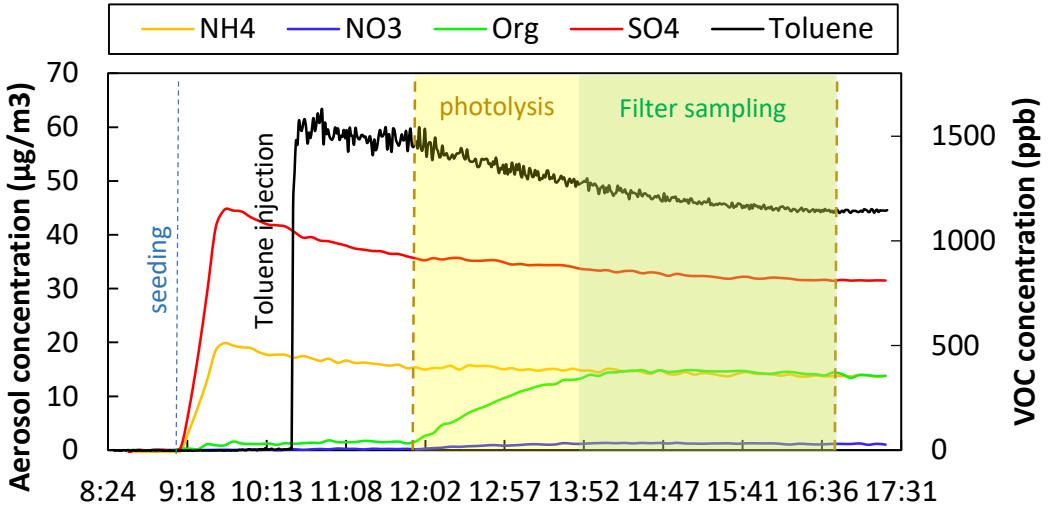
Chamber experiments and field measurements will be combined using the SOA tracer method (Kleindienst et al. 2007).

Chamber experiments to determine the f_{SOC}

CESAM CHAMBER

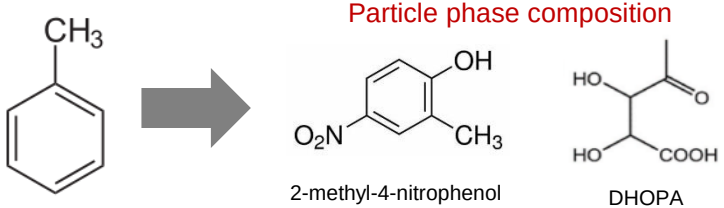
Wang et al. (2011)

Example of toluene photo-oxidation



Experiment was performed in the presence of seeding with $(NH_4)_2SO_4$ and NOx.

Particle phase composition



2-methyl-4-nitrophenol

DHOPA

Summary of the f_{SOC} obtained for different experiments of anthropogenic precursors

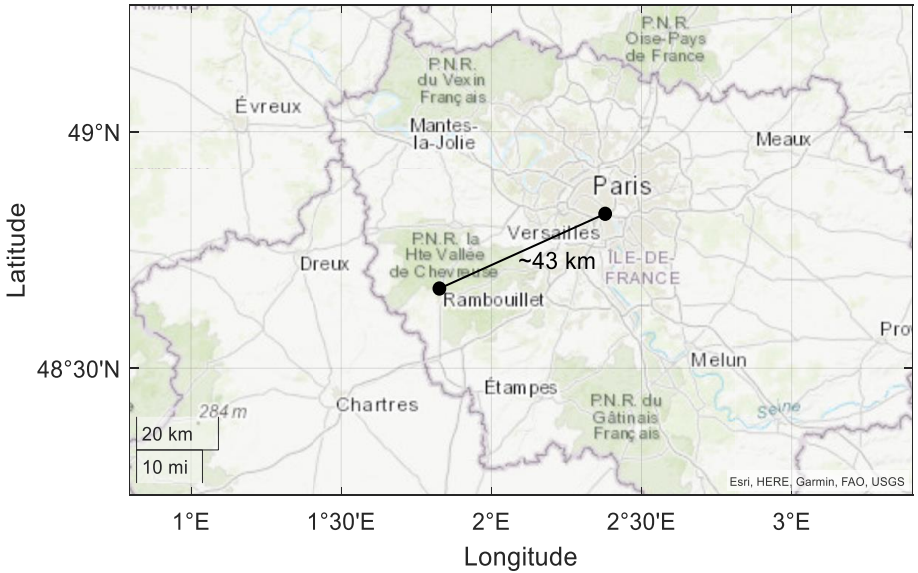
Summary of experiments performed at the CESAM chamber using $(NH_4)_2SO_4$ and H_2O_2 under different conditions of relative humidity and NOx.

VOC precursor	RH (%)	Temp. (°C)	VOCi (ppb)	NOx (ppb)	VOC/ NOx	*fsoc* MNP	*fsoc* NP	*fsoc* DHOPA	*fsoc* PA
toluene	8.9	20.7	662.8	149.3	4.4	0.0073	0.0087	0.0073	
toluene	8.9	20.8	624.0	167.4	3.7	0.0316		0.0125	
toluene	8	20.9	615.8			0.0103		0.0452	
toluene	11.9	20.7	545.2	103.1	5.2	0.0044		0.0029	
toluene	54.2	19.2	607.9					0.0361	
m-xylene	55.7	18.9	862.8	96.3	8.9			0.0371	
napthalene	59.9	19.4	150.8	73.3	2.0				0.1151
toluene	4.4	26.44	1068.5	164.6	6.4	0.0498	0.0015	0.0011	
toluene	7.25	23.98	1099.9	142.3	7.7	0.0431	0.0011		
toluene	38.5	26.81	1029.8	116.4	8.8	0.0281	0.0014	0.0082	
toluene	33.8	28.58	1019.0	125.9	8.0	0.0242	0.0007	0.0067	
toluene	31.3	28.91	1128.9	122.9	9.1	0.0177	0.0006	0.0125	

MNP= methyl nitrophenol, NP= nitrophenol, PA= phthalic acid, DHOPA=2,3-dihydroxy-4-oxopentanoic acid

No significate variations were observed for the f_{SOC} for different humidity conditions. However, they seem to be influenced by the NO_X presence.

Field measurements to address the aerosol composition in the real atmosphere



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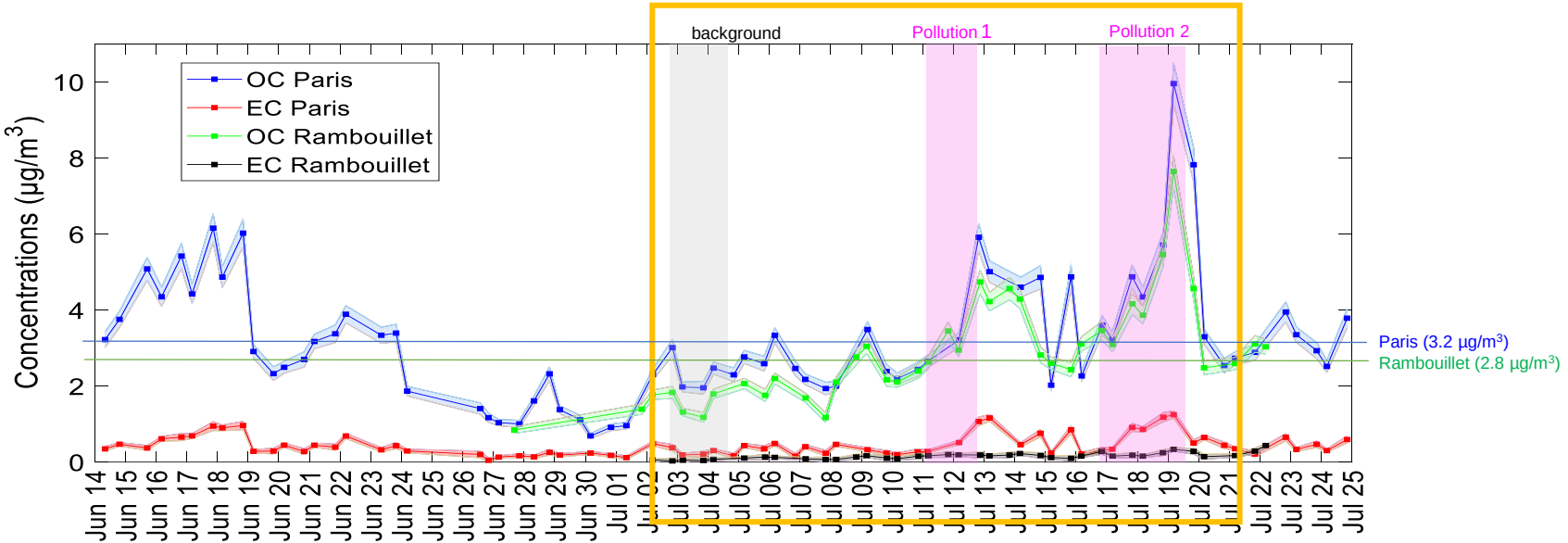
Rambouillet forest

PM1 samples were simultaneously collected in the day (4am - 8pm UTC) and night (8pm – 4am UTC) at the urban area of Paris and the forest of Rambouillet during the summer 2022 (Jun 13 to July 25)

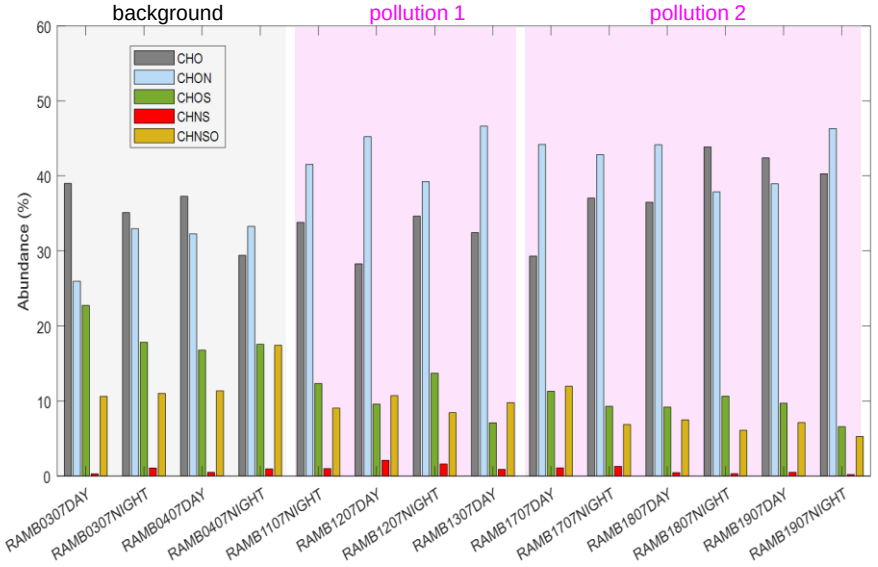
Organic carbon and elemental carbon concentrations derived from sunset analysis during the across campaign for filters collected at Paris and Rambouillet



Similar organic carbon concentrations were observed for the urban and forested area of Paris.

Compound class abundance comparison

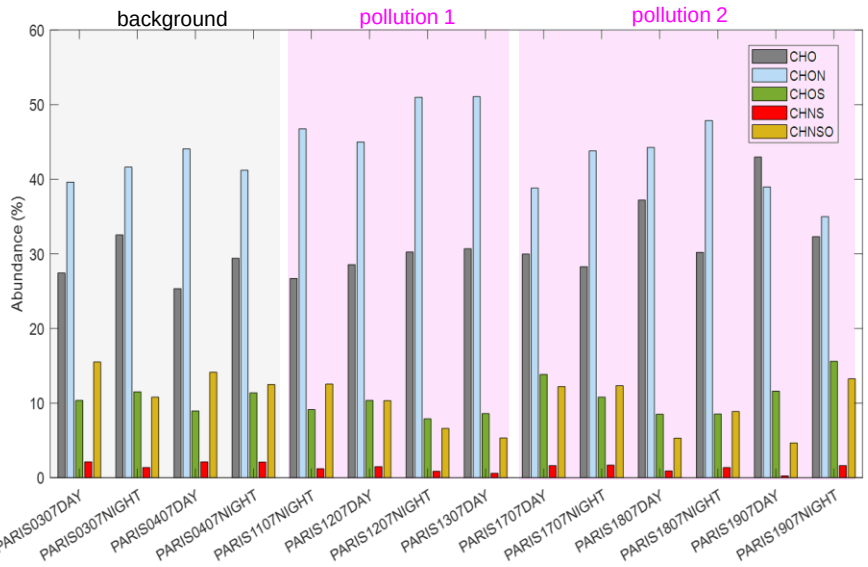
Rambouillet



$C_5H_{12}SO_7$ → Isoprene product (Kourchev et al. 2014)

$C_{10}H_{17}NSO_7$ → α/β-pinene product (Kourchev et al. 2014)

Paris



$C_6H_5NO_4$ → nitrocathecol (Kristensen et al., 2013)

$C_{10}H_{16}O_3$ → pinonic acid (Iinuma et al., 2010)

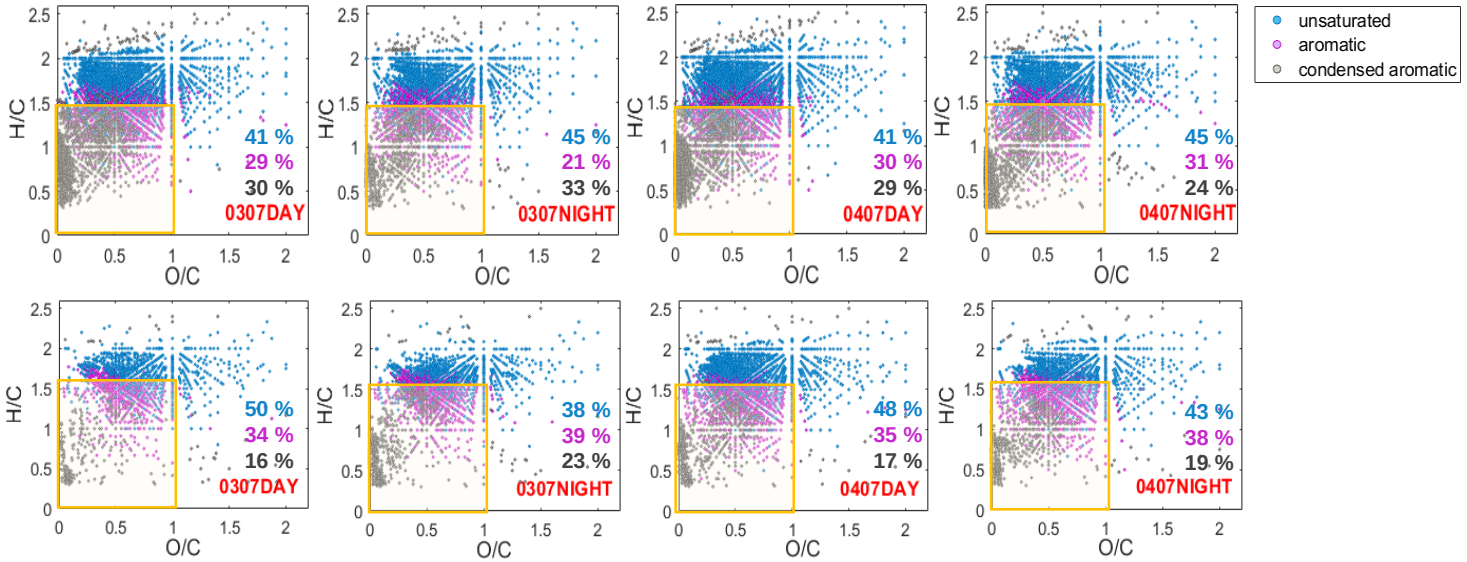
Background period: Rambouillet shows similar contributions of CHO and CHON compounds, with contributions of CHOS while Paris is mainly influenced by CHON compounds.

Pollution period: For both Rambouillet and Paris, the contribution of CHON compounds predominates.

Aromatic compounds presence on the samples of Paris and Rambouillet collected during the “background period” (derived from Orbitrap analysis)

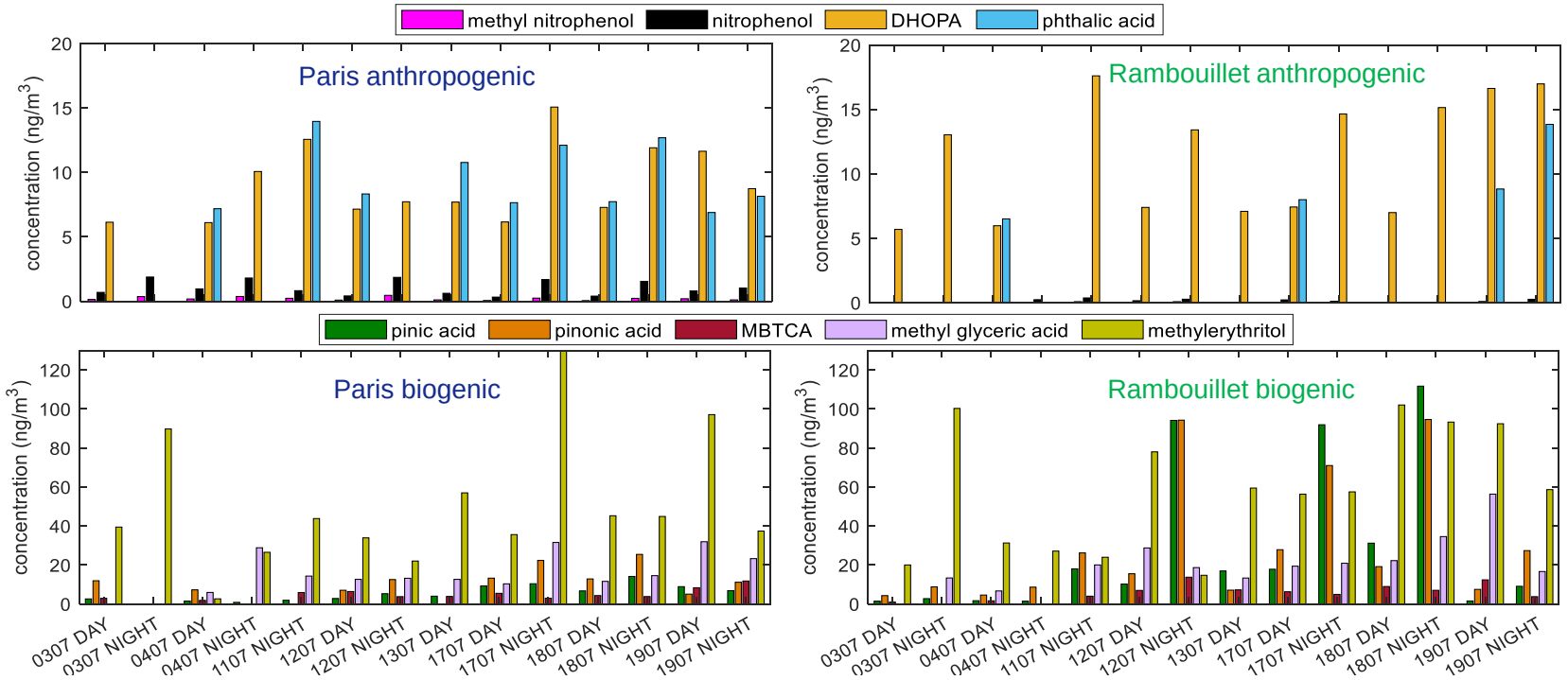
Paris

Rambouillet



Although Rambouillet and Paris represent different environments, they are both influenced by the presence of aromatic and condensed aromatic compounds distributed at O/C<1.

Quantification of the molecular tracers in the urban area of Paris and the forest of Rambouillet

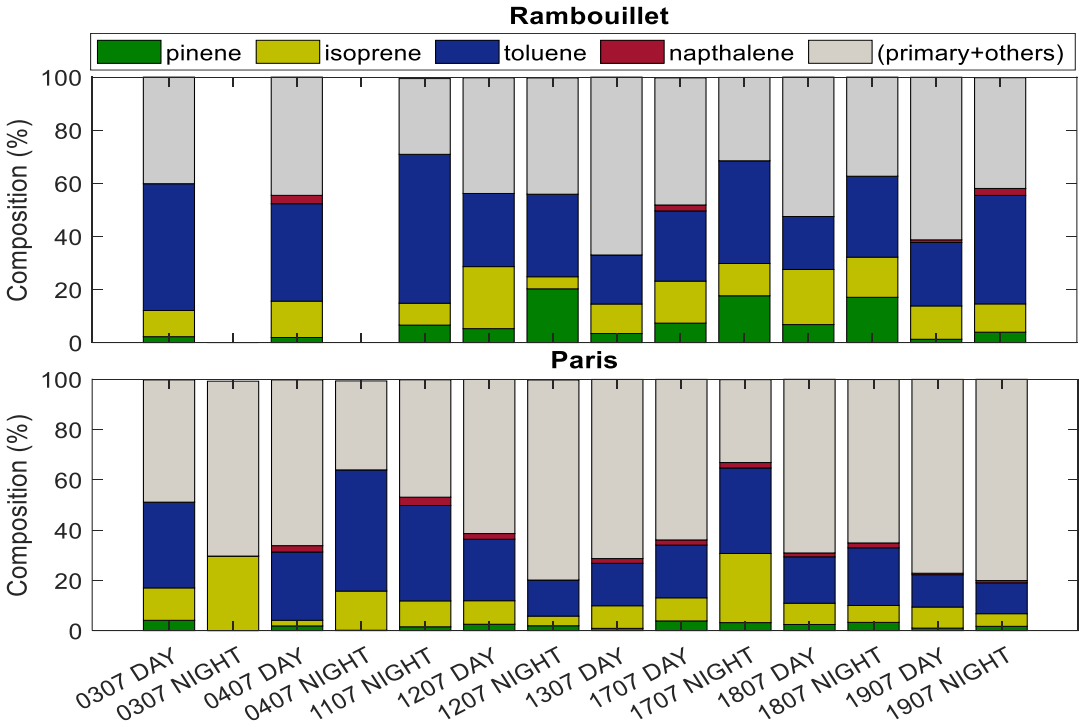


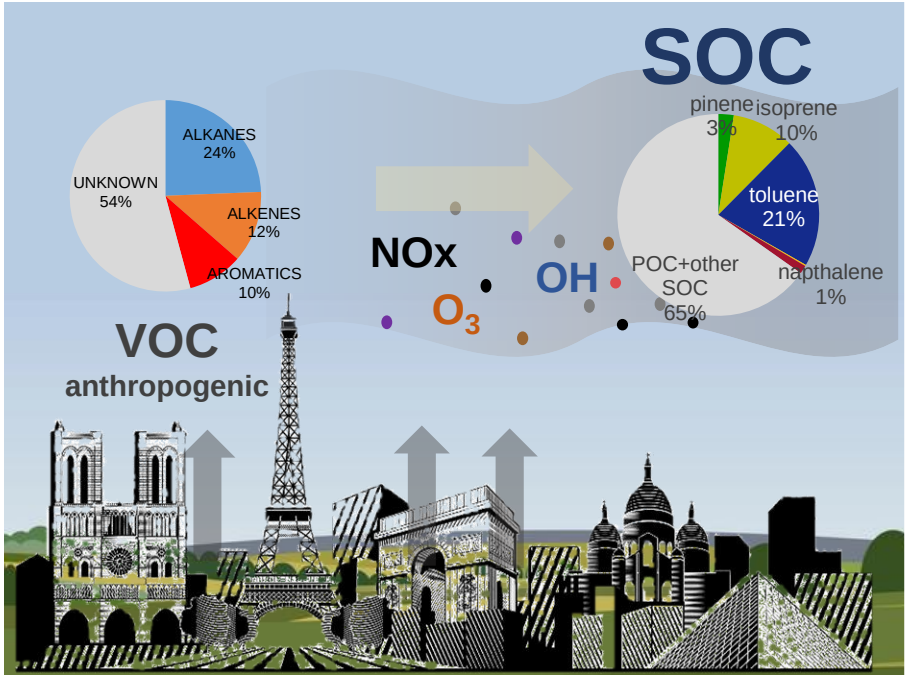
A similar concentration of DHOPA was observed for Paris and Rambouillet, while the nitrophenol was mainly present in the urban area. In the case of the biogenic compounds they were observed at higher concentrations in the forested area with the exception of the methylerythritol.

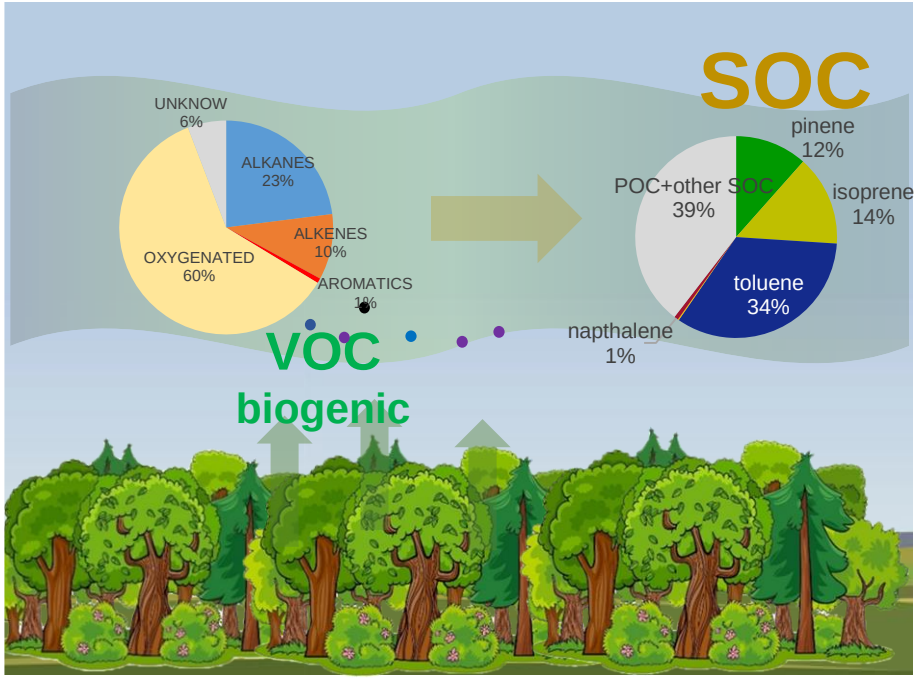
Application of the SOA tracer method to approach the aerosol composition

VOC	f_{SOC}
α-Pinene (Lanzafame et al. 2021)	0.231 for pinonic acid 0.124 for pinic acid 0.162 for MBTCA
Isoprene	0.155 (Kleindienst et al. 2007)
toluene	0.009 (this study)
Naphthalene	0.115 (this study)

Higher contribution of secondary organic aerosol is observed at Rambouillet. The SOA composition is highly influenced by the contribution of anthropogenic sources.







There is an homogeneity in the chemical composition for the urban area of Paris and the forest of Rambouillet with small differences observed during the background period, which highlights the nature of the local emissions of each place.

This work was supported through the project TRACAOS-A within the PN-LEFECHAT program, through the fellowship IDEX at the Université Paris Cité and the ACROSS project. The ACROSS project has received funding from the French National Research Agency (ANR) under the investment program ANR−17−MPGA−0002, and it was supported by the French National program LEFE of CNRS-INSU.

The authors acknowledge the CNRS-INSU for supporting the CESAM simulation chamber and the PEGASUS mobile platform as national facilities of the ACTRIS research infrastructure.