Atmospheric photochemistry and secondary aerosol formation of urban air in Lyon, France

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A B S T R A C T

Photochemical aging of volatile organic compounds (VOCs) in the atmosphere is an important source of secondary organic aerosol (SOA). To evaluate the formation potential of SOA at an urban site in Lyon (France), an outdoor experiment using a Potential Aerosol Mass (PAM) oxidation flow reactor (OFR) was conducted throughout entire days during January-February 2017. Diurnal variation of SOA formations and their correlation with OH radical exposure (OHexp), ambient pollutants (VOCs and particulate matters, PM), Relative Humidity (RH), and temperature were explored in this study. Ambient urban air was exposed to high concentration of OH radicals with OHexp in range of (0.2–1.2) × 1012 molecule/(cm3·sec), corresponding to several days to weeks of equivalent atmospheric photochemical aging. The results informed that urban air at Lyon has high potency to contribute to SOA, and these SOA productions were favored from OH radical photochemical oxidation rather than via ozonolysis. Maximum SOA formation (36 μg/m3) was obtained at OHexp of about 7.4 × 1011 molecule/(cm3·sec), equivalent to approximately 5 days of atmospheric oxidation. The correlation between SOA formation and ambient environment conditions (RH & temperature, VOCs and PM) was observed. It was the first time to estimate SOA formation potential from ambient air over a long period in urban environment of Lyon.

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Introduction

Omnipresent organic aerosols (OA) attract extensive concern due to their great burden on air pollution and related adverse health effects and pronounced climate forcing (Wu et al., 2020; Gao et al., 2012; Orru et al., 2017; Tong et al., 2020). A number of epidemiological and clinical studies have found a firm correlation between exposure to ambient OA and adverse health effects, including increased morbidity from respiratory and cardiovascular diseases as well as endpoint mortality (Tiet et al., 2017; Zhou et al., 2019; Cohen et al., 2017). In 2004, the World Health Organization (WHO) estimated 141,000 premature deaths per year due to OA emission and associated climate change with a forecast of 250,000 additional annual deaths that will occur from 2030 to 2050. About 9% of prema-
ture deaths in France are attributable to air pollution specifically by particles smaller than 2.5 μm (PM2.5), of which OA are the main contributor (Santé publique France, 2016). The toxicity of PM relates to the particle-bounded reactive oxygen species (ROS), which are enriched to a high degree in OA (Campbell et al., 2019).

High fractions of OA are generated secondarily (namely SOA) from heterogeneous transformations of primarily emitted OA and more via the gas-to-particle conversion mechanisms, often initiated from oxidation of diverse volatile organic compounds (VOCs) by oxidants, like O3, OH and NO3 radicals, etc. (Waring and Wells 2015; Watne et al., 2017). Photochemical reactions between OH radicals and VOCs are the main pathway to contribute SOA in the atmosphere, especially in urban air, where a large amount of anthropogenic VOCs sourced from traffic exhaust, residential emissions, and constructions generate SOA in photochemical aging, deteriorating urban air quality and associated health threat (Gulia et al., 2015; Zhang et al., 2020; Li et al., 2020).

Numerous studies have investigated urban air pollution and characterized photochemical resulted SOA (Luo et al., 2020; Wang et al., 2020; Weitkamp et al., 2020; Adon et al., 2019). However, assessments of SOA formation potency from urban air were seldom conducted due to practical complexity in urban air chemicals and environments and also due to constraints in poorly defined SOA formation mechanisms/models and in techniques (Liu et al., 2018; McFiggans et al., 2019). As mentioned above, urban air comprises more anthropogenic VOCs, which are strongly influenced by human activities, energy consumptions, and distribution of social facilities, such as industrial, residential, education, entertainment area, etc. (Montero-Montoya et al., 2018; Molina et al., 2019). Meanwhile, many inorganic pollutants (SO2, NOx, NH3, etc.) and particles (Primary OA, POA, and inorganic salts) specifically released from urban sites also add complexity to the transformations of VOCs and SOA formation (Hammes et al., 2019; Wang et al., 2020).

Moreover, there still lies great uncertainties in SOA formation assessments using VOCs compositions and SOA yield parameters, because many reaction pathways and kinetics, such as RO2 auto-oxidation, are not well studied or involved in current chemical models. The extensively studied SOA formation yields of typical VOCs shall be questioned when considering the mixing with other vapors and under various atmospheric aging pathways in the practical environment (Chen et al., 2018; Bianchi et al., 2019). McFiggans et al. (2019) reported reduced SOA formation from monoterpenes by mixture of atmospheric vapors, such as isoprene, carbon monoxide and methane, in photochemistry. Although environmental chambers are widely used to study SOA formation, the noteworthy disadvantages, including long residence time and high wall loss for chemicals, relative low oxidation ranges, and less efficient in operation and particle transformation response, demonstrate that environmental chamber can hardly capture the SOA formation potency for VOCs in urban air (Zhang et al., 2014; Krechmer et al., 2015). To investigate the formation of SOA over a wide extent of atmospheric aging, which is quantitativied as OH radical exposure (OHexp), the Potential Aerosol Mass (PAM) oxidation flow tube reactor (OFR) has emerged to rapid and efficiently simulate generation and transformation of SOA in wide range of oxidation degrees, that is comparable with ambient atmospheric photochemical oxidation from days to weeks (Li et al., 2019, 2015; Simonen et al., 2019; Peng et al., 2016). PAM measures the potential mass loading of SOA that can be produced from oxidation of the precursor gasses. SOA formation and extensively aging that takes hours to days in the atmosphere can be achieved in a few minutes through the PAM-OFR (Lambe et al., 2011).

According to Chu et al. (2016) SOA were mainly generated from local source atmospheric vapors rather than precursors that were transported far away. It was estimated urban-site vehicle exhausts contribute annual 2.9 ± 1.6 Tg SOA globally (Tkacik et al., 2014). Apart from diverse VOC precursors, SOA formation also correlates with photochemical extension. An urban-site study in Los Angeles has shown that the maximum net SOA productions were obtained at OHexp between (1.1–8.0) × 1013 molecule/cm²sec, equivalent to 0.8–6.0 days of ambient OH radical photochemical oxidation, taking ambient average OH radical concentration of 1.5 × 106 molecule/cm³ (Ortega et al., 2016; Mao et al., 2009).

This study investigates SOA formations from ambient VOCs and their subsequent aging via O3 and OH oxidation through the OFR. Diurnal trends of SOA formation potential from ambient air and associated influence of environmental parameters (e.g., ambient VOC, Ozone concentration, OHexp, temperature and humidity) were studied, the results can help predicate the mass concentration and transformation of urban ambient air pollution and SOA formation. Moreover, secondary aerosol formation from direct engine exhausts was also explored with respect to various traffic vehicles of different age, operation, and fuel consumption. The results can be helpful to assess the traffic sourced particle formation and related air pollution, as traffic engine emissions represent the major air pollutants in Lyon. For engine exhaust, the OFRs have been used in several studies (Friedman et al., 2016; Ihalainen et al., 2019; Jathar et al., 2017; Karjalainen et al., 2016), OFR was also used to study of emissions from a vehicle fleet (Liu et al., 2019; Saha et al., 2018; Tkacik et al., 2014).

1. **Experimental methods**

1.1. **Campaign site**

Lyon is the third largest city of France, it located in the southeastern quarter of France at the confluence of the Rhône and the Saône. It holds 1.9 million inhabitants (Eurostat, 2018) with an average population density of 2.9 per km² (Lucie Anzivino and Magali Venzac diagnostic santé environnement des habitants de la Métropole de Lyon, 2018). Lyon has one of the highest cars densities (720 car per thousand inhabitants) and bears large traffic throughput, implying the severe air pollution in the urban area. The campaign was carried out in the National Research Center of France (CNRS) next to the scientific campus of Doua (Lyon, Villeurbanne) during January-February 2017. The sampling site is 9 km from the industrial zone, it could be considered as typical urban environment that is influenced by daily shift traffic and industrial exhaust. A mobile monitoring station equipped with PAM-OFR system was deployed. Detailed location and surrounding environment are presented.
in Fig. S1 in the supporting information (SI). In this study, SOA formation potentials from ambient air and engine emissions via OH radical dominated photochemistry were extensively explored, accounting for their temporal, environment parameter, photochemical oxidation degree dependent characters.

1.2. Setup and experiments

1.2.1. PAM-OFR system
Photochemistry of ambient air was conducted in a Potential aerosol mass (PAM) oxidation flow reactor (OFR). Detailed description and operation of the PAM-OFR can be found elsewhere (Sbai and Farida, 2019; Li et al., 2019; Watne et al., 2018). Briefly, PAM-OFR provides controllable OH radical dominated photochemical environment to oxidize gaseous or/and particles rapidly and efficiently, the results can be compared to ambient photochemical aging of various precursors in compositions from several days to weeks (Kang et al., 2007; Lambe et al., 2011). Our PAM-OFR was equipped with two 254 nm UV lamps that were diagonal mounted against the quartz flow tube, hereby it was called OFR254. The OFR254 (GoPAM 2.0) is different from general Aerodyne OFR, which is made completely of coated aluminum with UV lamps horizontally inserted inside (Lambe et al., 2011). Our OFR254 consists of a vertical high-transmission Quartz cylindrical flow tube (Length: 95.0 cm, ID: 12.4 cm) with effective volume of approximately 11.5 L. The parallel mounted UV lamps (Philips TUV 30 W germ-killing tube, flux at 254 nm ~ 3.46 × 10^{15} photons cm^{-2} s^{-1}) output uniform and steady irradiation at 254 nm. The tube and lamps are sealed in an aluminum box, a powerful fan fixed at the bottom of the box cools the reactor system and removes outgas from the lamps. Two inlets allow introducing of auxiliary air (e.g., N2/air, moisture, external O3, SO2, seed particles, etc.) and precursors (e.g., VOCs, primary organic aerosols, etc.), separately. A teflon-coated static mixer at the input of the flow tube enables uniformly mixing of auxiliary gases and precursors before flowing through the OFR254.

External O3 was supplied using a low-pressure mercury UV lamp (Jelight Co. Inc. Model 610–220) to excite oxygen in high-purity air. Relative humidity in the OFR254 was mediated with a flow of humidified N2. Pristine ambient air without any further treatment was introduced into the flow tube reactor. A total flow of 5.0 LPM (liter per minute) containing 4.0 LPM ambient air streamed through the OFR254, maintaining a steady laminar flow (Reynolds number ‘57’) with a residence time (RT) of approximately 137 sec. The gaseous and particulate inputs and outputs were continuously monitored using some Thermo analyzers (O3, Model 49i; SO2, Model 43i) and a TSI scanning mobility particle sizer (SMPS, Model 3080) in combination of one extra ultrafine condensation particle counter (CPC, Model 3775 low). Additional physical parameters (e.g., RH, pressure, temperature) inside the flow reactor were recorded with specific environmental sensor (Poseidon, Model 64). More relevant atmospheric pollutants, such as general VOCs and NOx with moderate time-resolution (30 min) were referred to the nearby Air Quality Monitoring Stations, and the recorded pollutants are summarized in Table 1.2. The experiment setup and method are schematically graphed in Fig. 1. The OFR254 system was held in a temperature and humidity stable environment, and sampling tubes used were optimized in material (conductive rubber and stainless-steel/copper tubes for particle carrying, Teflon tube for gas flows), length, and connection to minimize wall loss of particles and gasses. Before test, particle loss to the inner wall of sampling tube and flow reactor were assessed to be negligible (Fig. S2).

The OFR254 system was loaded in an mobile air quality monitoring van. The vertical main sampling tube passed through the roof of the van, the distance between the sampling inport and the roof was above 50 cm, and the distance between the inport and the ground was around 3 m.

1.2.2. OH radical exposure parametrization
OH radicals in the OFR254 can be produced through photolysis of external O3 and further reaction of singlet oxygen (O1D) with humidity:

\[
O_3 \xrightarrow{hv} (254 \text{ nm}) \rightarrow O(1D) + O_2
\]  (1)

\[
O(1D) + H_2O \rightarrow 2OH
\]  (2)

The complicated photochemistry in the OFR254 (e.g., OH radical dominated oxidation pathways over O3, H2O, RO2 reactions and photolysis) can be simply characterized and quantitatively as OH exposure (OHexp).

Sensitivity tests confirmed the complex correlation of OHexp with many variables including external total OH reactivity, humidity (water vapor mixing ratio), RT, UV light intensity, and initial O3 or/and static endpoint O3 (Li et al., 2015; Peng et al., 2016). The total external OH reactivity (OHR) can be estimated via equation below:

\[
\text{OHR}_{\text{ext}} = \sum_i ((R_i \times k_i)
\]  (3)

where, \(k_i\) is the reaction kinetic constant for \(R_i\) species in reaction with OH radical, \([R_i]\) is molecular concentra-
the full power. Equations were used to retrieve the operational function for our OFR$_{254}$. It should be noted the UV intensity in the OFR can only be tuned by switching on one or two UV lamps at full power, therefore, $\text{OH}_{\text{exp}}$ was explored over a wide range of input conditions, such as external O$_3$ concentration in range of 0.1–30 ppmv, OHRext in range of 0.1–20, RH in range of 20%–65%, and RT in range of 1.5–4.5 min, otherwise. The $\text{OH}_{\text{exp}}$ estimation functions were retrieved and shown as Equation 4 and 5, corresponding to one and two UV lamps full-power irradiation.

$$\log(\text{OH}_{\text{exp}}) = 1.732 + 0.79292 \times \log(\text{RH}) + 0.023076 \times \log(\text{RH})^2 + 0.978 \times \log(\text{RT}) - \log \left(1 + \exp \left(-\frac{1.22 - \log(\text{RH})}{0.421}\right)\right)$$

(4)

$$\log(\text{OH}_{\text{exp}}) = 1.991 + 0.79292 \times \log(\text{RH}) + 0.023076 \times \log(\text{RH})^2 + 0.978 \times \log(\text{RT}) - \log \left(1 + \exp \left(-\frac{1.22 - \log(\text{RH})}{0.41}\right)\right)$$

(5)

The estimated $\text{OH}_{\text{exp}}$ ($\times 10^{15}$ molecule cm$^{-3}$ s$^{-1}$) fits well with the measured $\text{OH}_{\text{exp}}$ via the decay of SO$_2$, details referring to SI text and Fig. S3. $\text{OH}_{\text{exp}}$ can be converted to equivalent days of OH radical initiated atmospheric aging by dividing a 24 hr average ambient OH concentration of $1.5 \times 10^6$ molecule/cm$^3$. However, in air polluted urban area average OH radical can be much higher (Carpenter, 2010; Liu et al., 2018). $\text{OH}_{\text{exp}}$ in this experiment was stepped over a wide range by adjusting light intensity and also external ozone concentration.

### 2. Results and discussion

#### 2.1. Background

Diel variations of gaseous and particulate pollutants at the sampling site were collected from all four nearby urban stations (distribution shown in Fig. S1, SI). These four air quality monitoring stations could clearly describe the air pollutions and meteorological conditions of the sampling site (Table 1). Daily average concentrations for the pollutants and meteorological parameters are summarized and presented in Table 2. It is clear that ambient PM$_{10}$, PM$_{2.5}$, NO and NO$_2$ at Lyon all exceed the European Limit Values, which should be within 40, 25, 30 and 40 $\mu$g/m$^3$ on yearly

### Table 1 – Background information and data taken referring to the nearby monitoring stations.

<table>
<thead>
<tr>
<th>Station</th>
<th>Station type</th>
<th>Distance from sampling site (km)</th>
<th>Data</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Villeurbanne place</td>
<td>Urban Traffic</td>
<td>2.34</td>
<td>PM$_{10}$, NO and NO$_2$</td>
<td>45°46’00&quot; North, 4°52’49&quot; East 198 m.a.s.l.</td>
</tr>
<tr>
<td>Grandclément</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Est lyonnais / Vaux en Velin</td>
<td>Urban Traffic</td>
<td>2.71</td>
<td>PM$_{2.5}$ and O$_3$</td>
<td>45°46’36&quot; North, 4°55’07&quot; East 179 m.a.s.l.</td>
</tr>
<tr>
<td>Sud lyonnais / Feyzin Zi</td>
<td>Urban Traffic</td>
<td>8.60</td>
<td>VOCs and SO$_2$</td>
<td>45°40’25” North, 4°51’34” East 204 m.a.s.l.</td>
</tr>
<tr>
<td>Lyon Bron</td>
<td>Weather station</td>
<td>5.93</td>
<td>Solar radiation and Wind speed</td>
<td>45°43’49’ North, 4°56’19’ East 201 m.a.s.l.</td>
</tr>
</tbody>
</table>

Busiest traffic time is 8:00–9:00 AM and 6:00 PM, which is obtained from the TomTom© Traffic Index (https://www.tomtom.com/en_gb/trafficindex).

### Table 2 – Summary of general conditions and average results of pollutant concentrations and weather variables in the study period.

<table>
<thead>
<tr>
<th>Experiment type</th>
<th>O$_3$ (μg/m$^3$)</th>
<th>NO (μg/m)</th>
<th>NO$_2$ (μg/m$^3$)</th>
<th>Ambient VOCs (μg/m$^3$)</th>
<th>SO$_2$ (μg/m$^3$)</th>
<th>OHR (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient air (morning,14 February)</td>
<td>31</td>
<td>43</td>
<td>37</td>
<td>400</td>
<td>2.0</td>
<td>16</td>
</tr>
<tr>
<td>Ambient air (afternoon,14 February)</td>
<td>7.3</td>
<td>56.5</td>
<td>46.5</td>
<td>1600</td>
<td>2.7</td>
<td>52</td>
</tr>
<tr>
<td>Ambient air (noon; 14 February)</td>
<td>13.3</td>
<td>78.7</td>
<td>75.5</td>
<td>100</td>
<td>1.5</td>
<td>07</td>
</tr>
<tr>
<td>Electricity generator (at noon)</td>
<td>18.6</td>
<td>128</td>
<td>80.3</td>
<td>NA</td>
<td>10.0</td>
<td>NA</td>
</tr>
<tr>
<td>Traffic exhaust (afternoon)</td>
<td>72.7</td>
<td>37.5</td>
<td>58.0</td>
<td>NA</td>
<td>0.0</td>
<td>NA</td>
</tr>
<tr>
<td>LD vehicle (afternoon)</td>
<td>29.2</td>
<td>190.5</td>
<td>110.0</td>
<td>NA</td>
<td>37.0</td>
<td>NA</td>
</tr>
<tr>
<td>Motorbike (at noon)</td>
<td>60.0</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>2.0</td>
<td>NA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experiment type</th>
<th>PM$_{10}$ (μg/m$^3$)</th>
<th>PM$_{2.5}$ (μg/m$^3$)</th>
<th>Wind speed (km/hr)</th>
<th>Solar radiation (W/m$^2$)</th>
<th>Temperature (°C)</th>
<th>Relative humidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient air (morning)</td>
<td>48.0</td>
<td>36.6</td>
<td>3.6</td>
<td>367</td>
<td>13</td>
<td>55</td>
</tr>
<tr>
<td>Ambient air (afternoon)</td>
<td>42.5</td>
<td>35.6</td>
<td>3.6</td>
<td>161</td>
<td>17</td>
<td>45</td>
</tr>
<tr>
<td>Ambient air (noon)</td>
<td>56.3</td>
<td>33.0</td>
<td>10.8</td>
<td>30</td>
<td>20</td>
<td>37</td>
</tr>
<tr>
<td>Electricity generator (at noon)</td>
<td>58.7</td>
<td>30.1</td>
<td>3.6</td>
<td>NA</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Traffic exhaust (afternoon)</td>
<td>49.0</td>
<td>8.3</td>
<td>14.4</td>
<td>NA</td>
<td>18</td>
<td>38</td>
</tr>
<tr>
<td>LD vehicle (afternoon)</td>
<td>65.5</td>
<td>29.7</td>
<td>7.2</td>
<td>225</td>
<td>18</td>
<td>40</td>
</tr>
<tr>
<td>Motorbike (at noon)</td>
<td>65.0</td>
<td>20.6</td>
<td>3.6</td>
<td>33</td>
<td>18</td>
<td>40</td>
</tr>
</tbody>
</table>

Note: NA means not available.
average, respectively (https://ec.europa.eu/environment/air/quality/standards.htm). The relative high NOx concentration indicates traffic exhaust should be the primary air pollution source. While, daily O3 and SO2 were below the European Limit Values of 120 and 20 μg/m3, respectively (https://ec.europa.eu/environment/air/quality/standards.htm).

VOCs were characterized based on chemical natures as alkane, alkene, and aromatic compounds. Their contributions in urban air of Lyon were pie-chart displayed in Fig. S4. Meanwhile, the diurnal distributions of total VOCs during experiment period are presented in Fig. S5. Daily average concentrations of the major VOC species are collected in Table S1. Among the atmospheric organic vapors in Lyon, alkanes and alkenes contribute the dominant air pollutants. Daily average VOCs consist of 74.5% alkanes and 25.5% alkenes, while aromatic compounds make up about 2% of the VOCs. Of the detected aromatic compounds, BTEX (benzene, toluene, ethylbenzene and xylene) and trimethylbenzene are the main pollutants. In short, 25% of the detected urban VOCs in Lyon have at least one C=C double bond, implying their high reactivity towards oxidants like O3 and OH radicals. The precursor chemical structure orientated reactions have recently been studied in SOA formation by Chippini et al. (2019) they found the addition of ozone on the double bond (C= C) produces functionalized Criegee Intermediate (CI) with high volatility, while OH radicals attacking the unsaturated carbon bond following O3 addition produce peroxyalkyl radical (RO2•), then abundant RO2 radicals involve in a series of intramolecular and intermolecular reactions with O3, OH and HO2 radicals to produce oxygenated organic compounds with multifunctional groups and low volatility. These highly oxygenated multifunctionalized organic productions contribute to the formation and growth of SOA (Jokinen et al., 2015; Mentel et al., 2015; Molteni et al., 2019).

The VOCs present a clear and regular diurnal distribution pattern that increase sharply in the morning of working day and then gets a rapid decrease till noon. The mass loading of total detected VOCs increases from traceable amount to approximately 1.7 × 10^3 μg/m^3 at around 10:00 AM, exceeding the European Limit Values of 300 μg/m^3 greatly (Bearg, 1993) in morning and afternoon. This pattern overlaps well with morning rush in Lyon, specifically one-way traffic activity, indicating that traffic is an important source of the VOCs in the study area. Moreover, these traffic released VOCs (e.g., alkane, aromatic compounds) have high potential to produce secondary organic aerosol, thereby, influencing regional air quality and public health.

2.2. Diurnal variation of soa formation from photochemical oxidation of ambient air

The operation parameters and proper OHexp estimated based on ambient period-average OHR and humidity are summarized and compared in Table 2. Fig. 2 shows temporal trend of SOA formation from ambient air throughout the entire day on February 14, 2017. Three periods corresponding to different oxidation conditions were classified as P1, P2, and P3, respectively (Table 3). At each period, the initial O3 supply, 254 nm light irradiance, and residence time in the PAM were fixed with the only changes of ambient air composition. The result can depict daily character of secondary particle formation potency in urban area.

In Period 1, average total OHRex, including reactivity of NOx, SO2, and VOCs, was 28.3 ± 5. 1 sec^-1. However, OHRex attributed to VOCs was only 3.5 ± 1. 7 sec^-1, and SO2 contribution to the OHR can be neglected due to the ultra low concentration of SO2. Thus, OHexp in the OFR254 during this period was estimated to be approximately (6.9–8.9) × 10^11 molecule/(cm^3·sec), that is equivalent to 57 days of atmospheric photochemical exposure. Remarkable photochemistry occurred to the ambient urban air in the OFR, resulting in significant secondary particle formation. Considering the neglected SO2 mixing ratio and partition of nitric acid production (NOx in reaction with OH radicals) in the gas phase, the generated secondary particles should comprise dominant organic composition. At fixed UV radiation and external O3 supply in the OFR, secondary organic particle formation presented a specific pattern with more formations in the morning (before 11:30 am) and afternoon (after 15:00 pm), maximum mass concentration for the secondary aerosol was up to over 36 μg/m^3 (Fig. 2).

The continuous decrease in mass concentration after 11:00 can be explained by the decrease in RH in the OFR, the high humidity in the morning facilitated OH radical formation and enhanced VOCs oxidation. Fig. 2 displays a correlation between the SOA mass concentration and the RH since they follow the same trend by decreasing in parallel, indicating that RH accelerates the attenuation of SOA particles, this can be explained by the decrease of the adsorption of water molecules on the surface of particles. Thus the decrease in RH leads to a decrease in particle size (He et al., 2019). The adsorption of the water molecules on the hydrophilic functional groups in particle phase decreases with RH and therefore the SOA mass concentration (Yu et al., 2018), water vapor can initiate particulate coagulation and facilitated gas-particle transformation (Li et al., 2015). This suggests that the decrease in mass concentration is due to the decrease in RH (Fig. 2). In addition, the gas/particle partitioning of VOC is strongly dependent on RH, because RH enhance the coagulation and uptake of trace gases.

The diurnal pattern echoed to traffic rush hour, and also variation solar radiation. In the morning and later afternoon, traffic rush time produced much VOCs and NOx precursors (Fig. S5 and Table 2), moreover, the high humidity in the morning facilitated OH radical formation and enhanced VOCs oxidation. At noon and early afternoon, the strong solar radiation enhanced oxidation capacity of outdoor surface air, thus consuming more ambient VOCs and promoting gas to particle transformation, which can partly explain less particle formation in OFR254 from 11:30 am ’14:30 pm (Fig. 2, P1). Though secondary particle formation varied with time and air compositions, the geometric mean diameter (GMD) for the newly generated particles kept constant at around 25 nm, demonstrating the ultrafine or Aitken mode dominated the particle distribution.

The volatility of VOCs increases with temperature (Seinfeld et al., 2001). In the experiment, we noticed that there was an increase in temperature from around 10 °C in the morning to 25 °C in the afternoon), which could influence the partition of VOCs between the gas and particulate
Fig. 2 – Exemplary plot of SOA formation from ambient air in term of particle size distribution, number and mass concentration as a function of time and OHexp throughout the day. Diurnal temperature and humidity were also presented (February 14, 2017).

Table 3 – Oxidation conditions of the periods of the experiment shown in the Fig. 2.

<table>
<thead>
<tr>
<th>Period</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3 (ppmv)</td>
<td>2.6</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>254 nm photon flux (photons/cm²·sec)</td>
<td>$7.0 \times 10^{15}$</td>
<td>$3.5 \times 10^{15}$</td>
<td>$3.5 \times 10^{15}$</td>
</tr>
<tr>
<td>OHexp (10¹¹ molecule/cm³·sec)</td>
<td>6.9–8.9 a</td>
<td>5.2</td>
<td>3.9</td>
</tr>
<tr>
<td>Age Equivalent (Days)</td>
<td>5.3–7.0 a</td>
<td>4.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Note: The photon flux was cited from the manual of the Philip UV lamp that operates at full power for each lamp. OHexp was estimated using Eq. (4) and (5).

a maximum and minimum value.

phase and lead to an increase in the content of VOCs in the gaseous phase. Thus contributing to a loss of mass in the particulate phase, which may partly explain the decrease in mass concentration (Fig. 2). The effect of temperature on SOA formation was studied in a simulation chamber using anthropogenic VOCs (toluene, m-xylene, 1,2,4-trimethylbenzene) and biogenic VOCs ($\alpha$-pinene, $\beta$-pinene) (Takekawa et al., 2003), they concluded that the SOA yield is affected by the increase in temperature since the yield was doubled when the temperature increased from 283 K to 303 K. In addition, the increase in temperature leads to the evaporation of the low volatility species condensed on the surface of the particles which leads to a significant loss in SOA mass.

After 16:00 pm, ambient air conditions, such as humidity, temperature, ozone, OHexp and VOC, kept constant till the end of the field investigation by 19:30 pm. It was clear that secondary particle formation decreased with decreasing of OHexp in Period 2 and 3. Several studies have reported the relationship between SOA formation and OHexp in use of OFR (palm et al., 2016; Ortega et al., 2016; Liu et al., 2018). Commonly, before the critical OHexp, SOA formation was in line with the increase of photochemical oxidation. Yet, when OHexp was beyond the critical value, SOA formation decreased with increasing of OHexp. To better understand the SOA formation trend in Lyon, photochemistry to the urban air was conducted under large OHexp levels.

2.3. SOA formation as a function of OHexp

SOA formation potency with subtle atmospheric photochemical aging (OHexp) was explored in the late afternoon (after 16:00 pm) on February 18th, when the VOC mass is rela-
tively stable (Fig. S5). OHexp in the OFR was conditioned in the range of \((0.9–12.5) \times 10^{11}\) molecule/(cm\(^3\)·sec), corresponding to equivalent 0.7–9.7 days of field photochemical oxidation. Particle measurement in each oxidation condition last for around 20 mins. Mass concentrations of the SOA as a function of OHexp were presented in Fig. 3A, and the results were also compared with that in Beijing and Los Angeles. We found similar trends for SOA formation with OHexp for all these traced three studies in different cities whereas SOA formation from pristine urban air was higher nearly at all OHexp level in Lyon. Since VOC concentrations in Beijing were almost twice as high as in Lyon, the difference in SOA mass can be justified by several parameters such as the nature of VOCs precursors, NO\(_x\) and SO\(_2\) mixing ratios because the high mixing ratios of NO\(_x\) and SO\(_2\) competitively consumed OH radical and also participated in SOA formation, high external O\(_3\) mixing ratios was applied to achieve similar OHexp than the other study, which can significantly contribute to the SOA formation via O\(_3\) oxidation and leading to different oxidation pathways and ratios between OH radical reactions to O\(_3\) oxidation, UV irradiance, SOA mass analysis method because Liu et al. (2018) calculated the SOA mass using an aerosol mass spectrometer (AMS), the difference in PAM chamber design-operation (Go-PAM vs. Aerodyne PAM) and OHexp estimation should also be considered because OHexp in Liu et al. (2018) was monitored directly from decay of specific VOC species using Proton-Transfer-Reaction Mass Spectrometry (PTR-MS), the result should be more practical and precise than the OHexp estimation via empirical function in this study. Low SOA mass concentration found at Los Angeles (Ortega et al., 2016), was attributed to relative low VOC concentrations.

The critical value of OHexp was found in the range of \((5.0–7.4) \times 10^{11}\) molecule/(cm\(^3\)·sec) for all the traffic emission sourced SOA formation, below the critical value, SOA formation via functionalization and subsequent gas-particle transformation of precursors was enhanced at OHexp between \((0.5–4.0) \times 10^{11}\) molecule/(cm\(^3\)·sec), however with the increase OHexp level, fragmentation becomes more important and leads to the production of high volatility species, leading to the decrease in the SOA mass (Fig. 3A). Fig. 3B compared the POA distribution and the SOA distribution formed via O\(_3\)/OH oxidation. Particle number size distribution (PNSD) for SOA formed by ozonolysis was of bimodal mode with two peaks at 100 nm and within 20 nm. However, SOA formed by OH oxidation was of unimodal mode with a peak around 30 nm, in addition the OH oxidation shifted the particle to smaller size (aiken mode) by generating abundant ultrafine particles.

2.4. SOA formation from various engine emissions

Aforementioned study demonstrated transportation related and industrial sourced air pollutants exhibited high SOA formation potency via OH radical dominated photochemistry in Lyon, and the association between the SOA formation of urban air and OHexp was also confirmed. To tell exact photochemical results of traffic exhaust and acquire the knowledge of potential impact of transportation on air quality, the OFR system directly sampled traffic exhaust at the entrance of the underground parking and also oxidized individual vehi-
Particle emissions. In Lyon, car and motorcycle are tow main kinds of traffic vehicle. Here, we recruited two representative gasoline cars and one motorcycle. Two cars were of same brand but different ages, one was new model Renault car (Euro 5), the other was over 15-year old car (Euro 4). To simulate vehicle emissions in a manner sensitive to roadway traffic conditions, low-duty idling and high-duty operation of these vehicles were tested with exhaust pipe directing to the mobile air quality monitoring van (OFR254 system), the distance between the OFR254 and the tested vehicle was within 2 m. Moreover, emission from a diesel fueled electricity generator (500 KW) was also tested to represent industry related pollution. The electricity generator next to the van (3 m away) was operated in full power output for several hours. OHexp trace by SO2 decay in the OFR254 was mediated by changing external O3 supply or UV light strength, the final OHexp was set at approximately 7.0 \times 10^{11} \text{ molecule cm}^{-3} \text{ s} for all photochemical oxidation tests, under which the maximum SOA formation should be expected according to the above study and results in literature (Liu et al., 2018; Palm et al., 2016). According to previous research, the maximum SOA formation from vehicle exhaust is typically between OHexp approximately equivalent to 3 days and one week of photochemical aging in the atmosphere (Suarez-Bertoa et al., 2015; Nordin et al., 2013; Karjalainen et al., 2016).

Particle Number Size Distributions (PNSD) were measured in the upstream and downstream of the OFR254, representing the fresh and photochemical aged engine emissions. Some of the results are presented in Fig. 4 and compared in Table 4. We noticed that OH-oxidation shifted the PNSD to smaller size whatever the source of precursors in the OFR254. Aged PNSD were dominated by nucleation mode in any case, showing also high nanoparticles (diameter between 10 and 40 nm) formation. The same aged PNSD was found by Simonen et al. (2019) for the port fuel injection (PFI), a gasoline vehicle equipped with direct injection (GDI).

Vehicle exhausts contribute to PM mass in the atmosphere, not only by their direct emissions but, more significantly by photochemical reactions and gas-to-particle conversion of volatile species (Arnold et al., 2012; Rönkkö et al., 2013; Pirjola et al., 2015). The Geometric Mean Diameter (GMD), mass and number concentration for nucleation and accumulation mode designed for fresh and oxidized particles has been shown for various engine emissions (Table 4). Bimodal size distribution (peaks at 35 and 88 nm, GMD at 54.7 nm) with a much higher contribution of the accumulation mode than the nucleation for primary particle emission from Traffic exhaust (Fig. 4A) and Euro 4 & 5 vehicle exhaust (Fig. 4B). Regarding the fresh and oxidized PNSD for Euro 4 & 5, we show that Euro 4 vehicle produced more fresh and oxidized particle than Euro 5 vehicle (Fig. 4B), the bimodal distribution of secondary aerosols has also been observed during other study (Gu et al., 2011; Kasumba et al., 2009; Squizzato et al., 2019). Massive ultrafine particles were generated from electricity generator emission in the OFR to increase the Aitken mode by more than 10 times in mass and almost two orders magnitude higher in number concentration (Table 4). The formation of SOA from vehicle exhaust exceeds the SOA produced by ambient air by about 2 to 3 times. The high SOA formation from vehicle exhaust has been reported in several researches (Pieber et al., 2018; Karjalainen et al., 2016). The number and mass concentration of SOA formation via vehicle exhaust in the OFR seems to depend strongly on fuel type (diesel or gasoline), speed and engine technologies (Karjalainen et al., 2016).

Gasoline Direct Injection (GDI) vehicles (Euro4) produce more particles than Port Fuel Injection (PFI) vehicles (Euro5) (Chen et al., 2017; Zhu et al., 2016). However, Simonen et al. (2019) found the opposite, this disagreement has been attributed to the measurement technique, since their study was carried out under real driving conditions on a road. In addition, they measured all particles with a diameter greater than 3 nm, while this study was conducted for particles with a diameter greater than 14 nm. Saliba et al. (2017) have found the accumulation mode higher for the GDI against the nucleation mode is higher for PFI. The differences in SOA production between Old and New vehicle (Euro 4 & 5) cannot comes from the different injection technologies of fuel, because Zhao et al. (2018) have tested sev-
Fig. 4 - Particle number size distributions (PNSD) pattern for fresh and OH radical photochemical oxidized aerosols through OFR$_{254}$: (a) Traffic exhaust from the underground parking, (b) gasoline vehicle exhaust from two car with different ages, only low-duty idling results were displayed (c) motorcycle exhaust and (d) Diesel fueled electricity generator emission.
eral exhaust vehicles in the OFR and they showed no difference in SOA particle formation for PFI and GDI vehicles. Several research on exhaust vehicle SOA production and aging report SOA formation only for cold-start driving cycles (Simonen et al., 2019; Timonen et al., 2017), these authors have shown that fuel types had minor effects on the SOA formation while the lubricant represents an important source of SOA precursors that can be formed during the combustion process. According to Timonen et al. (2017) aromatic compounds content of fuel represent the main source of SOA formation from gasoline GDI.

Mass and number OA enhancement for aitken and accumulation mode particle from air ambient show a difference between afternoon, morning and noon. High solar radiation during morning and afternoon can contribute to ambient photochemistry and photonucleation. OA enhancement is maximum during morning this explained by the high VOC emission from road traffic. Mass and number OA enhancement are high for the aitken mode compared with accumulation mode regardless of particle source, indicating that accumulation mode particle formation is negligible in the OFR. Mass and number OA enhancement for HD Motorbike were highest, almost 9 times higher than the ambient air, which shows that HD Motorbike produces more VOC than other sources (Table 4).

We did not observe significant difference for the fresh emissions for motorcycle with respect to low-duty or high-duty driving from Fig. 4C, but the photochemical aged emission was much higher than that at low-duty idling. It could be deduced that motorcycle high-duty operation consumed more gasoline rapidly, thus more VOC precursors would generated even if particle emission dose not change much. Motorcycle engine emission had the highest potency in secondary aerosol formation. Particle mass enhanced by about 18 and 37 times in the Aitken mode for low-duty idling and high-duty operation, respectively, in photochemistry. Meantime, the particle number increased much more.

The fresh particle emissions from the diesel fuel electricity generator had high variation in unimodal distribution pattern (Fig. 4D). Its emission was much higher than those from traffic engine. Photochemical oxidation increased the particle mass concentration by about 15 times in Aitken mode and almost 2 times in the accumulation mode (Table 4).

3. Conclusions

We present in this study the formation of SOA from oxidation of ambient air using a GoPAM-OFR, in an urban area in Lyon for the first time to our knowledge. The measurements were carried out during January-February 2017. SOA formation was measured continuously and documented as a function of OHexp and photochemical atmospheric age equivalent. We found that SOA distribution in term of both number and mass concentration mainly depend on oxidation levels of the ambient VOC concentration. We noticed that the SOA mass concentration increases with OHexp between 2.3 × 10^{11} and 7.4 × 10^{11} molecule/(cm^3·sec), then it decreases, because at high OHexp the fragmentation leads to the formation of incondensable species of low molar mass and high volatility. The maximum SOA mass was obtained at OHexp between 4.0 × 10^{11} and 7.4 × 10^{11} molecule/(cm^3·sec). The SOA mass is higher than similar urban environments in countries like China (Beijing) and USA (Los Angeles) under the same level of OHexp. Moreover, secondary aerosol formation potency from practical traffic exhaust and emissions of representative individual vehicles with different age and operating mode were investigated in atmospheric photochemistry. The results confirm the high particle formation potency from transpiration related pollutants and associated influence on air quality in their atmospheric transformation.

4. Data availability

Data are available by contacting the corresponding author, the data for the pollutant measurement stations have been downloaded via the site Atmo Auvergne-Rhône-Alpes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this pape.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version.

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