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1 **Real-time assessment of wintertime organic aerosol characteristics and sources**
2 **at a suburban site in northern France**

3
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11

ABSTRACT

A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was deployed during wintertime (5 February to 15 March 2016) at a suburban site in Douai, northern France, in order to investigate the characteristics and sources of the organic matter (OM). The campaign average concentration of non-refractory submicron particulate matter (NR-PM₁) was $11.1 \pm 9.3 \mu\text{g m}^{-3}$, and composed of 38% OM, 36% nitrate, 16% ammonium and 9% sulfate. The average values for the OM:OC, O:C and H:C ratios were 1.60 ± 0.15 , 0.32 ± 0.11 and 1.55 ± 0.14 , respectively, indicating a moderate level of aerosol oxidation. The positive matrix factorization (PMF) source apportionment method was applied to the high-resolution organic aerosol (OA) mass spectra, resulting in four factors: a hydrocarbon-like (HOA) factor; one associated with oxidized biomass burning (oBBOA); and two oxygenated factors (OOA) denoted as less oxidized (LO-OOA) and more oxidized (MO-OOA), with average contributions to OA of 20%, 28%, 17% and 35%, respectively. The oBBOA factor was found to be mainly local as shown by non-parametric wind regression (NWR) analysis, and to correlate well with relative humidity (RH), suggesting fast aqueous processing of locally emitted primary biomass burning emissions. During most part of the campaign, the sampling site was affected by different air masses. However, during the last period of the campaign (5-16 March 2016) the site was heavily impacted by air masses from Eastern Europe which were rich in secondary inorganic and organic aerosols. The H:C versus O:C (Van Krevelen, VK) diagram highlighted that the aerosol followed an oxidation process throughout the whole campaign, with an average slope of -1.05. The impact of continental air masses towards the end of the campaign confined the aerosol towards a narrower space in the VK diagram, suggesting a homogenization of the different aerosol sources due to OA ageing during transport. Several nocturnal NPF (new particle formation)-like events were observed and associated to the fast processing of BBOA emissions and the formation of ammonium nitrate.

Keywords: AMS; organic aerosols; source apportionment; aqueous processing

1. Introduction

Atmospheric aerosols have gained attention worldwide due to their various impacts on human health (Kelly and Fussell, 2012), climate, visibility and ecosystems (Hallquist et al., 2009; IPCC, 2013; Watson, 2002). In the year 2016 only, air pollution was responsible for 7 million deaths worldwide (WHO, 2018), mostly due to inhalation of fine particulate matter (PM_{2.5}). In Europe, the premature mortality associated to air pollution is also alarmingly high, with estimations for the year 2016 ranging from 208,000 to 348,000 for high-income and low- to middle-income countries, respectively (WHO, 2018). The region of northern France is also affected by high levels of PM_{2.5}, particularly during winter and spring (Atmo Nord-Pas-de-Calais, 2014). These high levels are mainly attributed to its location amidst various emission source areas including an extensive highway network, a high urban density, and the proximity to several European capitals (London, Paris, and Brussels) as well as a significant influence of industry and agriculture.

While the elemental and inorganic fractions of ambient aerosols are rather well understood, the characterization of the organic matter (OM) still remains a challenge due to their complex nature, associated to numerous emission sources and atmospheric transformations (Hallquist et al., 2009; Jimenez et al., 2009). OM can represent from 20 to 90% of the total submicron aerosol (PM₁) mass (Jimenez et al., 2009), and hence understanding its sources and transformation processes is essential in order to develop effective mitigation policies. OM, also called organic aerosol (OA), is typically divided into primary (POA) and secondary organic aerosols (SOA). POA are directly emitted to the atmosphere by a variety of sources comprising anthropogenic ones such as traffic, industrial activities, and residential biomass combustion; and natural ones like sea spray, volcanic emissions, forest fires, etc. (Hallquist et al., 2009; Mohr et al., 2009). SOA are formed in the atmosphere through several physicochemical processes of gas phase VOCs (volatile organic compounds) or POA (Kanakidou et al., 2005).

Different techniques have been developed in the past decades to analyze the nature and composition of OA. Most of these techniques work in offline mode; post analysis of the collected samples. These techniques can provide more exhaustive information on the nature and characteristics of individual organic species, but they require large amounts of samples which generally result in a low time resolution (of several hours). Since most of the atmospheric reactions occur at a time scale of few tens of minutes, these offline techniques often fail to elucidate the underlying atmospheric processes (Hallquist et al., 2009). On the contrary, online techniques provide less exhaustive information on individual chemical species but can characterize bulk OA with a very high time resolution (of seconds to minutes). Among the available online techniques, aerosol mass spectrometry (AMS) has become quite popular, since it allows the measurement of the chemical composition and mass loading as a function of the particle size in the submicron range (Canagaratna et al., 2007).

Besides, the combination of AMS data with source apportionment techniques, mainly positive matrix factorization (PMF) and multi-linear engine (ME-2), has allowed for the study of the OA sources and characteristics (Ulbrich et al., 2009). Several AMS-PMF studies have shown

81 that OA can typically be separated into secondary or oxygenated OA (OOA), and several primary
82 OA types like hydrocarbon-like OA (HOA), biomass burning OA (BBOA) and cooking OA
83 (COA), depending on the site location and sampling season (Bozzetti et al., 2017; Crippa et al.,
84 2014; Florou et al., 2017; Lanz et al., 2010; Mohr et al., 2012; Poulain et al., 2011; Saarikoski et
85 al., 2012; Timonen et al., 2013). In France, a few studies have focused on the OA sources and
86 characteristics using real-time measurements in Paris (Crippa et al., 2013), Marseille (Bozzetti et
87 al., 2017), and in the north of France in Douai and Dunkirk which showed that winter OA was
88 moderately oxidized and mostly composed of OOA, while significant contributions of BBOA,
89 HOA and sulfur-containing OA (SCOA) were also found (Crenn et al., 2017a, 2017b).

90 In this context, this intensive campaign using a high-resolution time-of-flight aerosol
91 mass spectrometer (HR-ToF-AMS) and carried out in winter 2016 at a suburban site in Douai
92 was deployed with the aim of complementing ongoing long-term measurements with a Monitor
93 for Gases and AeRosols in ambient Air (MARGA) and other collocated instrumentation which
94 focused on the source apportionment of the PM_{2.5} inorganic aerosol with an hourly resolution
95 (Roig Rodelas et al., in press). This work focuses on the characterization of the chemical
96 composition of NR-PM₁ and of the sources of OA obtained by PMF analysis during winter in
97 Douai. In addition, the influence of meteorological characteristics and long-range transport on the
98 characteristics of NR-PM₁ is also evaluated.

99

100 **2. Materials and methods**

101

102 **2.1. Measurement site**

103

104 Observations of the chemical composition of atmospheric aerosols were carried out from
105 5 February to 16 March 2016 in Douai, northern France, at a suburban location outside the city
106 center (Figure S1) which is considered as representative of the background pollution of the area
107 (50°23'03''N, 3°05'08''E, and 20 m above sea level). The city of Douai is located in a fairly flat
108 land and is close (about 25-30 km south) to the European Metropolis of Lille. Lille is the second
109 most densely populated metropolis in France, after that of Paris, with about 1.2 million
110 inhabitants and a population density of 1,832 inhab. km⁻². The climate in northern France is
111 classified as temperate oceanic, characterized by low seasonal thermal amplitudes, and regular
112 precipitations along the year, with no dry season.

113

114 **2.2. Instrumentation**

115

116 The high resolution-time of flight-aerosol mass spectrometer (HR-ToF-AMS) (Aerodyne
117 Research, USA), hereafter named AMS, was deployed in order to measure in real-time the
118 chemical composition and concentrations of the non-refractory PM₁ (NR-PM₁) (DeCarlo et al.,
119 2006). The major species composing NR-PM₁ include NO₃, NH₄, SO₄, Cl and organic aerosols
120 (OA). Due to the principle of AMS data analysis, the non-refractory species are vaporized and
121 ionized by electron impact (70 eV). Hence, the names of these species as used throughout this

122 article (i.e. without charges) correspond to the sum of all the m/z fragments related to one given
123 species in the fragmentation table (Allan et al., 2004). The AMS operates in two modes according
124 to the trajectory of the ions: the low resolution but highly sensitive V mode and the high
125 resolution but less sensitive W mode. In this study, the time resolution of the AMS was set to 5
126 minutes, with 3 minutes for mode V and 2 minutes for mode W. Only the results for the V mode
127 are shown, since the lower sensitivity of the W mode delivered a too low signal-to-noise ratio
128 during most of the campaign.

129 The mass concentration measurement accuracy of AMS depends on collection efficiency
130 (CE) and ionization efficiency (IE) values. The CE considers the effects of incomplete focusing
131 of the particle beam and bouncing of some particles from the vaporizer (Drewnick et al., 2005).
132 Typically, a default CE value of 0.5 is used (Middlebrook et al., 2012). However, it has been
133 shown that the CE is dependent on particle phase, which is influenced by the relative humidity in
134 the sampling line above 80%, the acidity/neutralization of the sulfate, ammonium nitrate, and
135 organic content (Middlebrook et al., 2012). In this work a Nafion dryer was used in order to
136 reduce the relative humidity in the sampling line. In addition, a composition dependent CE
137 (CDCE), which recalculates the concentrations of all the chemical species by taking into account
138 the NO₃ fraction of the aerosol, was applied to the AMS data as proposed previously by
139 Middlebrook et al. (2012).

140 The IE is defined as the ratio between the number of ions detected and the molecules of
141 the parent species (Jimenez, 2003), and is species specific. Its value is determined through
142 calibrations. However, since it is not practical to perform individual calibrations for all
143 compounds in ambient aerosol, a reference calibration is typically performed for nitrate, and the
144 relative IE (RIE) of every species is obtained relative to that of nitrate (Alfarra et al., 2004). We
145 carried out calibrations every two weeks in order to determine IE(NO₃⁻) and RIE(NH₄⁺) using
146 aqueous solutions of 10⁻² mol L⁻¹ NH₄NO₃ (Sigma Aldrich, 99.0%). NH₄NO₃ particles were
147 generated by an atomizer (TSI 3076) and then dried by passing through a silica gel drier (TSI
148 3062). A dilution system composed of a set of valves and a HEPA (High Efficiency Particle Air)
149 filter was used in order to vary the particle concentration. In addition, an electrostatic classifier
150 (TSI 3080) and a differential mobility analyzer (TSI 3081) allowed selecting the particles with an
151 electrical mobility diameter of 300 nm. Finally, the particles entered simultaneously a
152 condensation particle counter (TSI, 3788) and the AMS. Additional calibrations were carried out
153 using aqueous solutions of 10⁻² mol L⁻¹ of (NH₄)₂SO₄ (Sigma Aldrich, 99.0%) and NH₄Cl (Sigma
154 Aldrich, 99.5%) in order to determine the RIE for SO₄ and Cl, respectively. The RIE values were
155 determined to be 4.0, 1.1 and 1.6 for NH₄, SO₄ and Cl, respectively.

156 The processing of the AMS unit mass resolution (UMR) and high resolution (HR) data
157 has been carried out by using the modules SQUIRREL (SeQUential Igor data RetRiEvaL,
158 version 1.60E) and PIKA (Peak Integration by Key Analysis, version 1.20E), respectively (D.
159 Sueper, University of Colorado-Boulder, Boulder, CO, USA) for Igor Pro v. 6.37 (Wavemetrics,
160 Inc. Portland, OR, USA).

161 A scanning mobility particle sizer SMPS Model 3936 (TSI) was also deployed in order to
162 obtain the particle number size distribution (PNSD) between 10 and 1083 nm every 7 min.

163 Additionally, several other instruments were used as part of a longer campaign (Roig
164 Rodelas et al., in press), whose data are used for comparison purposes and as external tracers to
165 validate the PMF identified factors. These included a MARGA 1S (Metrohm Applikon B.V,
166 Netherlands) (ten Brink et al., 2007) for the measurement of water-soluble ions (NO_3^- , SO_4^{2-} ,
167 NH_4^+ , K^+) and precursor gases (HONO) with an hourly resolution, a double-
168 wavelengthaethalometer AE42 (Magee Scientific, USA) for black carbon (BC) and Delta-C with
169 a 5-min time resolution, a chemiluminescence analyzer NOx 2000G (Seres environment, France)
170 for nitrogen oxides every 15 minutes and a BAM-1020 (Met One Instruments, USA) for the
171 $\text{PM}_{2.5}$ total mass concentration every hour. The Delta-C variable was determined as the difference
172 of light absorption between 370 and 880 nm, and represents the enhanced optical absorption of
173 some specific OA compounds (Allen et al., 2004). It has previously been found to correlate with
174 wood-burning markers such as levoglucosan and K^+ and therefore might be used as a tracer of
175 wood combustion (Allen et al., 2004; Wang et al., 2012). Meteorological parameters including
176 temperature, relative humidity (RH), and pressure were acquired from a BAM-1020 and a
177 TEOM-FDMS. The wind speed and direction, and precipitation were monitored on site with an
178 anemometer. The mixing layer height (MLH) was obtained from the GDAS meteorological data
179 (1 degree) on the NOAA website.

180

181 **2.3. Source apportionment of OA**

182

183 The Positive Matrix Factorization (PMF) method (Paatero and Tapper, 1994) was applied
184 to the V mode HR OA mass spectra ($m/z = 12$ to $m/z = 150$) in order to investigate the different
185 sources of OA using the PMF Evaluation Tool (PET) v. 3.00 integrated into Igor Pro (Paatero
186 and Tapper, 1994; Ulbrich et al., 2009). PMF analysis was carried out as per the guidelines of
187 Paatero and Tapper, 1994 and Ulbrich et al., 2009. Weak species, with a signal-to-noise ratio
188 (SNR) below 2 were down-weighted by a factor of 2. In addition, the errors of CO_2^+ as well as
189 the four ions associated with it in the fragment table (O^+ , HO^+ , H_2O^+ , CO^+) were downweighted
190 automatically using PET in order to prevent excessive weighting of the signal at m/z 44 (Allan et
191 al., 2004; Ulbrich et al., 2009). No fragments (SNR < 0.2) were removed from the database. We
192 examined PMF solutions between 2 and 8 factors. The selection of the most appropriate solution
193 was made by taking into account several criteria such as the variation of the Q/Q_{exp} ratio, the
194 physical meaningfulness of the mass spectra representing each factor, the time series and daily
195 cycles, and the relationship with external variables.

196

197 **2.4. Geographical determination of sources**

198

199 In order to get insight into the geographical origins of the sources of OA, we combined
200 the data obtained by the PMF analysis with the wind speed and direction and the back-
201 trajectories. The wind speed and wind direction were used by applying the non-parametric wind
202 regression (NWR), a hybrid source-receptor model which locates and quantifies local sources of

203 hourly averaged atmospheric concentrations of a pollutant based on wind speed (u) and direction
204 (θ) (Henry et al., 2009) following equation 1:

205

$$206 \quad E(C|\theta, u) = \frac{\sum_{i=1}^N K_1\left(\frac{\theta-W_i}{\sigma}\right) \cdot K_2\left(\frac{u-U_i}{h}\right) \cdot C_i}{\sum_{i=1}^N K_1\left(\frac{\theta-W_i}{\sigma}\right) \cdot K_2\left(\frac{u-U_i}{h}\right)} \quad \text{Eq. 1}$$

207 where E is the concentration estimate at a wind direction θ and wind speed u ; W_i , U_i and C_i
208 the wind direction, speed and atmospheric concentrations, respectively, measured at t_i ; σ and h
209 the smoothing factors (suggested by the software); and K_1 and K_2 are a Gaussian kernel function
210 for wind direction θ and an Epanechnikov kernel function for wind speed u , respectively, used to
211 get the smoothing (Henry et al., 2009).

212 The weighed concentrations obtained from Eq. 1 are then weighted by the wind
213 frequency. Hence, an empirical joint probability density of wind speed and direction is calculated
214 using the kernel density estimate, as shown in equation 2:

215

$$216 \quad f(\theta, u) = \frac{1}{N\sigma h} \cdot \sum_{i=1}^N K_1\left(\frac{\theta-W_i}{\sigma}\right) K_2\left(\frac{u-U_i}{h}\right) \quad \text{Eq. 2}$$

217 where N is the total number of points.

218

219 The Potential Source Contribution Function (PSCF) is a statistical source-receptor model
220 aiming at determining the geographical origins of high concentrations of air pollutants. It is based
221 on the analysis of the residence times of air masses using air mass trajectories back in time. The
222 main idea is that the longer an air mass stays over a pollution source, the higher the pollution
223 brought by the air mass to the receptor site. Generally, the domain covered by the backtrajectories
224 is meshed according to a regular grid. The PSCF model calculates the probability of having a
225 pollutant source located inside each gridcell of the domain and responsible for pollutant
226 concentrations measured at the receptor site above a given threshold, following equation 3:

227

$$228 \quad PSCF = \frac{m_{ij}}{n_{ij}} \quad \text{Eq. 3}$$

229

230 where m_{ij} is the number of backtrajectory endpoints passing over the ij^{th} gridcell at
231 latitude i and longitude j and associated to concentrations measured at the receptor site exceeding
232 a specific threshold (in this case the 75th percentile was used); and n_{ij} the total number of
233 trajectory endpoints passing over the ij^{th} gridcell.

234 A high value of the PSCF probability for the ij^{th} gridcell indicates a high probability that
235 this gridcell corresponds to a source location. The backtrajectories used for PSCF analysis were
236 calculated with HYSPLIT 4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) for an
237 arrival height of half of the planetary boundary layer, at 3-h intervals (8 trajectories per day at 0,
238 3, 6, 9, 12, 15, 18, 21 UTC), and 72 hours back in time. Due to spatial resolution, PSCF was
239 applied only to OA sources identified as regional by the NWR approach. In addition, a

240 sigmoidal-type weighing function was applied when using PSCF in order to decrease the
241 influence of grid cells with a few number of points.

242 The calculation of both NWR and PSCF was carried out using the Zefir v3.31 IGOR tool (Petit et
243 al., 2017).

244

245 **2.5. Ventilation coefficient**

246 Additionally, we calculated the ventilation coefficient (i.e. the product of the mixing layer
247 height and the wind speed; in $\text{m}^2 \text{s}^{-1}$) in order to evaluate whether the atmospheric conditions
248 favor dispersion or accumulation of the pollutants at the sampling location (Goyal and Chalapati
249 Rao, 2007). The dispersion condition in the site is considered as bad, moderate, good and
250 excellent for ventilation coefficients between 0 and 2,000, 2,001 and 4,000, 4,001 and 6,000 and
251 $> 6,000 \text{ m}^2 \text{ s}^{-1}$ respectively, according to the criteria of Eagleman (1991).

252

253 **3. Results and discussions**

254

255 **3.1. Overview of NR-PM₁**

256

257 The time series of the meteorological parameters, concentrations of the main components of
258 NR-PM₁ and OA elemental ratios are shown in Figure 1. The weather conditions during the
259 campaign were mostly humid and cold, with average values for RH and T of $82 \pm 12\%$ and
260 $5.7 \pm 3.3^\circ\text{C}$, respectively. Relatively low wind speeds were observed during the campaign, with
261 an average of $1.6 \pm 1.2 \text{ m s}^{-1}$, with calm winds from north and northeast alternating with strong
262 winds from the southwest.

263 Moderate to high levels of NR-PM₁ were observed during the measurement campaign, with
264 concentrations ranging from 0.23 to $50.9 \mu\text{g m}^{-3}$ and a campaign average concentration of
265 $11.1 \pm 9.3 \mu\text{g m}^{-3}$. The NR-PM₁ composition was dominated by OA (38.4%; $4.2 \pm 3.1 \mu\text{g m}^{-3}$)
266 and NO₃ (35.9%; $4.0 \pm 4.3 \mu\text{g m}^{-3}$) followed by NH₄ (15.9%; $1.8 \pm 1.8 \mu\text{g m}^{-3}$) and SO₄ (8.8%;
267 $1.0 \pm 0.9 \mu\text{g m}^{-3}$). The contribution of Cl was particularly low (1.0%, $0.23 \mu\text{g m}^{-3}$) throughout the
268 campaign, and hence will not be further discussed. Previous studies in northern France carried
269 out in winter also observed similar compositions for NR-PM₁ (Crenn et al., 2017b, 2017a);
270 Zhang et al., in prep.). In addition, the major inorganic species in NR-PM₁ measured by the AMS
271 (NO₃, NH₄ and SO₄) are well correlated ($r > 0.95$) to those measured in PM_{2.5} by a MARGA 1S
272 (Roig Rodelas et al., in press). Some interesting changes were observed between the first part (5
273 February – 4 March 2016) and the second part (5-16 March 2016) of the campaign. During the
274 second period, particularly high concentrations of NR-PM₁ (up to $50 \mu\text{g m}^{-3}$) were observed. This
275 was attributed to an impact of air masses originating from continental Europe and rich in
276 secondary aerosols, as will be discussed in detail in section 3.4.

277 The daily profiles of the average concentrations and fractional contributions for the main
278 species of NR-PM₁ are shown in Figure S2. Concentrations of NO₃ and NH₄ are higher during the
279 nighttime, in accordance with the lower temperatures and higher RH favoring the partitioning of
280 ammonium nitrate to the aerosol phase. On the other hand, the concentrations of sulfate do not

281 show noticeable differences throughout the day, suggesting that it might be a result of
282 transformation of regionally emitted SO₂. In addition, the daytime production of SO₄ might have
283 been masked by the expansion of the boundary layer, and the nighttime lower boundary layer
284 values might have caused higher SO₄ thus the similar levels between daytime and nighttime. The
285 daily cycle of OA shows two maxima, one in the early morning which could be linked to the
286 vehicular emissions during the traffic rush hours, and one in the evening, which could be
287 attributed to emissions from biomass burning, as will be further discussed in section 3.3. The
288 difference in composition of the NR-PM₁ between daytime and nighttime was small, although the
289 contribution of OA was higher through the night (41% compared to 35% during daytime; Figure
290 S2b), which could be attributed to a higher contribution of OA sources such as biomass burning
291 during the nighttime, as will be discussed later.

292 The origin of the main components of NR-PM₁ was assessed with the use of polar plots,
293 shown in Figure S3. We observed higher concentrations of NO₃ and NH₄ for low and moderate
294 wind speeds from the NE sector, suggesting that a combination of local and regional sources
295 could have contributed to the observed concentrations. High levels of SO₄ are observed for low
296 and moderate wind speeds in the NE sector. However, high concentrations of SO₄ are also
297 observed for other directions, implying that its origin could be rather regional, in agreement with
298 its daily cycle. The polar plot for OA shows highest concentrations for very calm winds
299 (<1m s⁻¹), pointing out significant local contributions. However, high concentrations of OA are
300 also observed for moderate wind speeds from the NE and SE sectors, suggesting that regional
301 sources are also important.

302 The acidity of the NR-PM₁ aerosol was evaluated by using the neutralization ratio (NR)
303 (Figure S4). This is defined as the ratio between the observed ammonium and that required for
304 the full neutralization of nitrate and sulfate. NR was close to 1 during most of the campaign,
305 implying that there was always enough NH₄ to neutralize NO₃ and SO₄.

306

307 **3.2. OA characteristics**

308

309 Calculation of OA elemental ratios indicates that OA was moderately oxidized during the
310 campaign. The elemental ratios were calculated based on the calibration factors from Aiken et al.
311 (2008). The average values for the OM:OC, O:C and H:C ratios were 1.60 ± 0.15 , 0.32 ± 0.11
312 and 1.55 ± 0.14 , respectively. These values are consistent with previous wintertime observations
313 at urban sites in France (Chakraborty et al., in prep.; Crenn et al., 2017b; Crippa et al., 2013).

314 The daily profiles of the elemental ratios are shown in Figure 2. The OM:OC and O:C ratios
315 are found to be slightly higher during nighttime than daytime hours, which could be attributed to
316 aqueous processing during nighttime due to very high RH levels and occurrence of some fog
317 events. Higher or comparable nighttime OM:OC and O:C values have also been observed in
318 previous studies (Brown et al., 2013; Florou et al., 2017; Hayes et al., 2013). High humidity and
319 fog events can create a suitable environment for aqueous oxidation leading to higher O:C ratios.
320 Li et al. (2013) and Chakraborty et al. (2015) reported oxidation of OA and possible changes in
321 oxidation mechanism (functionalization vs fragmentation) from two moderate to highly polluted

322 locations of Asia via AMS observations. Ge et al. (2012) and Dall'Osto et al. (2009) reported
323 formation of organosulfates during fog events from Fresno, California, and London using AMS.
324 Sullivan et al. (2016) detected aqueous SOA formation even in dark under high RH conditions.
325 So, under foggy and high RH conditions night-time oxidation can also produce highly oxidized
326 SOA. Stagnant conditions during winter nights, suggested by ventilation coefficient values lower
327 than $1000 \text{ m}^2 \text{ s}^{-1}$ (Eagleman, 1991) (Figure S5b), may have also allowed more time for the
328 processing of local air masses. For instance, aqueous oxidation of primary biomass burning
329 aerosols has already been reported (Gilardoni et al., 2016) and this will be discussed further in
330 section 3.3. Relatively lower solar radiation (and thus less photochemical activity) may have led
331 to the observed lower OA oxidation levels during daytime. The minima for OM:OC and O:C are
332 found in the early morning (7-8 am UTC, that is to say 8-9 am local time) and afternoon (5-6 pm
333 UTC), during the traffic rush hours. On the contrary, the H:C ratio presents higher values during
334 daytime, with maximum values during the traffic rush hours. In the literature, H:C usually shows
335 a sharp decrease after reaching its maximum in the morning (Crippa et al., 2013; Docherty et al.,
336 2011; Florou et al., 2017; Saarikoski et al., 2012). However, in this study H:C shows only a
337 minor dip after its morning maximum, and remains steady until the afternoon traffic rush hours.
338 This could be linked to the substantial contribution from some primary sources such as traffic
339 outside rush hours (the road next to the sampling site is situated between an industrial zone and a
340 commercial zone, implying that there is always some traffic of cars, trucks and buses).

341 The Van Krevelen plot (H:C vs O:C) can reveal some important information on the aging of
342 the atmospheric OA (Heald et al., 2010). In Figure 3, OA elemental ratios are observed to move
343 towards the lower right (higher O:C and lower H:C) as the campaign proceeds. Some inferences
344 can be drawn on OA aging based on the slope of this change of OA elemental ratios. In the same
345 plot, reactions involving the addition/subtraction of several functional groups are illustrated with
346 straight lines of different slope values. For instance, a slope of -2 is obtained when an aliphatic
347 carbon group ($-\text{CH}_2-$) is replaced by a carbonyl group ($-\text{C}(=\text{O})-$), representing the loss of 2
348 hydrogens and the gain of 1 oxygen. The replacement of one hydrogen atom with an alcohol
349 group ($-\text{OH}-$) results in a slope value of 0. Lastly, a slope of -1 is obtained by the simultaneous
350 addition of the carbonyl and alcohol groups (Heald et al., 2010). The data plotted in Figure 3
351 presented an average slope of -1.05, which is in the range of values reported for other field
352 campaigns (-0.8 to -1.1) (Hayes et al., 2013; Heald et al., 2010; Timonen et al., 2013). It is also
353 observed that the elemental ratios of OA tend to be confined within a narrow area towards the
354 end of the campaign, when aged air masses were arriving from continental Europe, as will be
355 discussed in detail in section 3.4. This observed tendency implies that with the atmospheric aging
356 due to transport, the chemical characteristics of bulk OA tend to be homogenized, as reported in
357 several previous studies (Pan, 2015; Williams et al., 2007).

358

359 **3.3. Source apportionment of OA**

360

361 The PMF analysis was applied to the high resolution mass spectra of OA by varying the
362 number of factors from two to eight. The four factor solution was chosen based on the Q/Q_{exp}

363 ratio, the chemical signatures of the different mass spectra, the time series and daily cycles, and
364 the correlation with tracers and external variables. Reasoning behind this choice is presented in
365 Table S1. The PMF diagnostics for the chosen solution are shown in Figure S6. The four factors
366 were identified as hydrocarbon-like OA (HOA), oxidized biomass burning OA (oBBOA), more
367 oxygenated oxidized OA (MO-OOA) and less oxygenated oxidized OA (LO-OOA).

368 When the number of factors was increased up to five, a HOA-COA mixed factor was
369 obtained, which entailed the decrease of residuals at m/z 55 among others. The mass spectra, time
370 series and daily profiles are shown in the supplementary material (Figure S7). However, the
371 Q/Q_{exp} barely decreased with respect to the four factor solution, and hence the four factor solution
372 was finally chosen.

373 The mass spectra profiles and time series for each factor are shown in Figure 4a and b,
374 respectively. The higher contributions are observed for MO-OOA (33%) and oBBOA (28%),
375 while LO-OOA (17%) and HOA (20%) constituted the remaining OA mass. The time series of
376 each PMF factor and their correlation with tracer(s) are shown in Figure S8. In addition, in Table
377 S2 the correlations between the PMF factors and the additionally available external variables are
378 also presented.

379 As mentioned in section 2.4, linking the wind speed and direction data to the PMF factors can
380 bring additional information on the sources of OA. Hence, in Figure 6 the NWR plots for each
381 PMF factor are shown.

382

383 3.3.1. HOA

384

385 The HOA mass spectrum is dominated by the $C_nH_{2n-1}^+$ and $C_nH_{2n+1}^+$ ion series (Figure 4a),
386 which are characteristic of OA mass spectra from vehicular exhaust emissions (Canagaratna et
387 al., 2004). Accordingly, the HOA factor has the highest H:C ratio (2.03), and lowest OM:OC
388 (1.36) and O:C (0.13) ratios among all the factors. The daily profile of HOA (Figure 5a) shows
389 two prominent peaks in the morning and evening hours corresponding to higher traffic activities
390 during the rush hours. HOA is observed to be strongly correlated with m/z 57 ($r = 0.94$; Figure
391 S8a), which is typically used as an internal tracer for HOA. Good correlations are also observed
392 with external traffic tracers like BC ($r = 0.70$) and NO_x ($r = 0.72$) (Figure S8a and Table S2). The
393 obtained HOA mass spectrum is also compared to reference ambient spectra (Crippa et al., 2013;
394 Docherty et al., 2011; Mohr et al., 2012; Struckmeier et al., 2016) obtained from the High
395 Resolution AMS Spectral Database (<http://cires1.colorado.edu/jimenez-group/HRAMSsd/>) and
396 excellent correlations are obtained ($r = 0.89-0.98$) (Figure S9). As shown in the NWR plot for
397 HOA in Figure 6a, the highest concentrations are observed for very low wind speeds, suggesting
398 that most of the HOA was locally emitted. In fact, a two-lane road is located adjacent to the
399 sampling site and likely contributed notably to the observed HOA.

400

401 3.3.2. oBBOA

402

403 An oxidized BBOA factor was also retrieved by the PMF analysis. This factor is
404 characterized by the presence of characteristic fragments of biomass burning at m/z 60 and 73,
405 associated to $C_2H_4O_2^+$ and $C_3H_5O_2^+$, respectively (Figure 4a) (Alfarra et al., 2007). Accordingly,
406 oBBOA is well correlated with its main tracer m/z 60 ($r = 0.88$; Figure S8b). In addition, good
407 correlations are observed between oBBOA and Delta-C ($r = 0.69$; Figure S8c and Table S2) and
408 water-soluble K^+ from MARGA measurements ($r = 0.61$) (Table S2). As explained in section 2.2,
409 Delta-C can be used as a tracer of wood combustion.

410 oBBOA has a high degree of oxidation (OM:OC = 1.93 and O:C = 0.58), with notable peaks
411 in its mass spectrum at m/z 28 (CO^+), 29 (CHO^+) and 44 (CO_2^+). The observation of a unique
412 oxidized BBOA factor in OA PMF analysis is not common. Instead, most studies typically report
413 a primary BBOA factor or two separate primary and oxidized BBOA factors. However, a recent
414 study conducted in Houston, USA (Wallace et al., 2018), also reported the presence of a single
415 oxidized BBOA factor (OM:OC and O:C of 2.03 and 0.65, respectively).

416 One previous field study has provided evidence of aqueous processing of primary BBOA
417 (Gilardoni et al., 2016), mainly through its correlation with RH. Sun et al. (2010) and Li et al.
418 (2014) observed the rapid formation of oxidized compounds and enhancement in O/C ratios via
419 laboratory aqueous oxidation of phenolic compounds (phenol, syringol, guaiacol, etc.) originating
420 from biomass burning activities, and identified similar signatures in ambient aerosols as well. So,
421 both field and laboratory studies provide evidence that the aqueous oxidation of BBOA is
422 possible under suitable atmospheric conditions. RH values during the present measurement
423 campaign were particularly high, with an average of $82 \pm 12\%$, which could promote aqueous
424 processing of the OA. Indeed, when the correlation between the PMF factors and the RH (by
425 bins) is evaluated (Figure 7), the concentration (and relative contribution) of oBBOA increases
426 from $0.47 \mu\text{g m}^{-3}$ (12% of OA) for $RH < 60\%$ to $2.27 \mu\text{g m}^{-3}$ (31%) for $RH > 95\%$. This positive
427 trend is observed between oBBOA and RH, while it is not observed for the other PMF factors.
428 This, together with the NWR graph for oBBOA (Figure 6b) where higher concentrations are
429 associated with low wind speeds, suggests that aqueous processing possibly led to the rapid
430 oxidation of locally emitted biomass burning emissions forming oBBOA.

431 The daily profile of oBBOA (Figure 5) shows an increase of the concentration in the late
432 afternoon and a maximum before midnight, after which the concentrations show a sharp decrease.
433 This profile is in agreement with the time of biomass burning activities (in the evening), then
434 lower MLH and higher RH values during the night, promoting the aqueous processing of fresh
435 BBOA emissions.

436 437 3.3.3. LO-OOA and MO-OOA 438

439 Two OOA factors were obtained and denoted as LO-OOA and MO-OOA (Figure 4a). Even
440 though their mass spectra are similar ($r = 0.83$), they are being considered as two separate factors
441 since their degree of oxidation and time series are different ($r = 0.62$; Figure 4b). The mass
442 spectra of both factors are characterized by major peaks at m/z 28 and 44, attributed to CO^+ and
443 CO_2^+ , respectively. However, the MO-OOA also includes a peak at m/z 29 associated to CHO^+ ,

444 whereas the LO-OOA does not and instead presents small contributions from alkyl fragments at
445 m/z 29 and 64, attributed to $C_2H_5^+$ and $C_3H_4^+$, respectively. Therefore, the MO-OOA factor
446 presents higher OM:OC and O:C ratios (2.41 and 0.95, respectively) in comparison to the LO-
447 OOA factor (2.00 and 0.61). However, both factors have very similar H:C values (around 1.5)
448 suggesting there was no evolution of the LO-OOA towards the MO-OOA, but rather that each
449 OOA factor has a different origin and/or has been processed over a different timescale. While
450 both factors showed a high correlation with NO_3 ($r = 0.79$ and 0.86 for MO-OOA and LO-OOA,
451 respectively), the LO-OOA factor correlated better with SO_4 ($r = 0.84$) than MO-OOA ($r = 0.59$).
452 This suggests that the LO-OOA could have a more regional origin. Even though the majority of
453 AMS studies have reported correlations between sulfate and MO-OOA higher than with nitrate,
454 there are a few exceptions. For instance, in China, Zhou et al. (2018) reported a poor correlation
455 between MO-OOA and sulfate and concluded that both were being produced by aqueous
456 oxidation. In addition, in more humid and colder conditions (similar to our sampling period),
457 nitrate can stay longer in the particulate phase due to relatively lower evaporative loss, so it can
458 be transported over longer distances just as sulfate (Seinfeld and Pandis, 2006; Zhou et al., 2018).
459 Xu et al. (2016) reported higher MO-OOA vs. nitrate correlation than with sulfate, while LO-
460 OOA correlated well with both sulfate and nitrate. They attributed this finding to the fact that the
461 nitrate formation was primarily occurring via photochemistry owing to lower temperature and
462 humid conditions. In this study, a similar phenomenon has been observed, so most likely MO-
463 OOA and nitrate were both produced via photochemistry and showed good correlation, while
464 LO-OOA, which has some significant regional contribution, correlates better with sulfate.

465 The time series of the MO-OOA factor shows similar concentrations throughout the whole
466 campaign (Figure 4b). However, the LO-OOA factor presented low concentrations during most
467 of the time except in the last period, where its contribution showed a remarkable increase (Figure
468 4b) due to the impact of air masses from continental Europe, as will be further discussed in
469 section 3.4. The daily profiles of both factors showed a similar cycle, with smaller concentrations
470 in the daytime (Figure 5a). For MO-OOA, the concentrations are observed to be steady during
471 the night and early morning, but showed a decrease until the evening, and then started to increase
472 again. For LO-OOA, the observed daily profile showed a similar but less pronounced trend.
473 Concentrations of oxygenated factors are expected to be usually observed in the daytime,
474 particularly in the afternoon, due to higher solar radiation which promotes photochemistry
475 leading to the formation of secondary organic aerosols. However, in this study, the concentrations
476 of OOA factors have decreased over the day (Figure 5a). This could be attributed to the strong
477 dilution effect of the mixing layer, the values of which are higher in the afternoon (Figure S5a).
478 Besides, although their concentrations are going down, their contributions to total OA are
479 increasing (Figure 5b) indicating that OOA is produced but somewhat masked by the enhanced
480 ML heights.

481 The NWR plots for the MO-OOA and LO-OOA factors show higher concentrations for low-
482 to-moderate wind speeds from the NE sector (Figure 6c-d). This suggests that the origin of both
483 factors is rather regional. The PSCF plots show that higher probabilities are observed for air
484 masses from Belgium and Germany (Figure S10).

485
486 **3.4. Impact of meteorological parameters and long range transport on NR-PM₁**
487 **characteristics**
488

489 The entire campaign was further divided into two different periods based on mass
490 loadings and meteorological conditions to gain further insights about the impact of meteorology
491 and long range transport on aerosol characteristics. Period I (5 February to 4 March 2016) was
492 characterized by moderate NR-PM₁ (average of $8.8 \pm 7.3 \mu\text{g m}^{-3}$), ranging from 0.4 to $31.5 \mu\text{g m}^{-3}$.
493 On the other hand, period II (5 to 16 March 2016) showed high concentrations of NR-PM₁
494 (average of $17.2 \pm 10.9 \mu\text{g m}^{-3}$) with values up to $50 \mu\text{g m}^{-3}$. The average temperatures and RH
495 values were similar between both periods. However, period II was associated with anticyclonic
496 conditions, with atmospheric pressure values higher than 1020 hPa, no precipitations (4 mm in
497 comparison to 73 mm for period I) and calm winds from the N and NE. In addition, during period
498 II significantly lower values were observed for the mixing layer height during the nighttime
499 (Figure S5a), which could favor the accumulation of pollutants. The ventilation coefficient
500 (Figure S5b) also shows a similar trend, with lower nighttime values in period II ($< 500 \text{ m}^2 \text{ s}^{-1}$)
501 which indicate adverse conditions for the dispersion of pollutants (Eagleman, 1991). The
502 backtrajectory density maps for each period (Figure S11) show that during period I higher
503 probabilities of occurrence are observed for air masses from the north of France, suggesting that
504 there is a higher influence from local areas. On the contrary, in period II high probabilities are
505 observed for Belgium, Germany and Western Poland. Overall, this combination of factors
506 contributed to the long-range transport of NR-PM₁ and its accumulation over the region of
507 northern France.

508 The composition of the NR-PM₁ was also significantly different between both periods
509 (Figure 8). In period I, the NR-PM₁ was dominated by OA, with an average of 43%, while the
510 inorganic ions constituted the rest of the mass, with 33% NO₃, 15% NH₄, 8% SO₄ and 1% Cl. In
511 period II the OA contribution decreased to 32%, and the percentage of the inorganic ions
512 increases notably, particularly of NO₃ to 39%, but also of NH₄ (18%) and SO₄ (10%). This
513 suggests that during period I, local sources contributed more significantly to OA, while during
514 period II the long-range transported air masses led to an increase of the levels of the inorganic
515 aerosols.

516 While the total OA mass in period II was not significantly higher in comparison to period
517 I (as opposed to the inorganic part of the aerosol), we observed significant differences in its
518 composition (Figure 8). On the one hand, in period I the OA was dominated by local sources
519 (59%) with average contributions of 33% for oBBOA and 23% for HOA. Among the rather
520 regional OA factors, MO-OOA clearly dominates (35%) over LO-OOA (9%) (Figure 8). This
521 confirms that period I was mainly influenced by local sources.

522 In addition, what seems to be a nocturnal new particle formation (“NPF-like”) event was
523 distinguished in period I, and will be discussed in the next section. On the other hand, in period II
524 the total contribution from local OA decreased significantly to 32%, with average contributions

525 of 18% for oBBOA, and 14% for HOA. The lower contribution of oBBOA during period II (i.e.
526 under the influence of transported air masses from continental Europe) proves that primary
527 biomass burning emissions are locally processed. The contribution of the regional factors
528 increased up to 68% during period II. However, though the contribution of the MO-OOA factor
529 is similar to that of period I (33%), the contribution of LO-OOA sharply increased to 34%.
530 Therefore, it seems that the increase in LO-OOA in period II could be attributed to the impact of
531 aged air masses transported from continental Europe.

532 Despite a significantly different composition of OA between both periods, the elemental
533 ratios were rather similar. This could be attributed to a compensation of these ratios between the
534 different OA factors (i.e. lower oBBOA and higher LO-OOA during period II).

535

536 **3.5. Nocturnal NPF-like event**

537 During the period where the SMPS was deployed, several nocturnal NPF-like events were
538 detected, presenting a characteristic banana shape (Heintzenberg et al., 2007). This type of event
539 corresponds to the growth of previously formed nanometer-sized particles. It may be
540 characterized based on the apparent growth rate $g(t, D_p)$ of particles calculated from Eq. 4:

541

$$542 \quad g(t, D_p) = \frac{\Delta D_p}{\Delta t} \quad \text{Eq. 4}$$

543 where ΔD_p is the geometric mean diameter of the particles (nm) between the beginning
544 and the end of the event and Δt is the duration of the event (h).

545 In total, four significant NPF-like events were identified, all of them during nighttime. A
546 summary on the characteristics of each event is given in Table 1 together with information on
547 other NPF or NPF-like events observed in urban environments. The initial growth rates of these
548 events were similar (ranging between 5.1 and 6.4 nm h⁻¹), and well within the range of 0.25-39
549 nm h⁻¹ observed for other NPF events (Cheung et al., 2011; Fiedler et al., 2005; Hamed et al.,
550 2007; Iida et al., 2008; Man et al., 2015; Salimi et al., 2017; Stolzenburg et al., 2005; Wu et al.,
551 2007).

552 In this article, the results for the most representative event, which occurred from 15 to 16
553 February 2016, are presented. The event took place under anticyclonic conditions, with clear sky,
554 calm winds, low temperatures and high RH values. Additionally, the ambient concentrations of
555 PM_{2.5} in the previous hours of the NPF-like event were particularly low due to the occurrence of
556 precipitations and marine air masses with little anthropogenic influence impacting the site. This
557 low level of pre-existing particles favored the growth of newly-formed particles by limiting the
558 sink linked to their collision with larger pre-existing ones, which generally hinders the
559 observation of this kind of event at urban sites.

560 In Figure 9, the time series of the particle number size distribution (PNSD) and the
561 geometric mean diameter of PM₁ obtained with a scanning mobility particle sizer (SMPS) are
562 shown together with the time series of the PMF factors and PM_{2.5} total mass and main inorganic
563 ions and black carbon (BC). The NPF-like event started at 6 pm and finished at 4 am (local time),
564 with an average growth rate of 5.1 nm h⁻¹ reaching a geometric mean diameter of 70 nm. Two

565 phases of growth can be observed (Figure 9b): a first one with a steeper slope ($g = 6.4 \text{ nm h}^{-1}$),
566 between 18:00 and 23:00, corresponding to a stronger increase of the aerosol size and a second
567 one less pronounced ($g = 2.8 \text{ nm h}^{-1}$), between 23:00 and 04:00 the next day. During the growth
568 phase, for a given diameter in the upper range of the nucleation mode (e.g. 20 nm) the particle
569 number concentration decreased with time, whereas it increased in the Aitken mode (e.g. 60 nm).
570 At the same time, the concentrations of OA increased simultaneously up to $14 \mu\text{g m}^{-3}$, with
571 oBBOA clearly dominating with a contribution higher than 50% during most of the event. The
572 concentrations of soluble K^+ (not shown in the Figure) measured with the MARGA also showed
573 the same increasing trend. This suggests that fast processing of organic matter from biomass
574 burning emissions was strongly involved in this event. Simultaneously, increasing concentrations
575 of NO_3 , SO_4 , and NH_4 were observed (Figure 9d). It is likely that NH_4NO_3 played a major role in
576 the event by condensing on the emitted fine particles from combustion processes, given the
577 simultaneous increases – by a factor of 5.4 and 4, respectively – in the concentrations of NO_3 and
578 NH_4 during the event. The observation of NH_4NO_3 as one of the main components in particle
579 growth is quite rare. Indeed, previous studies having reported measurements of the main species
580 responsible for particle growth have shown that the main constituents at urban and regional sites
581 are OA and SO_4 (Kerminen et al., 2018 and references therein). However, almost none of these
582 studies have been conducted in North-Western Europe, where the contribution of NH_4NO_3 is
583 typically higher and as high as 30% (Putaud et al., 2004). Only one study carried out in Melpitz,
584 Germany, determined SO_4 , NH_4 and OA as the main components responsible for particle growth,
585 although their fractional contributions were not estimated (Wu et al., 2015). In addition, most
586 NPF events have occurred during daytime, and hence linked to a photochemical origin, in which
587 OA and SO_4 are the main species involved (Kulmala and Kerminen, 2008). Therefore, the nature
588 of nighttime NPF events is likely to differ from daytime NPF events, where compounds that
589 predominate during nighttime such as NH_4NO_3 and the oBBOA fraction of OA can play a key
590 role. However, up to date, fewer than 10 measurement sites worldwide have reported nighttime
591 NPF observations, and their main components are still not well-known (Kerminen et al., 2018).
592 Among these, Man et al. (2015) also related ammonium nitrate and OA to nocturnal particle
593 growth in Hong Kong.

594

595

596 **4. Conclusions**

597 In this study, the characteristics and sources of submicron OA were investigated during an
598 intensive winter (5 February to 16 March 2016) in northern France. Moderate concentrations of
599 NR-PM_1 ($11.1 \pm 9.3 \mu\text{g m}^{-3}$) were observed, generally dominated by inorganic ions (62%).
600 Nitrate was the dominant inorganic ion (35.9%), followed by NH_4 (15.9%) and SO_4 (8.8%). In
601 addition, the NR (neutralization ratio) of the aerosol was close to 1 during most of the campaign,
602 implying that there was always enough NH_4 to neutralize NO_3 and SO_4 .

603 OA was found to be moderately oxidized ($\text{O:C} = 0.32$) and evolving along a slope of -1 in
604 the Van Krevelen plot (H:C vs O:C) indicating that the simultaneous addition of carbonyl and
605 alcohol groups could be predominant in the oxidation of OA. Application of the PMF analysis to

606 the OA mass spectra revealed the presence of several types of OA at the sampling location.
607 Identified OA were denoted as hydrocarbon-like (HOA), oxidized biomass burning (oBBOA),
608 and two oxygenated factors classified into less oxidized (LO-OOA) and more oxidized (MO-
609 OOA). The concentrations of the oBBOA factor were positively correlated with relative
610 humidity, suggesting aqueous processing of primary biomass burning emissions took place. This
611 was supported by high values of OM:OC and O:C during nighttime and by the NWR analysis
612 which showed higher oBBOA concentrations for calm winds indicating local origins. On
613 average, OA was dominated by MO-OOA (35%) and oBBOA (28%). In addition, oBBOA,
614 water-soluble K^+ and NH_4NO_3 were shown to be involved in a nighttime NPF-like event during
615 period I, suggesting a condensation of SIA on freshly emitted fine particles. However, during the
616 last part of the campaign (5 to 16 March 2016) the contribution of the LO-OOA factor increased
617 up to 34%. During the first period of the campaign (5 February to 4 March 2016) the origin of the
618 air masses alternated from oceanic and continental, which led to low to moderate concentrations
619 of NR-PM₁. However, during the second period of the campaign (5 to 16 March 2016) the
620 sampling site was heavily impacted by air masses from Eastern Europe rich in aged aerosols,
621 evidenced by the high contributions from secondary inorganic and organic aerosols. In
622 combination with an anticyclonic situation and low ventilation coefficient values, this favored the
623 presence of high NR-PM₁ concentrations in the north of France. Lastly, the OA confined into a
624 narrower space in the VK diagram during the last period of the campaign, suggesting a
625 homogenization of the different aerosol sources due to ageing of OA during transportation.

626 These results indicate that during winter, aqueous processing of primary biomass burning
627 emissions in North-Western Europe could be more important than what was previously thought,
628 and even involved in NPF-like events during nighttime under specific meteorological conditions
629 (clean and stagnant air masses, low temperatures, high relative humidity). In addition, air masses
630 arriving from Eastern Europe have a considerable impact in the region of northern France, with
631 higher concentrations of secondary inorganic and organic aerosols. Hence, the improvement of
632 the mitigation policies in neighboring countries of France, mainly Belgium, Germany and
633 Poland, should exert a significant impact on the air quality.

634

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644

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646

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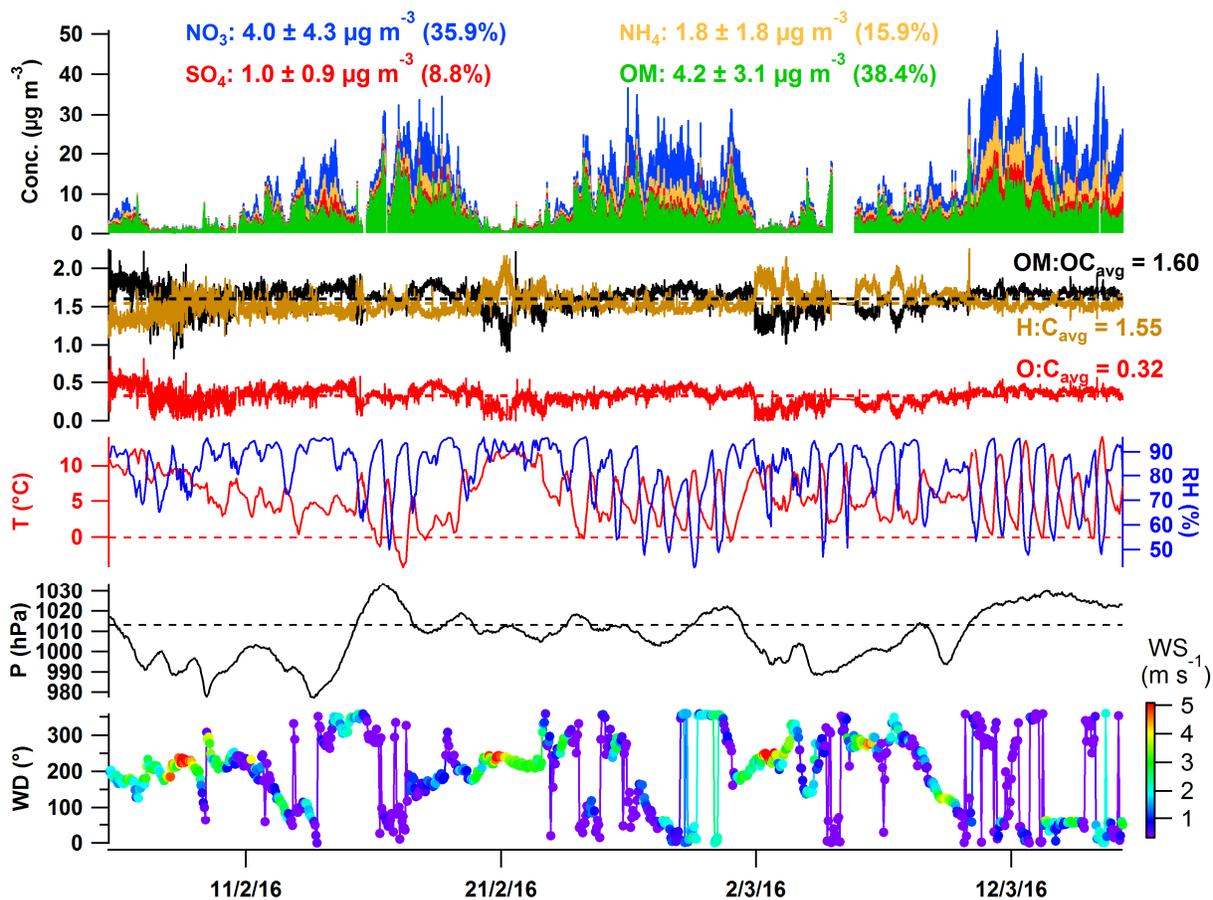
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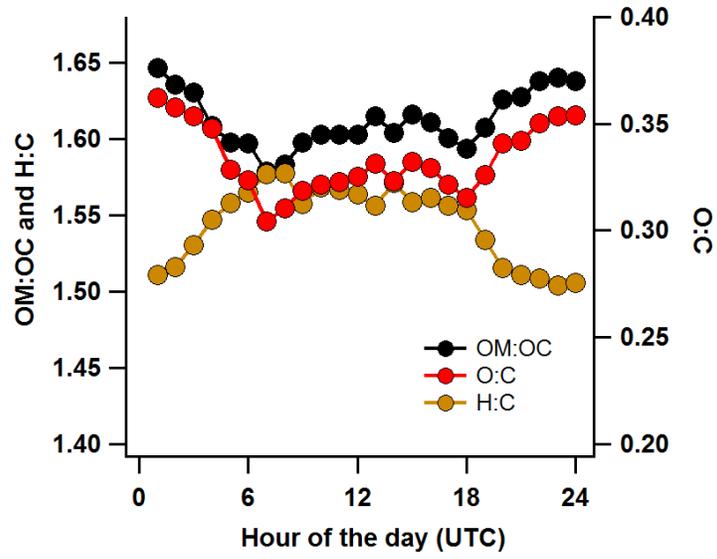
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FIGURES

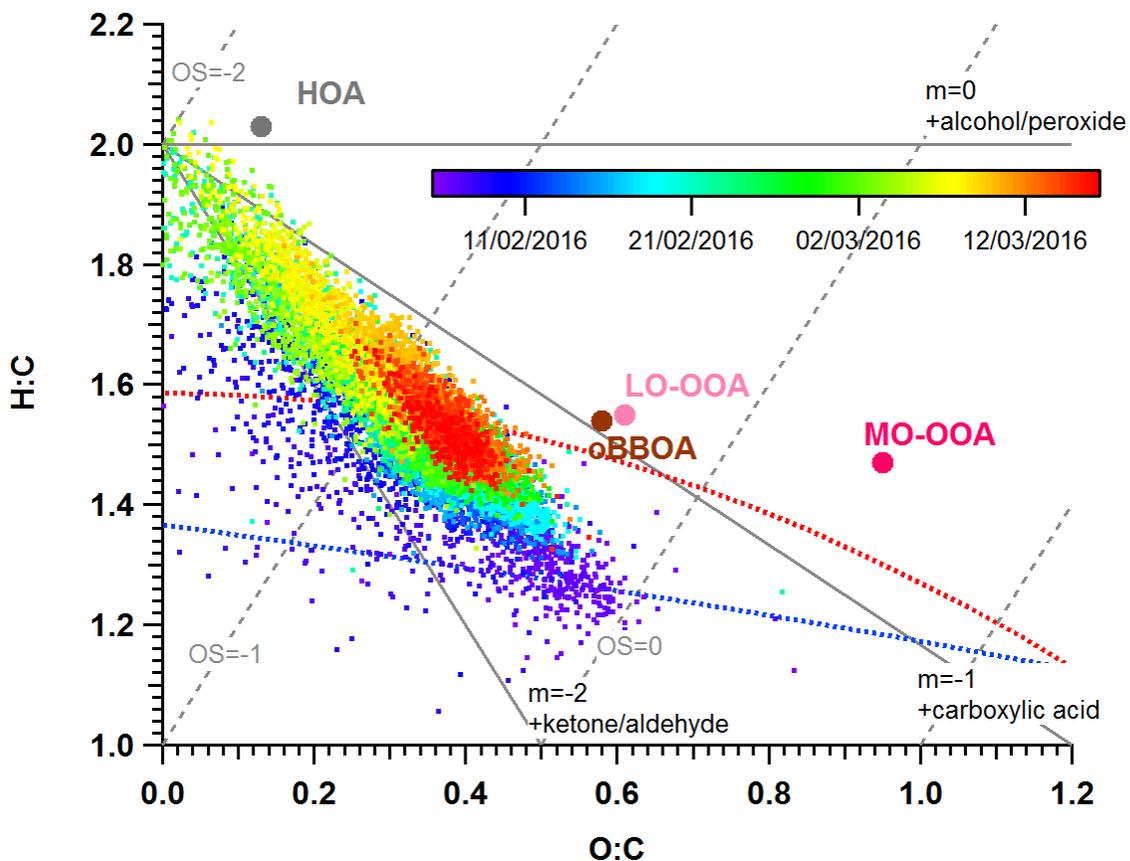


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 922 Figure 1. Time series of NR-PM₁, elemental ratios (OM:OC, H:C and O:C) and of the main
 923 meteorological parameters (T: temperature, RH: relative humidity, P: atmospheric pressure, WD:
 924 wind direction and WS: wind speed)
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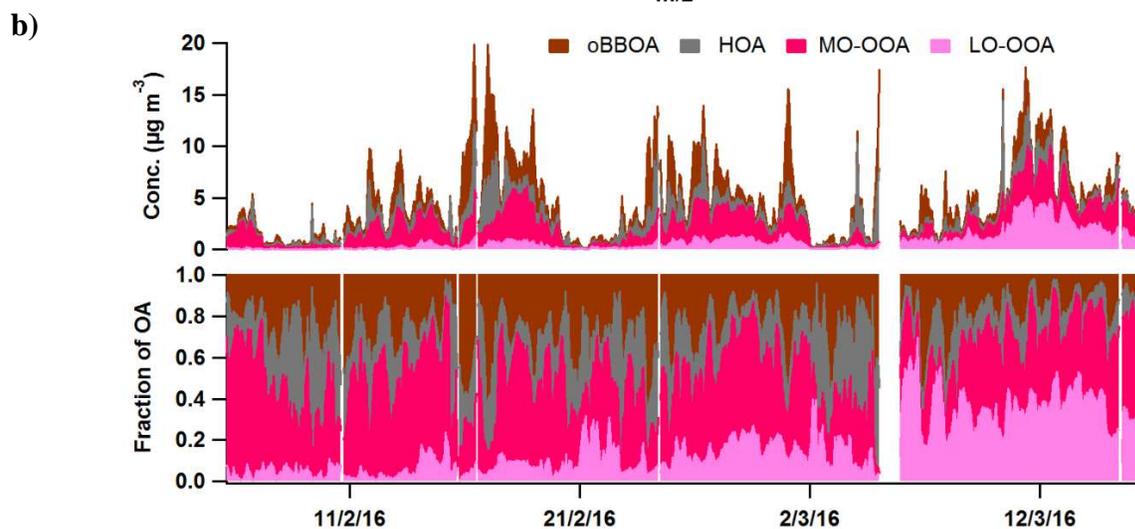
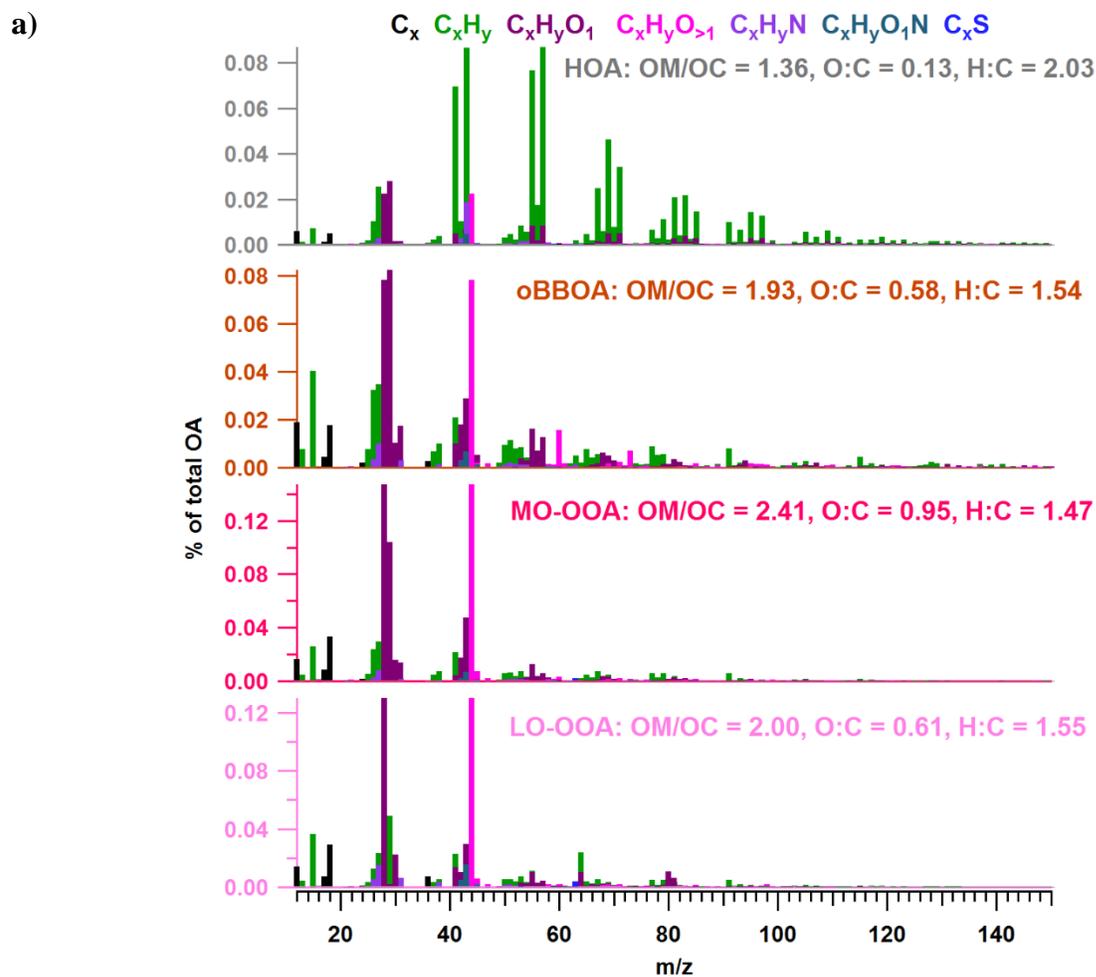
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Figure 2. Median daily profiles for OM:OC, O:C and H:C



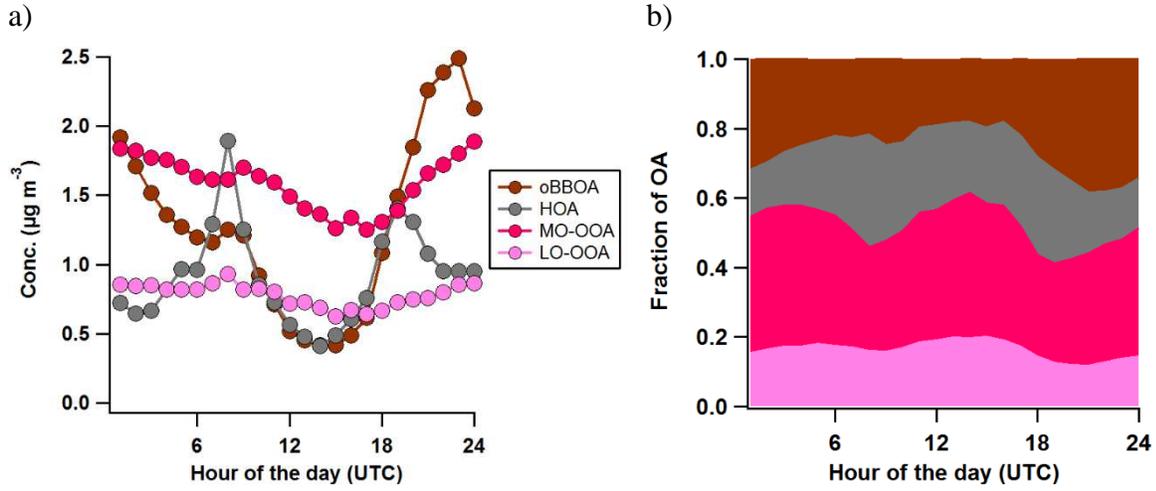
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Figure 3. Van Krevelen diagram for all the data colored by time, with identified PMF factors (HOA: Hydrogen-like OA, oBBOA: oxidized biomass burning OA, MO-OOA: more oxidized - oxygenated OA, LO-OOA: less oxidized - oxygenated OA).

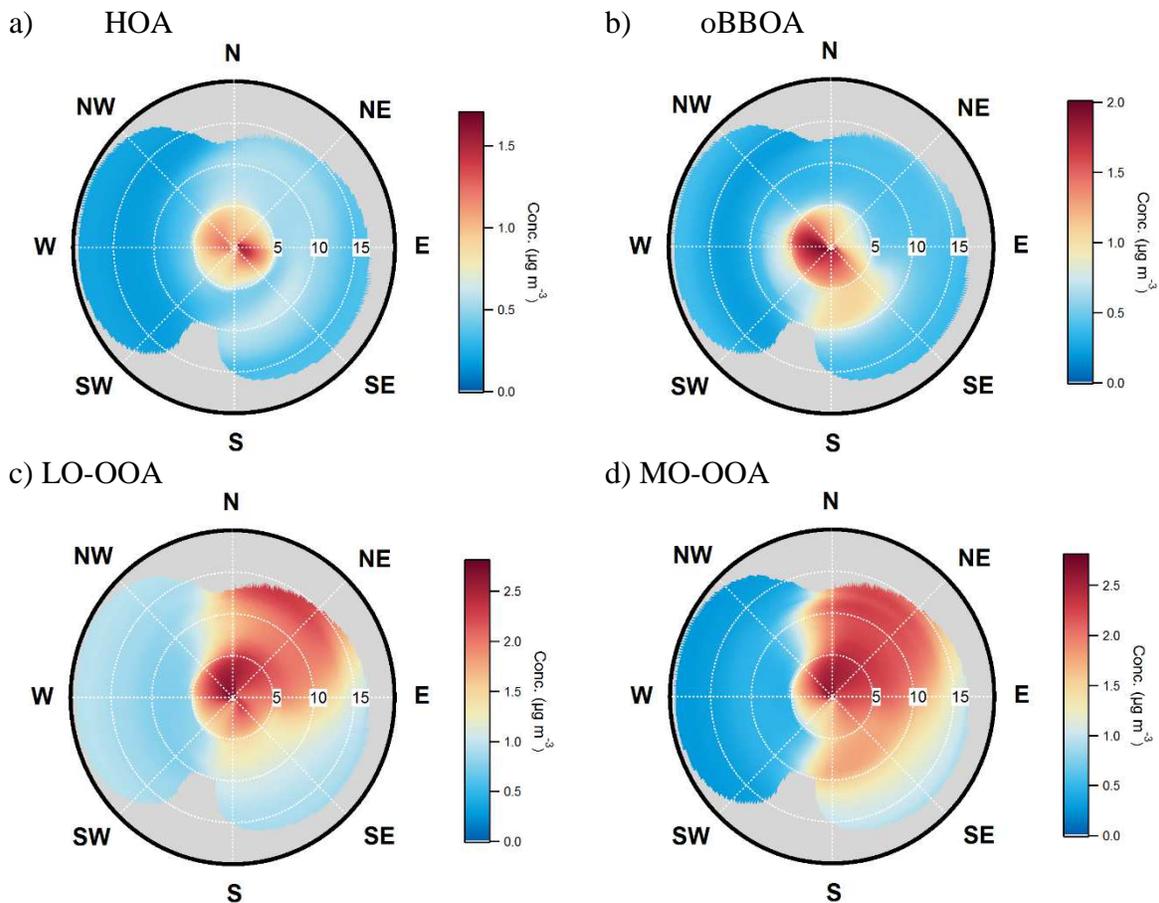


936 Figure 4. (a) Factor profiles with fragments colored by chemical families, and (b) time series of
 937 the concentrations and mass fractions of the PMF factors (HOA: Hydrogen-like OA, oBBOA:
 938 oxidized biomass burning OA, MO-OOA: more oxidized - oxygenated OA, LO-OOA: less
 939 oxidized - oxygenated OA).

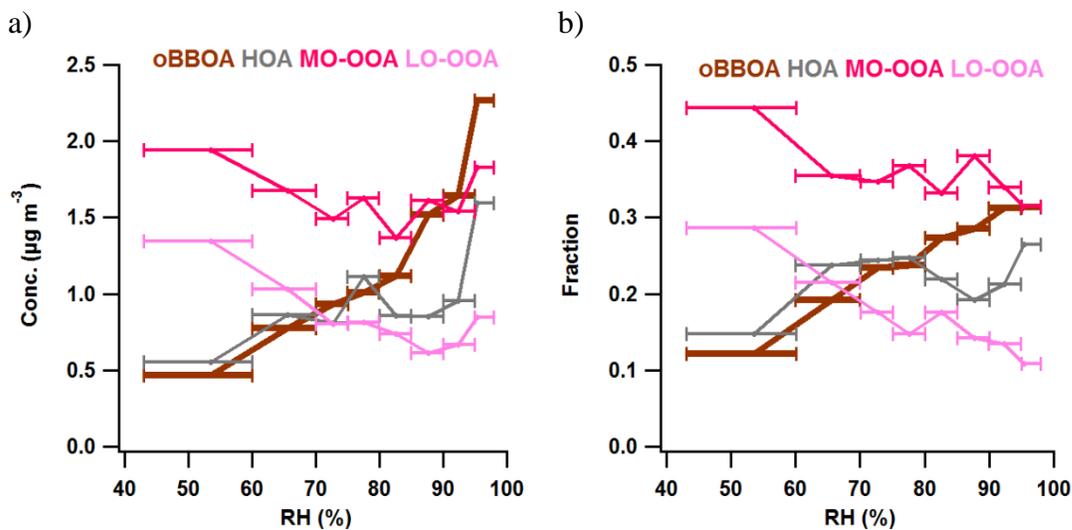
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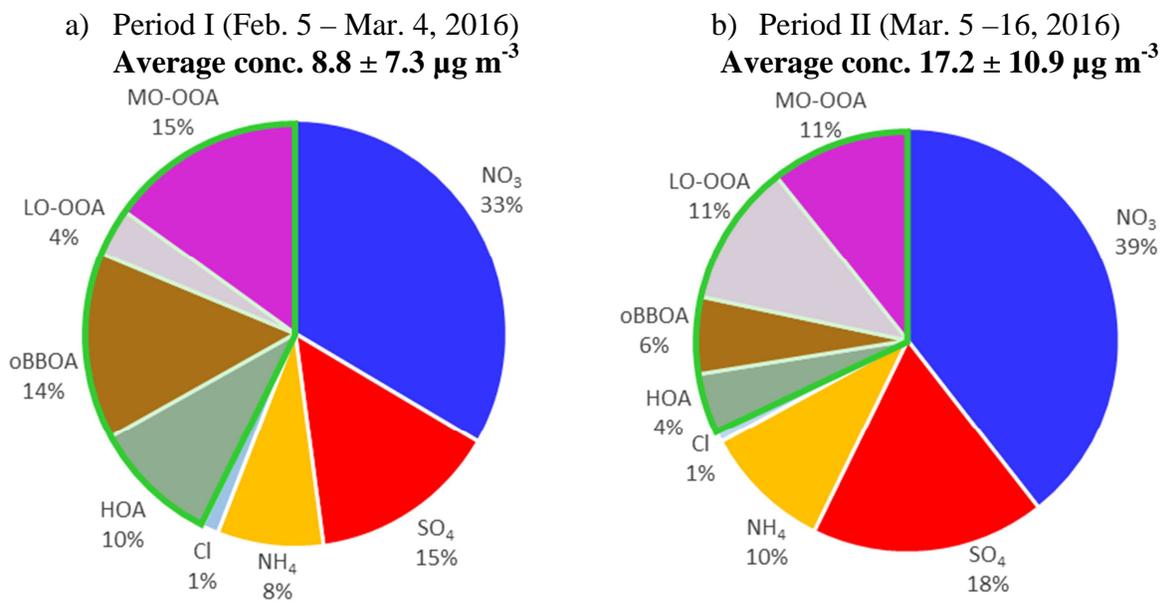
941
 942 Figure 5. Daily profiles of PMF factors by (a) concentration and (b) contribution to OA (HOA:
 943 Hydrogen-like OA, oBBOA: oxidized biomass burning OA, MO-OOA: more oxidized –
 944 oxygenated OA, LO-OOA: less oxidized – oxygenated OA).
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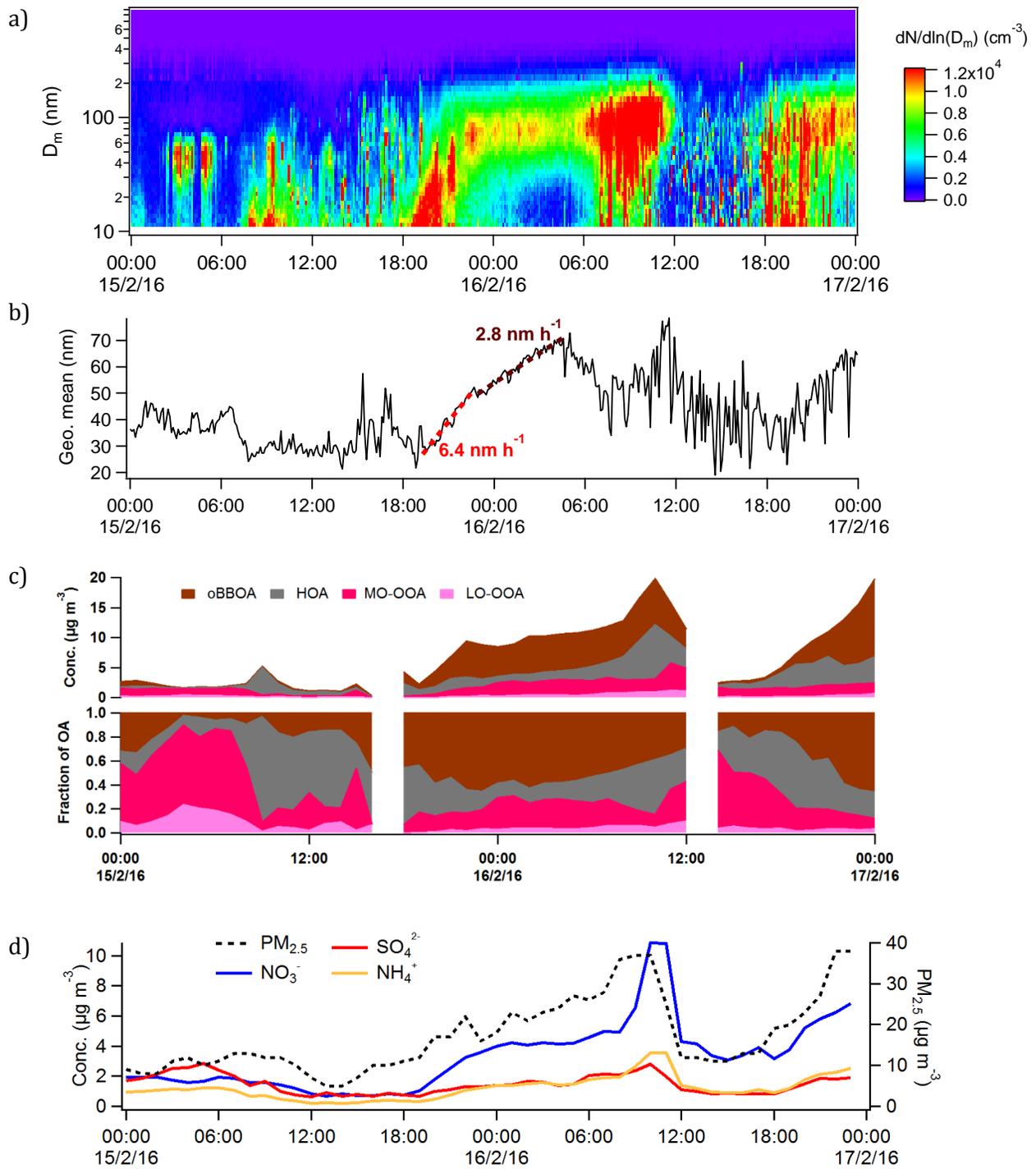
946 Figure 6. NWR plots for AMS PMF factors, colored by mass concentration (radius: wind speed
 947 in km h^{-1}). HOA: Hydrogen-like OA, oBBOA: oxidized biomass burning OA, MO-OOA: more
 948 oxidized - oxygenated OA, LO-OOA: less oxidized - oxygenated OA.
 949



950 Figure 7. Averaged mass concentrations and relative contributions of PMF factors as a function
 951 of RH bins (the width of the bins, represented by the horizontal bars, was chosen to increase the
 952 representativeness of each interval, with $n \geq 40$). HOA: Hydrogen-like OA, oBBOA: oxidized
 953 biomass burning OA, MO-OOA: more oxidized - oxygenated OA, LO-OOA: less oxidized -
 954 oxygenated OA.
 955



956 Figure 8. Average chemical composition of NR-PM₁ for (a) period I and (b) period II. The OA
 957 fraction (highlighted in light green) is subdivided into its PMF factors.
 958



959 Figure 9. (a) Time series of the particle number size distribution (PNSD), (b) geometric mean
 960 diameter, (c) PMF factors, (d) $\text{PM}_{2.5}$, NO_3^- , SO_4^{2-} , NH_4^+ , BC mass concentrations for the Feb.15-16,
 961 2016 NPF-like event

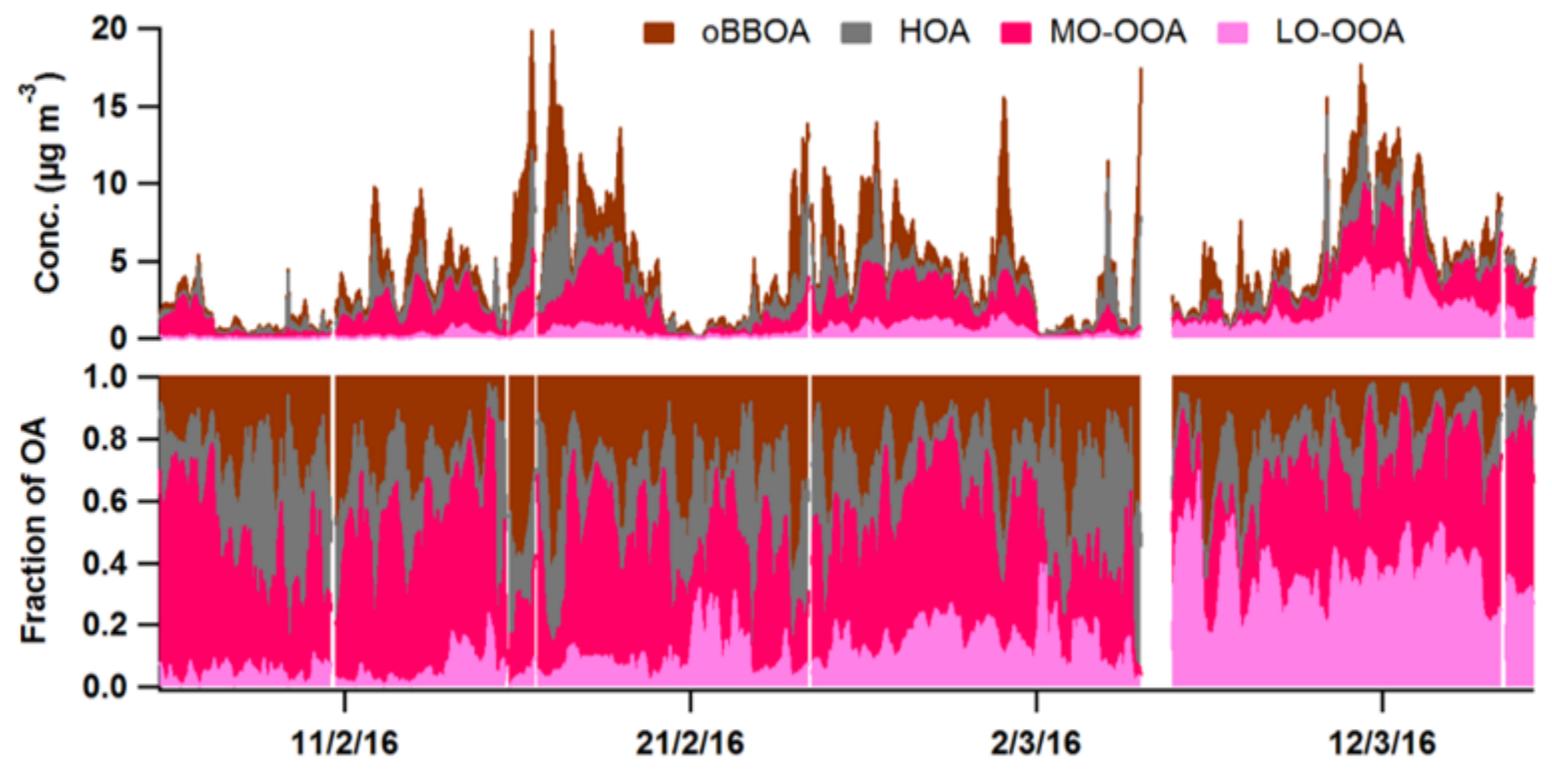
Table 1. Summary of growth rates (g) recorded during NPF or NPF-like events at urban or polluted sites

Reference	Mean g (nm hour ⁻¹)	Range of g (nm hour ⁻¹)	Size range (nm)	Site	Measurement period
This study	(1) 5.1 (6.2 ^a – 2.8 ^b) (2) 5.1 (3) 6.4 (4) 6.3	2.8 – 6.4	(1) 30-70 (2) 30-60 (3) 20-80 (4) 20-50	Douai, France	(1) 15-16/02/16 (2) 23-24/02/16 (3) 04-05/03/16 (4) 04-05/04/16
Fiedler et al. (2005)	7.7 9.0	1.3-12 2.1-23	1.3 3-25	Heidelberg, Germany	Feb.-Apr. '04
Stolzenburg et al. (2005)	9.3	2.9-22	10-90	Atlanta, United States	Jul.-Aug. '02
Hamed et al. (2007)	7	2.9-23		Po Valley, Italy	Mar. '02 – Mar. '05
Wu et al. (2007)		0.1-11		Beijing, China	Mar. '04 – Feb. '05
Iida et al. (2008)	18	6-40	3.7-25	Tecamac, Mexico	Mar. '06
Cheung et al. (2011)	4.6	1.8-7.8		Brisbane, Australia	Jan.-Dec. '09
Man et al. (2015)		2.4-39		Hong Kong, China	Mar.-Apr. and Nov.-Dec. '11
Salimi et al. (2017)		0.015-13 ^c 0.25-11.5 ^d		Brisbane Metropolitan Area, Australia	Oct. '10 – Aug. '12

963 ^a initial growth rate; ^b second growth rate; ^c daytime; ^d nighttime

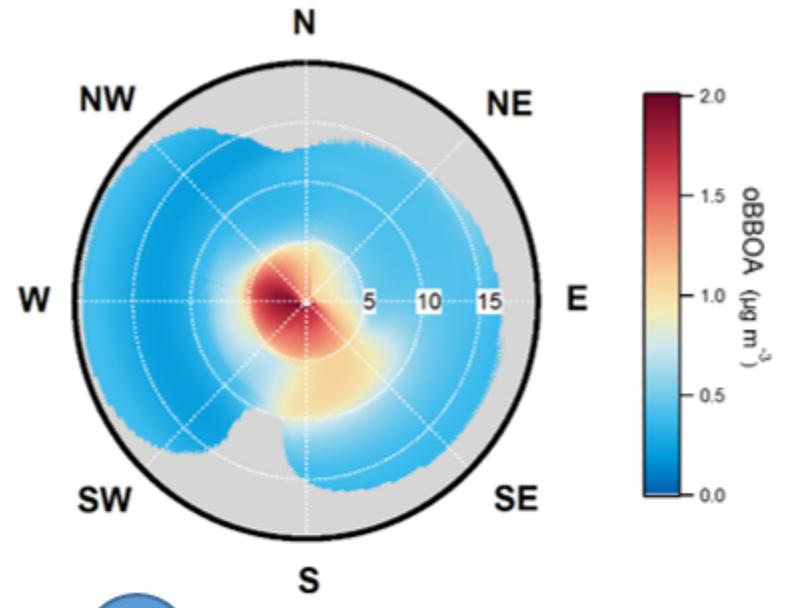
1

AMS measurements and source apportionment



2

Identification of local vs. regional sources



3

Analysis of specific periods / events

