Supplementary information

Investigating the role of anthropogenic terpenoïds on urban secondary pollution under summer conditions by a box modeling approach

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Table S1 : List the measured parameters, the associated instruments and their time resolutions and detection limits.

Maarina	T	Time	2σ	Limit of
Measurements	Instruments	resolution (min)	uncertainties	detection
		(11111)	(70)	
Meteorological parameters (Temperature, relative humidity, Pressure, Wind speed and direction)	Wind sensor and multi- plate radiation shield (Young) ^(a)	1	_	_
Boundary Layer Height (BLH)	ALS450 Lidar ^(b)	60	_	_
Photolysis frequencies (J(NO ₂), J(O ^{1D}), J(HONO)	Filterradiometers and spectroradiometer (LI-1800) ^(b)	1 – 10	20-25	10 ⁻⁷ - 5.10 ⁻⁵ s ⁻¹
ОН	Chemical Ionization Mass Spectrometry ^(b)	5	35	$3 \times 10^{5} \text{ cm}^{-3}$
NO	AC31M analyzer (Environment S.A.) ^(c)	1	5	0.5 ppb
NO ₂	NOxTOy (MetAir) (c)	1	5	0.5 ppb
O ₃	Ultraviolet absorption analyzer (41M, Environment SA) (c)	1	5	1 ppb
СО	Gas Chromatography	15	10	1 ppb

	with Reduction			
	Detection ^(b)			
	Gas Chromatography			
PAN	with Electron Capture	15	10	0.01 ppb
	Detection ^(b)			
	2 Gas Chromatography			
VOC (C2-C6)	with Flame Ionization	30	15 - 20	0.04 - 0.09
VOC (C7-C10)	Detection			ppb
	(Chromatotec ®) ^(a)			
	Proton Transfer Reaction			
Ovuganated VOC	 Mass Spectrometry 	5	20	
Oxygenated VOC	(Ionicon Analytik	5		
	GmbH)			
^(a) : Ait-Helal et al. ¹ , ^(b) :	Michoud et al. ² , ^(c) : Baudic et al.	3		

<u>Note</u>: All the measurements were done at urban background site of LHVP ("Laboratoire d'Hygiène de la Ville de Paris") except O_3 and OH that were monitored at SIRTA ("Site Instrumental de Recherche par Télédétection Atmosphérique"), a suburban site at 14 km southwest of Paris (see map above).



2. Presentation of the emissions implemented in the model

a. Anthropogenic emissions

i. Emissions of Volatile Organic Compounds (VOCs)

Following the works from Borbon et al. ⁴, deGouw et al.^{5, 6}, emission ratios were determined for the Paris and Los Angelescities. To do this, a linear regression fit was performed to calculate the slope of the scatterplot between VOC versus CO during nighttime (8 PM – 4 AM UTC). During this period, reactivity with OH is extremely low and can be neglected. Moreover, we consider nighttime chemistry not significant for most measured VOCs except for butenes.

Compounds	MCM species	VOC / CO (ppb/ppm)
Ethane	C2H6	23.4 ^(a)
Propane	С3Н8	9.02 ^(a)
n-Butane	NC4H10	10.1 ^(a)
i-Butane	IC4H10	4.53 ^(a)
n-Pentane	NC5H12	3.08 ^(a)
i-Pentane	IC5H12	10.8 ^(a)
2-methyl-pentane	M2PE	1.29 ^(a)
3-methyl-pentane	M3PE	1.39 ^(b)
n-Hexane	NC6H14	1.15 ^(a)
2-methyl-hexane	M2HEX	0.58 ^(b)
3-methyl-hexane	M3HEX	0.58 ^(b)
cyclo-hexane	CHEX	0.33 ^(a)
n-heptane	NC7H16	2.03 ^(a)
n-Octane	NC8H18	0.19 ^(a)
n-Nonane	NC9H20	0.26 ^(a)
n-Decane	NC10H22	0.46 ^(a)
Undecane	NC11H24	0.32 ^(b)
Acetylene	C2H2	4.74 ^(a)
Ethene	C2H4	7.64 ^(a)
Propene	C3H6	2.07 ^(a)
1-Butene	BUT1ENE	0.39 ^(b)
cis-2-Butene	CBUT2ENE	0.28 ^(b)
trans-2-Butene	TBUT2ENE	0.34 ^(a)
2-methyl-propene	MEPROPENE	0.90 ^(b)
1,3-Butadiène	C4H6	0.39 ^(a)
3-methyl-1-butene	ME3BUT1ENE	0.07 ^(b)
Benzene	BENZENE	1.07 ^(a)
Toluene	TOLUENE	12.3 ^(a)
m+p-Xvlenes	MXYL + PXYL	4.59 (a)
o-Xvlene	OXYL	1.09 ^(a)
		1····

Table S2: Urban emission ratios (ER) of VOCs relative to CO in Paris calculated by ^(a): Borbon et al. ⁴ and Los Angeles calculated by ^(b): deGouw et al. (2017) ⁶, and ^(c): deGouw et al. (2018) ⁵.

Ethylbenzene	EBENZ	0.95 ^(a)
n-propyl-benzene	PBENZ	0.87 ^(a)
i-propyl-benzene	IPBENZ	0.03 ^(b)
o-ethyl-toluene	OETHTOL	0.12 ^(b)
m+p-ethyl-toluene	METHTOL + PETHTOL	0.44 ^(b)
1,3,5-trimethyl-benzene	TM135B	0.38 ^(a)
1,2,3-trimethyl-benzene	TM123B	0.59 ^(a)
1,2,4-trimethyl-benzene	TM124B	0.74 ^(a)
Butanal	СЗН7СНО	0.23 ^(c)
2_methyl-propanal	IPRCHO	0.15 ^(c)
Hexanal	C5H11CHO	0.57 ^(c)
Benzaldehyde	BENZAL	0.89 ^(c)
ACR	ACR	1.40 ^(c)
2,3-Butadione	BIACET	0.13 ^(c)
Ethanol	С2Н5ОН	45.7 ^(c)
n-propanol	NPROPOL	0.32 ^(c)
i-propanol	IPROPOL	9.90 ^(c)
Formic acid	НСООН	1.20 ^(c)
Propionic acid	PROPACID	3.10 ^(c)

In addition to the available ER ratios in the literature, we also determined the ER of thirteen additional OVOC relative to carbon monoxide (CO) following the same method of Borbon et al. ⁴ based on a linear regression fit (<u>Table S3</u>) using VOC measurements by PTR-MS from the MEGAPOLI campaign. For β -pinene and limonene, since no data were available, we used data from Los Angeles.

As commented below, the scatterplots of OVOC-to-CO can be affected by photochemistry. By applying a nighttime-daytime filter on Paris data, Borbon et al. showed that there was no clear evidence of an effect of chemistry on primary non-methane hydrocarbon data. However, for OVOC, Baudic et al. ³ showed the secondary feature of their diel cycle in Paris with maxima concentrations at noontime due to their secondary production and primary biogenic emissions. The nighttime filter was applied to OVOC. Isomeric VOC like cannot be distinguished by PTR-MS measurements. To establish specific OVOC-to-CO emission ratios and constraint their emissions for the simulations, we applied the mean distribution of individual OVOC reported at the SIRTA surburban site ¹.

Three examples of scatterplots are provided in <u>Figure S2</u>. The scatterplot has been color-coded with hour. Two patterns are observed. First, the nighttime scatterplot of acetone and acetaldehyde is diffuse with an R^2 around 0.6. The late night (midnight to 04 :00) data points are in the upper part of the scatterplots suggesting an enrichment in OVOC compared to CO due to their non-combustion emissions (ie., solvent use). This period is outside of the rush hours of the late evening period when CO shows its highest concentrations above 300 ppb ³. Secondly, the R^2 is lower for methylglyoxal, MEK, and butanal. These latter are co-eluted by PTR-MS for the mass m/z 73. It is due to a few

number of extreme OVOC concentrations. However, the linear fit fall into most of the scatterplot data points; the emission ratio can be derived from the value of this linear fit slope.

To conclude, the ERs of OVOC-to-CO is derived from the slope of the least square linear fit which is a good compromise to constraint the emission ratios by at least representing 60% of the variance of the data for most OVOC.

Table S3: Additional Emission Ratios of VOCs relative to CO obtained by calculating a linear regression fit to data measured in Paris (MEGAPOLI), except for β -pinene and limonene which are measured in Los Angeles.

Compounds	МСМ	VOC / CO (ppb/ppm)
	species	
Methanol (m/z 33)	СНЗОН	24.2
Proxy Formaldehyde (m/z	НСНО	3.2
31)		
Acetone (m/z 59)	CH3COCH3	5.1
Acetaldehyde (m/z 45)	CH3CHO	7.2
Methyl Vinyl Ketone (m/z	MVK	1.3
71)		
Methacrolein (m/z 71)	MACR	0.3
Methyl Ethyl Ketone (m/z	MEK	1.1
73)		
Methylglyoxal (m/z 73)	MGLYOX	0.04
Glyoxal (m/z 59)	GLYOX	0.2
Propanal	C2H5CHO	0.3
Styrene	STYRENE	0.2
Isoprene	C5H8	1.6
α-pinene	APINENE	0.1
β-pinene	BPINENE	0.13
Limonene	LIMONENE	0.26



Figure S2 : Scatterplots of (a) acetone, (b) acetaldehyde, and (c) methylglyoxal versus CO in ppb; the color code represents the hours of the day.

ii. Emissions of CO, NOx, and SO₂

Emissions in tons/year are extracted from the AIRPARIF inventory for Paris Intramuros (<u>**Table S4**</u>). In this inventory, annual emissions are classified into different sectors. Each emission sector is supplied with a time key to calculate the quantity of compound emitted during a given period (month, day, hour) (<u>**Table S5**</u>). Emissions for the month of July E_{July} was chosen to represent the summer emission of each species. Then, a mean emission flux was calculated using the following equation:

$$F = \frac{E_{July}}{S \times t} \tag{eq. 1}$$

Where F is the mean flux for summer emissions in molec cm⁻² s⁻¹; S is the Paris Intramuros surface area in m²; t is the time of the July month in s. Here, Paris Intramuros surface area is equal to 105.4 km² and July is 31 days long.

Table S4 : Annual, monthly, and daily emission fluxes of CO, SO₂, and NOx.

Snecies	Annual emission	July emission	Emission flux
species	(tons/year)	(tons/month)	(molec cm ⁻² s ⁻¹)
СО	1.90 104	1.41 10 ³	1.07 1013
SO ₂	1.38 10 ³	9.82 10 ¹	3.27 1011
NO _x	8.78 10 ³	6.35 10 ²	2.94 1012

To represent the evolution of emission during a day, time keys were used to define a diel profile for each compound. Only dominant sectors (**Table S5**) were used to calculate the emission profiles (they represent 98.7% of the total emissions). For each sector, a time key gives the percentage of emissions for each hour. The daily profile is the average of each time key, weighted by the contribution of each sector. The standard deviation represents the variation of the different time keys. The standard deviation is also weighted by the contribution of each sector. The NO_x and CO profiles are nearly the same (same dominant sectors).

Table S5 : Time keys for each emission sector taken into account to calculate the emission profile of CO, SO₂, and NOx.

Sectors	CO	SO ₂	NOx
Energy industry combustion	0%	51.8%	5.4%
Non-industrial combustion	20.6 %	14%	18%
Combustion in the manufacturing industries	0%	32.9%	2.3%
Road transport	77.5%	0%	71.2%
Other mobile sources and machinery	1.5%	0%	3.2%





Figure S3: Temporal distribution in % of the emission of CO, NOx, and SO₂ over 24h. The solid line and envelope correspond to the mean and standard deviation; respectively, of the diel emission profile derived from the AIRPARIF database. Rectangular functions (dotted lines) are considered in the model to reproduce these diel emissions.

iii. <u>Deposition</u>

Table S6 :	Deposition	rates from	Michoud	et al.	2
	,	./			

MCM Species	Deposition rates (cm s ⁻¹)
NO ₂	0.15
O ₃	
SO_2	
CO	
CH3COCH3	
MEK	0.5
MVK	0.5
CH3OH	
C2H5OH	
HCOOH	
CH3CO2H	
PAN	
MPAN	0.2
HMPAN	
PPN	
PBZN	
PBN	1.1
PIPN	
H2O2	
НСНО	
CH3CHO	
C2H5CHO	
C3H7CHO	
MXYLAL	
PXYLAL	0.22
BENZAL	0.33
C5H11CHO	
ACR	
MACR	
GLYOX	
MGLYOX	
HNO3	2
N2O5	2
CH3OOH	0.55

Note: Following the work from Michaud et al.², we supposed a deposition rates equal to 0.5 cm s^{-1} for all other species in the MCM gas mechanism.

iv. Addition of the O₃ advection



Figure S4 : Comparison of diel profile of ozone before and after integration of its advection.

b. **Biogenic emissions**

Biogenic emissions in urban environments are usually poorly or incompletely considered in inventories. Recently, a modelling study using the CHIMERE model focused on the description of biogenic emissions in Paris in the frame of the STREET (Impact of STress on uRban trEEs on ciTy air quality) project ⁷ where an intensive field campaign was recently conducted over the Paris region during summertime. This study described the development of an emission inventory to model biogenic emissions in Paris during the month of the field campaign using a detailed vegetation map and measured meteorological parameters (temperature, humidity, etc.). Biogenic emissions were also described in the model based on Maison et al. ⁷ study. Gaseous emissions of 8 chemical compounds (isoprene, α -pinene, β -pinene, limonene, acetone, NO, CO, and methanol) were implemented in the model; 3 diurnal profiles were implemented in the model to describe their emissions (**Figure S5 (a), (b), and (c)**).





Figure S5 : Biogenic emissions diel profiles derived from Maison et al. ⁷ for isoprene, α -pinene, β pinene, limonene, acetone, NO, CO, and methanol; solid line represents the mean emission and the envelope corresponds to the standard deviation. These biogenic emissions are considered in the model as rectangular functions (doted lines).

3. Comparison of simulated concentrations vs measurements

In order to evaluate the simulation results in relation to the measurements in situ, we created an excel file (**Comparison_Obs_Model.xls file**) listing the hourly concentrations of the various compounds in the simulation for the last day where the photo-stationary phase is reached. A color code was assigned to measure the deviation between the simulated concentration and the median concentration measured during the campaign.

To ensure relevant comparison, only compounds with a percentage below the detection limit of less than 75% were considered; therefore, we eliminated compounds from the analysis. They are marked in red in **Table S7**.

Measured Compounds	% < Limit of
-	Detection
Ethane	5%
Propane	4%
n-Butane	5%
i-Butane	6%
n-Pentane	5%
i-Pentane	4%
2-methyl-pentane	22%
3-methyl-pentane	81%
n-Hexane	
2-methyl-hexane	_
3-methyl-hexane	0%
cyclo-hexane	41%
n-heptane	0%
n-Octane	85%
n-Nonane	52%
n-Decane	8%
Undecane	_
Acetylene	5%
Ethene	9%
Propene	18%
1-Butene	78%
cis-2-Butene	97%
trans-2-Butene	44%
2-methyl-propene	5%
1.3-Butadiène	39%
3-methyl-1-butene	
Benzene	36%
Toluene	0%
m+n-Xylenes	1%
m p-ryienes	1 / 0

Table S7 : The percentage of VOCs concentration values below the detection limit.

o-Xylene	29%
Ethylbenzene	26%
n-propyl-benzene	36%
i-propyl-benzene	_
o-ethyl-toluene	62%
m+p-ethyl-toluene	_
1,3,5-trimethyl-benzene	77%
1,2,3-trimethyl-benzene	_
1,2,4-trimethyl-benzene	30%
Butanal	0%
2_methyl-propanal	0%
Hexanal	0%
Benzaldehyde	0%
ACR	0%
2,3-Butadione	0%
Ethanol	0%
n-propanol	0%
i-propanol	0%
Formic acid	0%
Propionic acid	0%





Estimation of the SOA production from BTEX

The data from the simulations performed with the model have been used to calculate the SOA production: the rate constants of BTEX with oxidants computed in the model as well as the time evolution of the simulated concentrations of oxidants and BTEX. SOA formation yields of the selected compounds (benzene, toluene, ethyl benzene, xylene) were also evaluated based on the review of the literature. Only the reactivity of BTEX compounds with OH has been considered in our calculations. As in the MCM, all BTEX compounds react with OH, with some of them undergoing reactions with NO₃. Specifically, benzene and toluene react exclusively with OH, while xylenes and ethylbenzene also react with NO₃. However, there is a notable lack in yield data concerning the reactions between xylenes, ethylbenzene, and NO₃. The yields extracted from the literature and used in this study are presented in the Table S8. Figure S9 presents the time evolution of potential SOA mass concentrations produced from BTEX for the "Reference" case.

Table S8: SOA formation yields of BTEX precursors and rate constants with OH in the model.

Oxidant	BTEX	Benzene	Ethylbenzene	Toluene	O- xylene
ОН	SOA yield (µg m ⁻³ ppm ⁻¹)	2089	791	1694	254
	k(OH) (cm ³ molec ⁻¹ s ⁻¹)	1.2 10 ^{-12 (a)}	5.6 10 ^{-12 (b)}	7.0 10 ^{-12 (a)}	1.36 10 ^{-11 (b)}

(a) 8; (b) 9

Figure S9: Potential SOA mass concentrations produced from oxidation of BTEX by OH predicted with the model in the "Reference" case.

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