Paramétrisations simples pour représenter les SVOC/IVOC du trafic routier et impact sur la qualité de l'air en Île-de-France

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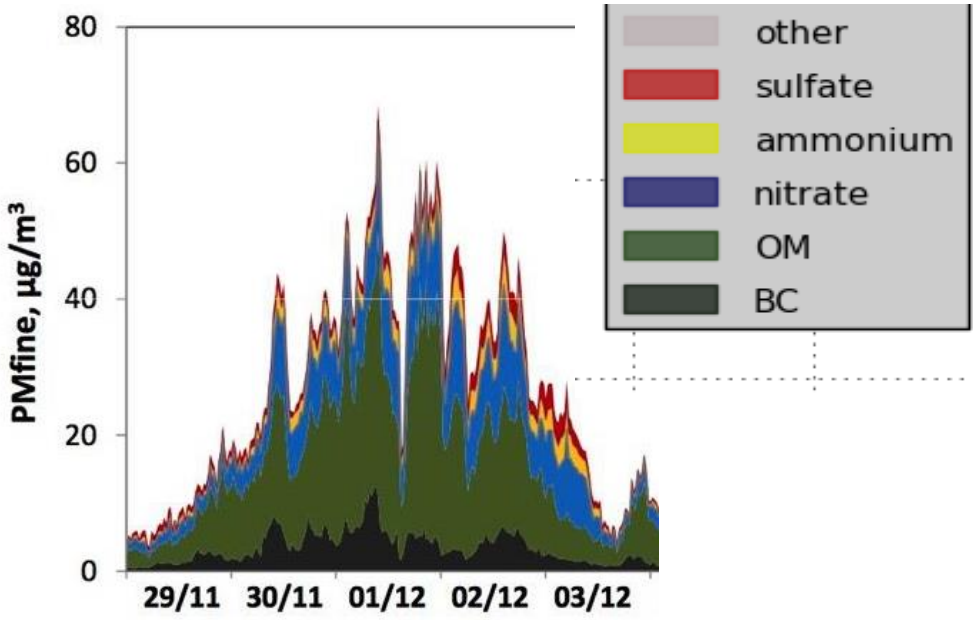
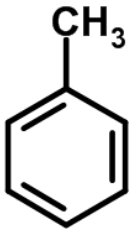
Introduction: composition of particles during a pollution episode in Paris in December 2016



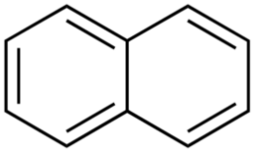
Observations at SIRTA (Greater Paris)
(Source : SIRTA / IPSL – LSCE / INERIS)

- High concentrations of organic matter (OM)
- Simulations show that about 85% of pollution is local
- Organic precursors from traffic and residential heating

Organics in the emissions



Range of molecular weights and functionalities



Volatile

Gas

Condensable products

Particles

Non-volatile

VOC (Volatile organic compounds)

Regulated

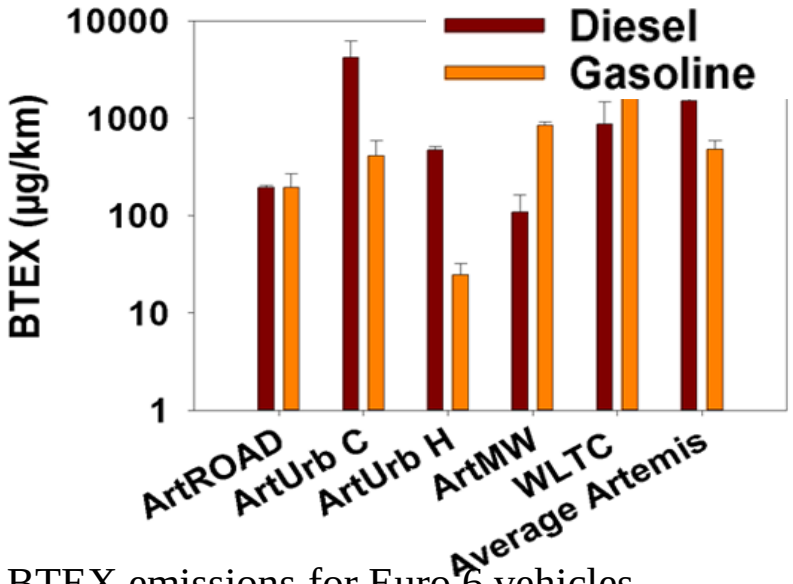
IVOC

SVOC

Not regulated

PM - OM

VOC and I/S-VOC precursors of SOA

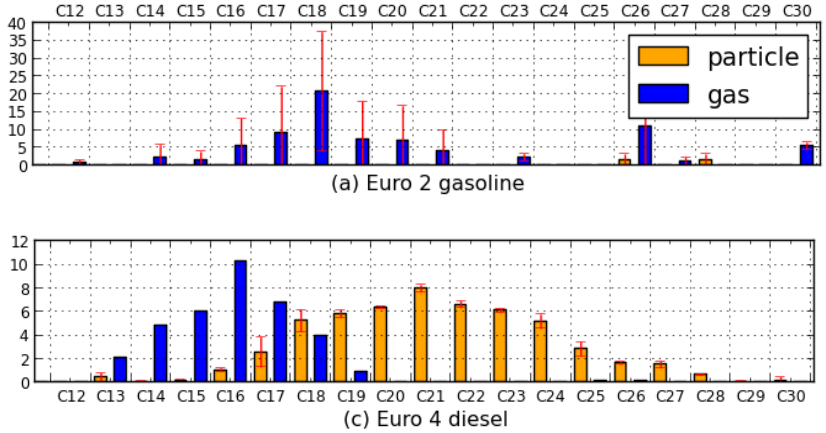


BTEX emissions for Euro 6 vehicles
Source: Martinet et al., Environ. Sci. Tech., 2017

- Amongst VOC, not all chemical species are SOA precursors.
- The main known precursors are aromatics: the so-called BTEX (benzene, toluene, ethylbenzene, and xylenes), and HAP.

I/S-VOC precursors of SOA are high molecular weight molecules, aromatics and cyclic alkanes …

Estimation of I/S-VOC emissions for linear alkanes



Emission factors of gas- and particle-phase alkanes for an urban cycle with cold start (Source: Kim et al. Atmos. Env., 140, 176-187, 2016).

Kim et al. (2016) measured alkane emissions in gas/particle phases:

- Gas IS-VOC/OM ~ 0.8
  for Euro 4 diesel vehicle
- Gas IS-VOC/OM ~ 23
  for Euro 2 gasoline vehicle
- Gas IS-VOC/OM ~ 116
  for Euro 4 DPF diesel vehicle

$\Rightarrow$ For passenger cars in France,

Gas IS-VOC emissions ~ 1.5 OM emissions.

These gas SVOC emissions are missing from emission inventories.

Estimation of I/S-VOC emissions using VOC emissions

- I/S-VOC estimated using I/S-VOC/OM
- But OM measurements depend on temperature => use I/S-SVOC/VOC instead
- Zhao et al (2015, 2016) =>
  - SVOCI/VOC* = 0.04 ± 0.02 for cold-start gasoline vehicles,
  - SVOCI/VOC* = 0.17 ± 0.12 for hot-start gasoline vehicles,
  - SVOCI/VOC* = 0.6 ± 0.1 for diesel vehicles,
  - SVOCI/VOC* = 1.5 ± 0.8 for diesel vehicles with particle filters.

* VOC are measured as NMHC, which may include a fraction of SVOC

Simple model to represent I/S-VOC emissions and ageing

- Only 3 species, the volatility distribution based on measurements of May et al. (2013)

$\log(c^*)$	Fraction of POA_{total}	Model species	Model $\log(c^*)$	Model fraction of POA_{total}
< -1	0.034	POA-lv	−0.04	0.041
−1	0.007			
0	0.008			
1	0.025	POA-sv	1.93	0.058
2	0.025			
3	0.079			
4	0.203	POA-iv	3.5	0.612
5	0.330			
6	0.289			

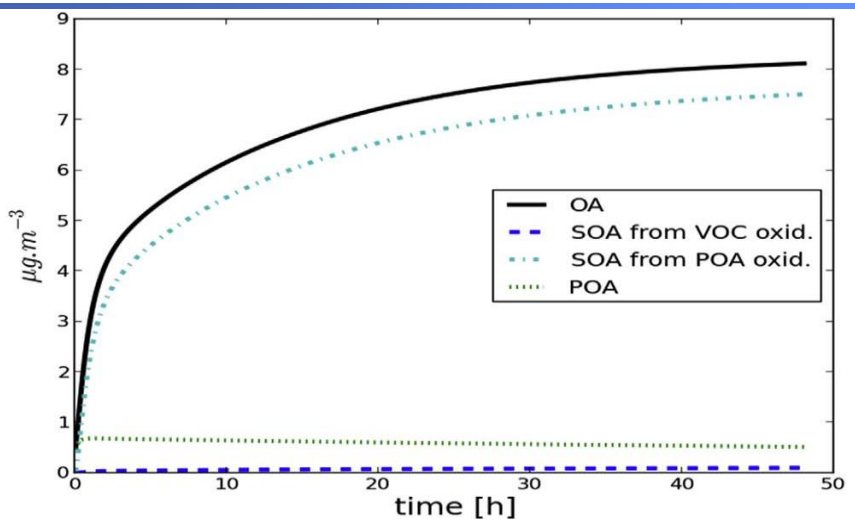
- Simple one-step ageing scheme

$$POA_{vapor}\text{-lv} + OH \rightarrow SOA_{vapor}\text{-lv}$$

$$POA_{vapor}\text{-sv} + OH \rightarrow SOA_{vapor}\text{-sv}$$

$$POA_{vapor}\text{-iv} + OH \rightarrow SOA_{vapor}\text{-iv}$$

Ageing of I/S-VOC emissions

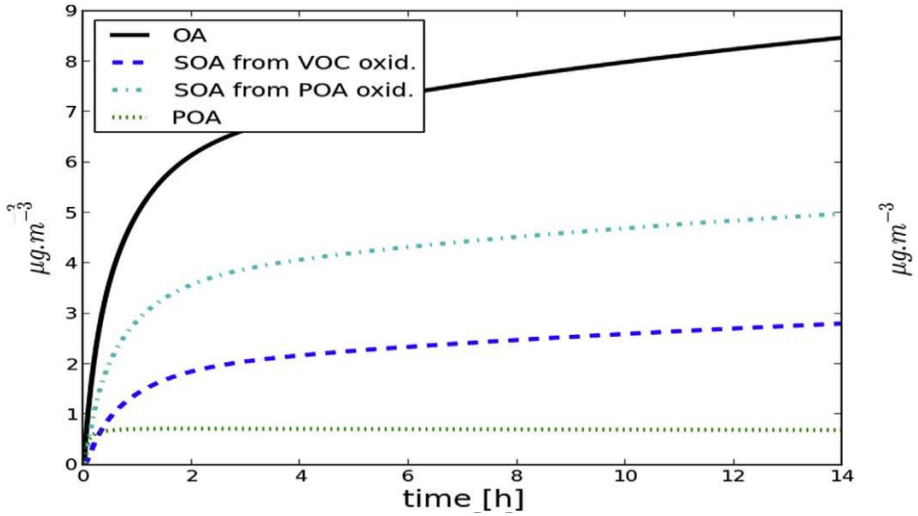


Organic concentrations from ageing of idle driving diesel vehicle without DPF emissions. Source: Sartelet et al. Atmos. Env., 2018

- Comparisons to the measurements of Gordon et al. (2014) and more sophisticated model of Zhao et al. (2015)
- For idle driving diesel vehicles: EF VOC = 6 200 mg/kg fuel

- After 11h of ageing (same OH exposure time as Gordon et al. 2014), SOA/POA= 8.6 in the experiment and 6.6 in the simple model
- After 48h of ageing,
  - Zhao et al. (2015) => OA = 1500 mg/kg fuel of SOA
  - Our model => OA = 1574 mg/kg fuel
- Most of SOA from I/S-VOC oxidation for diesel vehicles

Ageing of I/S-VOC emissions

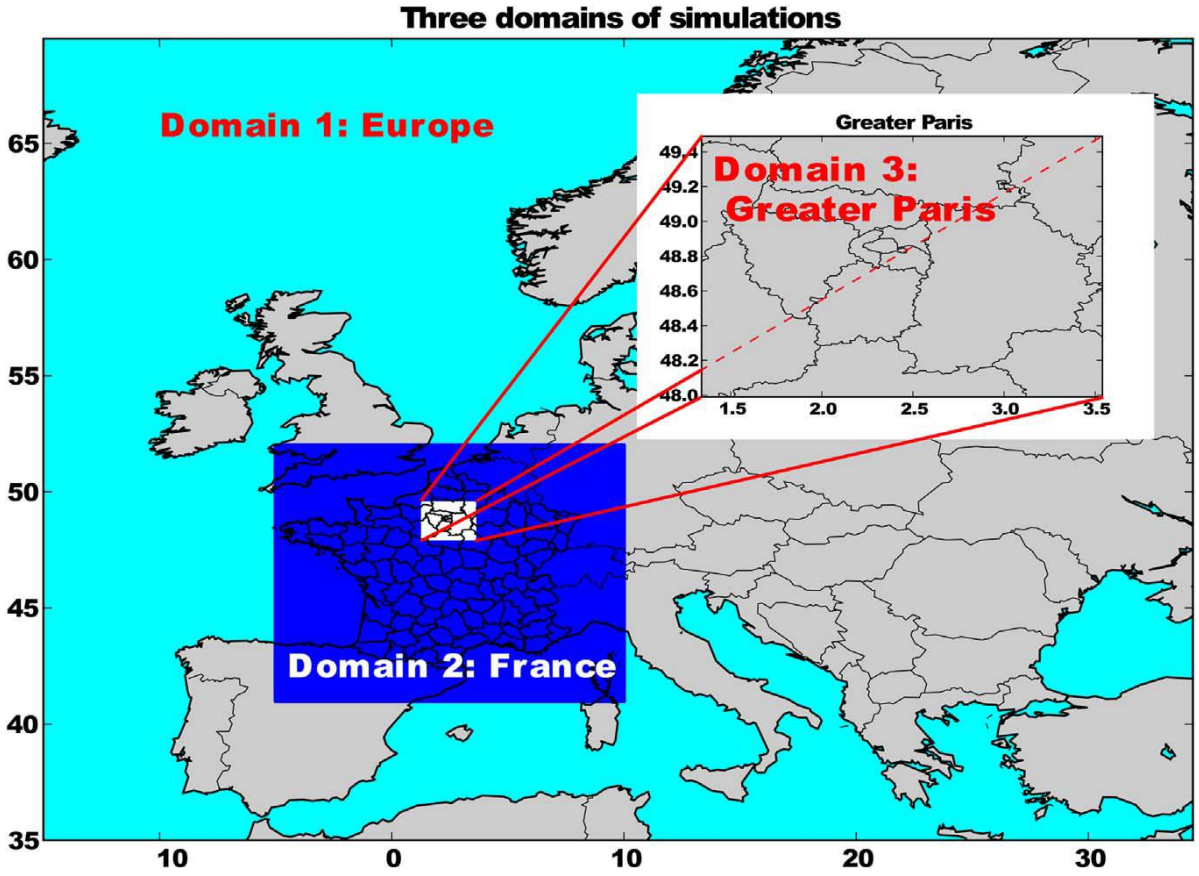


Organic concentrations from ageing of gasoline vehicle emissions (simulation of the experiments of Gordon et al. 2014). Source: Sartelet et al. Atmos. Env., 2018

- Comparisons to the measurements of Platt et al. (2013) for Euro 5 gasoline vehicle
- THC = POA_{total} + VOC initialised as in Platt et al. (2013)
- IVOC initialised by IVOC/VOC = 0.17 (Zhao et al. 2016)
- NOx initialised such as having VOC/NOx = 5.6 as in Platt et al. (2013)

- After 5 h of ageing, 197 µg m^{-3} of OA are simulated in good agreement with the measurements of Platt et al. (2013), who estimated OA to be about 200 µg m^{-3} after wall loss corrections.

Application to Greater Paris



- Polyphemus air-quality platform
- ECMWF Meteorology over Europe and France
- WRF Meteorology over Île-de-France
- EMEP emissions over Europe
- CITEPA emissions over France
- Airparif emissions over Île-de-France

Mozart 4 boundary conditions for European domain

I/S-VOC emissions

- Similar total emissions over Île-de-France by using the I/S-VOC/POA or the I/S-VOC/VOC methods
- Larger emissions over urban areas and lower over motorways using the I/S-VOC/VOC method

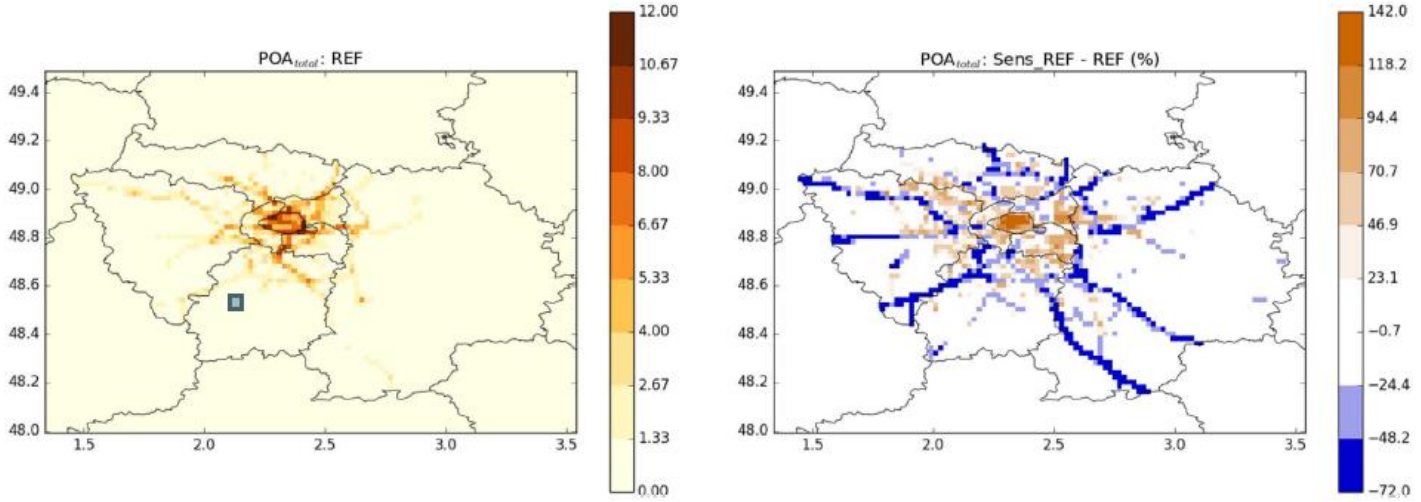


Fig. 3. POA_{total} emissions due to traffic in tonnes per year estimated from emissions of POA (reference simulation, left panel), and relative difference between the POA_{total} emissions estimated from the emissions of VOC (sensitivity study) and the emissions of POA (reference) (right panel).

Impact on OA concentrations

- Impact on OA concentrations is lower than on emissions

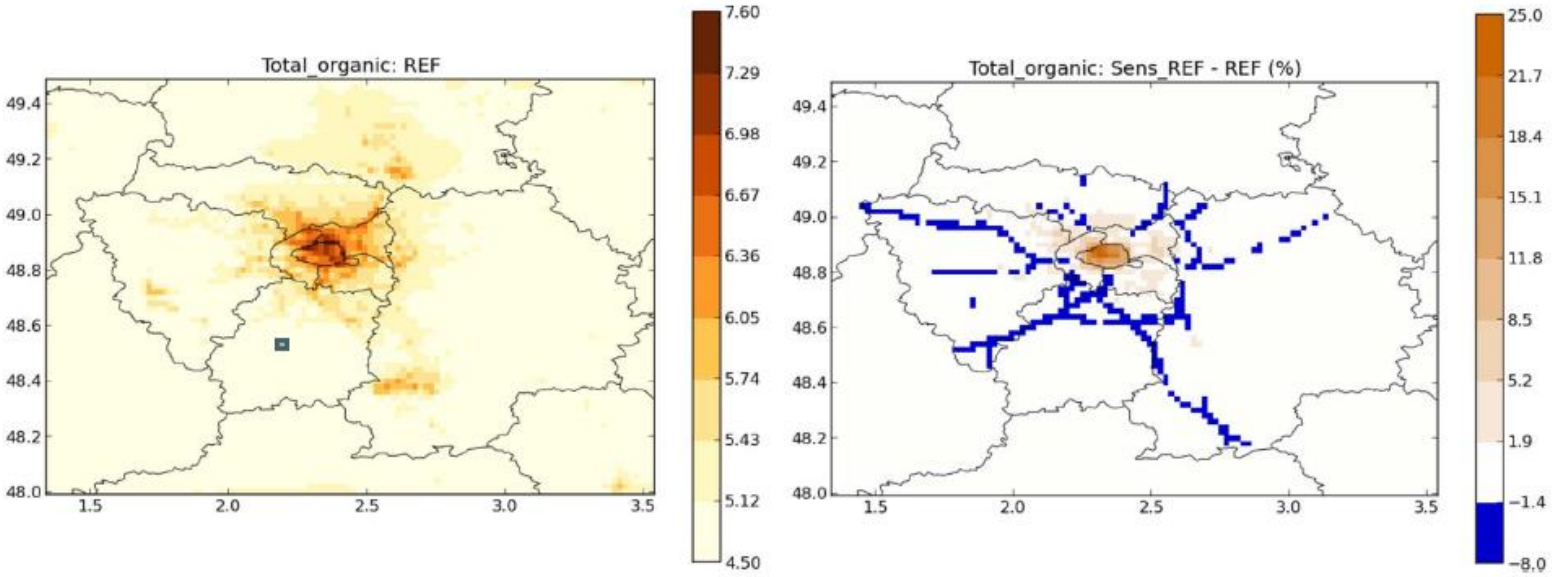


Fig. 8. Total organic concentrations (gas + particle phase OA_{total}) in $\mu g\ m^{-3}$ simulated with emissions estimated from the POA_{total}/POA emission ratio (left panel) and relative differences (in %) between concentrations simulated with emissions estimated from the POA_{total}/VOC emission ratios and those simulated with emissions estimated from the POA_{total}/POA emission ratio (right panel).

Contributions to OA concentrations

- Low contribution of VOC (toluene, xylenes)

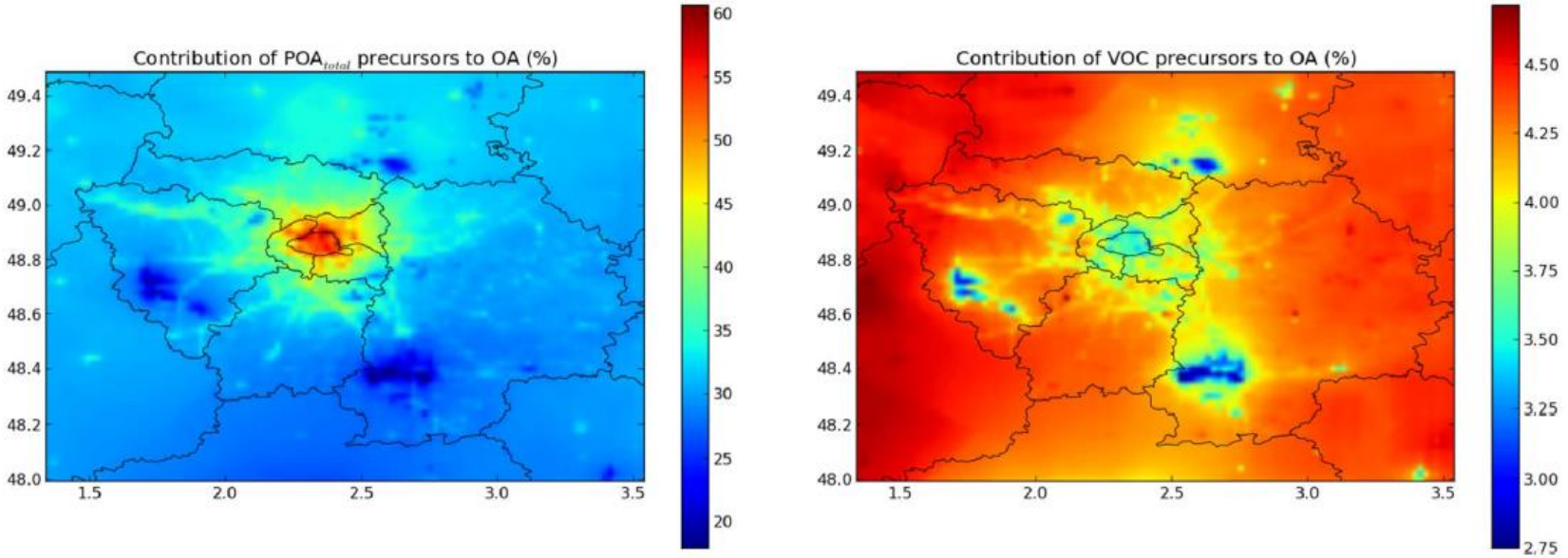


Fig. 6. Contribution in % of POA_{total} emissions (left panel) and VOC emissions (right panel) to OA concentrations.

Comparisons to measurements

Table 2
Statistics of comparisons to measurements for PM_{10}, $PM_{2.5}$, BC and OA. The statistics are derived from daily concentrations for a year.

	Number of stations	Meas. mean ($\mu g\,m^{-3}$)	Sim. mean ($\mu g\,m^{-3}$)	Correlation (%)	mfe (%)	mfb (%)
PM_{10}	14	21.1	17.3	32	43.6	−23.8
$PM_{2.5}$	7	12.4	14.2	36	45.4	21.6
BC	3	1.2	0.6	75	64.6	−60.9
OA	1	3.2	2.2	41	50.9	−29.8

Source: Sartelet et al. Atmos. Env. 2018

- SIRTA site not much affected by traffic I/S-VOCs

=> Need measurements in Central Paris

Conclusion

- OM precursors are emitted in the gas phase, with different volatilities and characteristics.
- A simple model of I/S-VOC emission and ageing represents well some chamber experiments.
- Need to better characterize the OM precursors. Low contribution of single-ring aromatic VOCs.
- Need to differentiate the potential of SOA formation depending on the Euro norm, regime (motorway, road, urban).
- More observations in central Paris required.