1   **Speciation of organic fractions does matter for aerosol source**

2   **apportionment. Part 3: combining off-line and on-line measurements**

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Abstract

The present study proposes an advanced methodology to refine the source apportionment of organic aerosol (OA). This methodology is based on the combination of offline and online datasets in a single Positive Matrix Factorization (PMF) analysis using the multilinear engine (ME-2) algorithm and a customized time synchronization procedure. It has been applied to data from measurements conducted in the Paris region (France) during a PM pollution event in March 2015. Measurements included OA ACSM (Aerosol Chemical Speciation Monitor) mass spectra and specific primary and secondary organic molecular markers from PM_{10} filters on their original time resolution (30 min for ACSM and 4 h for PM_{10} filters). Comparison with the conventional PMF analysis of the ACSM OA dataset (PMF-ACSM) showed very good agreement for the discrimination between primary and secondary OA fractions with about 75% of the OA mass of secondary origin. Furthermore, the use of the combined datasets allowed the deconvolution of 3 primary OA (POA) factors and 7 secondary OA (SOA) factors. A clear identification of the source/origin of 54% of the total SOA mass could be achieved thanks to specific molecular markers. Specifically, 28% of that fraction was linked to combustion sources (biomass burning and traffic emissions). A clear identification of primary traffic OA was also obtained using the PMF-combined analysis while PMF-ACSM only gave a proxy for this OA source in the form of total hydrocarbon-like OA (HOA) mass concentrations. In addition, the primary biomass burning-related OA source was explained by two OA factors, BBOA and OPOA-like BBOA. This new approach has showed undeniable advantages over the conventional approaches by providing valuable insights into the processes involved in SOA formation and their sources. However, the origins of highly oxidized SOA could not be fully identified due to the lack of specific molecular markers for such aged SOA.

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47   **1.   Introduction**

48   Particulate matter originates from a wide range of sources and atmospheric processes, and has

49   significant impacts on air quality and climate change (Boucher et al., 2013; Heal et al., 2012).

50   Particulate organic matter (POM) makes up a large, and often dominant, fraction (typically 20–

51   60% in the continental mid-latitudes) of fine particulate mass in the atmosphere (Kanakidou et

52   al., 2005). Primary organic aerosol (POA) refers to those organic aerosols (OA) directly emitted

53   from natural or anthropogenic sources. OA that formed in the atmosphere through the oxidation

54   of gas-phase precursors, known as secondary organic aerosol (SOA), also contributes

55   substantially (20-80%) to the carbonaceous aerosol mass (Carlton et al., 2009; Ziemann and

56   Atkinson, 2012). Therefore, the discrimination of POA and SOA sources is crucial to develop

57   and apply efficient air quality control policies.

58   Positive matrix factorization (PMF), a bilinear factor analytic model that constrains the factors

59   to be non-negative (Paatero et al., 2002; Paatero and Tapper, 1994), has been widely used with

60   traditional speciation data (i.e., organic carbon (OC), elemental carbon (EC), major ions and

61   elements) for source apportionment. The use of molecular markers within PMF has opened new

62   perspectives for filter-based source apportionment studies (Heo et al., 2013; Hu et al., 2010;

63   Shrivastava et al., 2007; Srivastava et al., 2018a; Srivastava et al., 2018c; Wang et al., 2012;

64   Zhang et al., 2009). Nevertheless, short-time resolution of filter measurements is not able to

65   reveal the rapid atmospheric processes (Srivastava et al., 2018a). Development of online

66   instrumentation (e.g. AMS (Aerosol Mass Spectrometer) and ACSM (Aerosol Chemical

67   Speciation Monitor)) (DeCarlo et al., 2006; Jayne et al., 2000; Ng et al., 2011) have successfully

68   improved the real-time measurements of the aerosol chemical composition. The PMF analysis of

69   OA mass spectra from such measurements also permits the differentiation of various POA and

70   SOA sources (Lanz et al., 2007b; Srivastava et al., 2018b; Ulbrich et al., 2009; Zhang et al.,

71   2011). However, online approaches often resolve SOA components based on their volatility

72   and/or oxidation state, and do not offer any direct link to the sources.

73   Combining datasets from several measurement systems has emerged as a new opportunity to

74   refine the source apportionment of OA. Slowik et al. (2010) were the first ones to combine the

75   AMS and PTR-MS (proton transfer reaction-mass spectrometer) data, leading to the

76   identification of additional OA factors including additional information on photochemical

77   processes linked to secondary sources. This approach has also been explored in other studies as

78   well (Crippa et al., 2013a). A few researchers have explored the combination of AMS or ACSM

79   data with other measurements, such as ambient and thermally denuded OA spectra (TD-PMF-

80   AMS) (Docherty et al., 2011), or with single particle mass spectrometry (Healy et al., 2013), by

81   merging high resolution mass spectra of organic and inorganic aerosols from AMS measurements

82   (McGuire et al., 2014; Sun et al., 2012), combining off-line AMS data and organic markers or [14]C

83   measurements (Huang et al., 2014; Vlachou et al., 2017), or including on-line single particle

84   aerosol time-of-flight mass spectrometry (ATOFMS), on-line EC-OC analysis, and off-line gas

85   chromatography/mass spectrometry with AMS data (Dall'Osto et al., 2014). In addition, the

86   combination of PMF-ACSM outputs with inorganic species and black carbon (BC) measurements

87   (Petit et al., 2014) or ACSM mass spectra with metal concentrations (Sofowote et al., 2018),

88   allowed the source apportionment of PM rather than only OA.

89   In this context, a novel approach has been developed to refine OA sources and to provide

90   more comprehensive information on the associated atmospheric processes. This refinement was

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91 accomplished by performing the PMF analysis using time synchronization multilinear engine

92 (ME-2) algorithm on the combined dataset including the ACSM OA matrix and specific primary

93 and secondary organic molecular markers from PM_{10} filters on their original time resolutions.

94 The identified OA sources, their oxidation state and formation processes are discussed in this

95 paper. In addition, results from the PMF-combined data analysis are also compared to the

96 conventional PMF-ACSM analysis.

97

2. Methodology

2.1. Monitoring site

100 Measurements were conducted at the SIRTA atmospheric supersite (Site Instrumental de

101 Recherche par Télédétection Atmosphérique, 2.15° E; 48.71° N; 150 m above sea level;

102 http://sirta.ipsl.fr). This site provides long-term, in-situ observations of the chemical, optical, and

103 physical properties of the atmospheric aerosol and illustrates the background air quality of the

104 Paris region (France) and belongs to the European Research Infrastructure for the observation of

105 Aerosol, Clouds and Trace Gases, ACTRIS (Crippa et al., 2013a; Haeffelin et al., 2005; Petit et

106 al., 2017a; Petit et al., 2014; Petit et al., 2015; Sciare et al., 2011; Srivastava et al., 2018a). An

107 intensive campaign was performed from 6th - 21st, March 2015 during a severe PM pollution

108 event (PM_{10} > 50 µg m^{-3} for at least 3 consecutive days). A detailed description of the site and the

109 sampling campaign can be found elsewhere (Petit et al., 2017a; Srivastava et al., 2018a).

110 Similarly, all datasets used for the present work, including filter-based chemical speciation,

111 online measurements and meteorological parameters, have been already reported in these same

112 papers. They are then described only briefly hereafter.

2.2. Online instrumentation

PM_{10} and PM_1 using tapered element oscillating microbalances equipped with the filter dynamic measurement system (TEOM-FDMS, Thermo; 15-min time resolution), black carbon (BC) by multi-wavelength aethalometer (AE33 model, Magee Scientific, 1-min time resolution), NO_X, and O_3 concentrations using T200UP and T400 monitors (Teledyne API, 15-min time resolution), have been respectively monitored at SIRTA. Further, BC was discriminated between its wood burning and fossil fuel fractions (BC_{wb} and BC_{ff}, respectively) using the so-called "aethalometer model" (Drinovec et al., 2015; Sandradewi et al., 2008). The chemical composition of non-refractory submicron aerosols ($NR\text{-}PM_1$) has been measured using ACSM (Aerodyne Research Inc.) at a 30-min time resolution since 2011 (Petit et al., 2015; Zhang et al., 2018). Details on the ACSM measurement principles and operation at SIRTA during the campaign can be found elsewhere (Petit et al., 2017a). Finally, meteorological variables such as temperature, relative humidity (RH), wind direction, and wind speed have been measured at the main SIRTA facility (about 5 km distance).

2.3. Filter sample collection and analysis

PM_{10} samples (Tissuquartz fibre filter, Pallflex, Ø=150 mm) were collected every 4 h from 6-21, March 2015 using a high-volume sampler (DA-80, Digitel; 30 m^3 h^{-1}). PM_{10} filter samples were analysed for a large set of chemical species (n=71) including EC/OC, anions/cations, methanesulfonic acid (MSA), oxalate (Ox, $C_2O_4^{2-}$), cellulose combustion markers (biomass burning) (levoglucosan (Levo), mannosan, and galactosan), 3 polyols (arabitol, sorbitol, and mannitol), 9 polycyclic aromatic hydrocarbons (PAHs), 14 oxy-PAHs, 8 nitro-PAHs and 13 SOA markers (e.g. α-methylglyceric acid (α-MGA), 2,3-dihydroxy-4-oxopentanoic acid (DHOPA),

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136   methylnitrocatechols, etc…), following the protocols described elsewhere (Albinet et al., 2019;

137   Albinet et al., 2006; Albinet et al., 2014; Albinet et al., 2013; Cavalli et al., 2010; Guinot et al.,

138   2007; Srivastava et al., 2018a; Srivastava et al., 2018c; Tomaz et al., 2016; Verlhac et al., 2013;

139   Yttri et al., 2015).

140

2.4.   Source apportionment

2.4.1.   Model description

144   Receptor modelling, including PMF, is based on the principle of mass conservation. A mass

145   balance between the measured species concentrations and source profiles is solved as a linear

146   combination of factors p, species profile f of each source and the amount of mass g contributing

147   to each individual sample (Hopke, 2016; Paatero and Tapper, 1994). "Multi-time/time

148   synchronization" factor analysis has been developed to merge datasets with different time

149   resolutions, and take each measured concentration data into account (Crespi et al., 2016; Kuo et

150   al., 2014; Liao et al., 2015; Liao et al., 2013; Ogulei et al., 2005; Sofowote et al., 2018; Zhou et

151   al., 2004). To achieve this, the main source-receptor model equation has been modified as below

152   (Zhou et al., 2004) (Eq. (1)).

153   $$X_{sj} = \frac{1}{t_{s2}-t_{s1}+1}\sum_{k=1}^{p} f_{kj} \sum_{ts1}^{ts2}(g_{sk}\eta_j) + e_{sj} \qquad (1)$$

154   where X_{sj} represents measured data for species j in sample s, and e_{sj} is the residual of each

155   sample/species not fitted by the model. j represents the measured species, t_{s1} and t_{s2} are the

156   starting and the ending times for sample s, respectively. The time unit (i.e. time resolution of the

157   ME-2 outputs) corresponds to the shortest sampling interval from the available data (30 min in

158   this work). η_j is an adjustment factor for replicated species measured by more than one analytical

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159 method with different time resolutions. Since it was not the case in this work, there was no

160 duplication between ACSM and filter measurements, η_j has been set to 1.

161 A smoothing parameter was used in order to eliminate unrealistic residuals, as explained by

162 Ogulei et al. (2005) and implemented by Sofowote et al. (2018).

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164 **2.4.2. Error estimation/ Input matrix**

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166 Uncertainties related to the ACSM OA dataset were calculated according to the procedure

167 usually used for PMF analysis on AMS data (Ng et al., 2011). "Weak" and "bad" variables were

168 defined based on the signal-to-noise ratio lower than 3 and 1, respectively.

169 The calculation and optimization of the uncertainties for the filter molecular markers were

170 performed following the procedure explained by Sofowote et al. (2018). The uncertainties (u_{sj})

171 have been calculated using the ME-2 error model (Eq. (2)) (Paatero, 2000) (error code -14 in

172 ME-2 was used).

173 $$u_{sj} = c_1 + c_3 max\left(\left|x_{sj}\right|, \left|y_{sj}\right|\right) \hspace{3cm} (2)$$

174 where, c_3 is a multiplier to add an extra uncertainty (set to 0.1 here), x_{sj} and y_{sj} are the observed

175 and modelled values, respectively, and c_1 is the measurement or estimated error. Adjustments to

176 the detection limit (DL) have then been done accordingly in order to get distributions of scaled

177 residuals centred around 0 with an acceptable range between -5 and 5 (Zhou et al., 2004).

178 Instrumental DL of the molecular markers (evaluated from standard solutions) analysed on the 4-hr

179 PM_{10} filter samples were used as first estimates for c_1. DL for actual samples are usually 10 times

180 higher or greater (Saadati et al., 2013). Therefore, DL of the molecular markers were adjusted by a

181 factor ranging from 10 to 100. Higher adjustment factors were used for very low concentration

182 compounds (pg, nitro-PAHs), while for the compounds with DL based on field blanks (MSA and Ox)

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183   and standard solutions, a factor from 1 to 10 was considered. For the compounds with DL obtained

184   from inter-laboratory comparisons (levoglucosan and EC) (Chiappini et al., 2014; Panteliadis et al.,

185   2015; Verlhac et al., 2013), no major adjustments were required. The original and adjusted DLs are

186   given in the supplementary material (SM, Table S1).

187   The scaled residuals obtained for each molecular marker are presented in Fig. S1. In the ideal

188   scenario, these scaled residuals should be normally distributed between -3 to 3. However, large

189   residuals can be expected when using this kind of complex models. Here, we chose to keep all the

190   data points - i.e., even the ones with high residuals for one or several molecular markers - in order to

191   avoid any alteration in the physical meaning of the given dataset. For ACSM m/z's, each of the major

192   ones has been included in the input matrix except m/z 29 which caused too high instability within the

193   combined PMF results. It was assumed that that no scaling factor was needed to adjust for m/z 29

194   and other minor ones not accounted within the combined PMF analysis. Eventually, the input

195   data matrix included 774 discrete time units, 866 samples (rows), and 72 variables (57 m/z from

196   the ACSM, 14 organic molecular markers and EC) (Table S2).

197   Note, the organic markers used here were analysed in the PM_{10} extracts while the PM_1 fraction

198   was measured using the ACSM. However, it has been demonstrated that the organic molecular

199   markers including secondary and primary markers such as levoglucosan, PAHs, oxy-PAHs, nitro-

200   PAHs, MSA, nitrophenols, dicarboxylic acids (oxalic acid, phthalic acid and succinic acid) are

201   mainly associated (>90%) with the fine aerosol fraction (below PM_1) (Agarwal et al., 2010;

202   Albinet et al., 2008; Allen et al., 1996; Kerminen et al., 1997; Li et al., 2016; Pszenny, 1992;

203   Ringuet et al., 2012; van Drooge and Grimalt, 2015). Hence, the assumption of using ACSM

204   measurements and PM_{10} organic markers in a combined source apportionment approach is

205   acceptable.

206

2.4.3. Selection and optimization of the final solution

The selection of the factors was based on the investigation of the chemical profiles, the temporal evolutions of the contributions, and the prior knowledge available for the same site (Crippa et al., 2013a; Fröhlich et al., 2015; Petit et al., 2017b; Srivastava et al., 2018a) (Figs. S2 to S7). Solutions with a number of factors below or equal to eight were less explanatory. Therefore, only solutions with more than eight factors were assessed. Solution with nine, ten, and eleven factors were carefully examined including the study of G-plots (Figs. S8-S10 and discussion in SM (S.B sub-section)). The ten-factor solution eventually provided the most reasonable solution for this combined ME-2 analysis.

The ME-2 algorithm allows the implementation of constraints. The general framework for applying constraints to PMF solutions has already been discussed elsewhere (Amato and Hopke, 2012; Amato et al., 2009). A subsequent run was performed on the base results in which different constraints and number of constraints were applied (Table S3). The ratio of observed Q_{aux}, i.e., auxiliary terms in the object function (Q) that is minimized in PMF, to the expected Q_{aux} (Q_{aux-o}/Q_{aux-e}) (see SM for details) can be investigated to decide the number of constraints that could be applied (Sofowote et al., 2015). Finally, only one constraint has been applied. 1-Nitropyrene (1-NP, marker for diesel emissions) (Keyte et al., 2016; Schulte et al., 2015; Zielinska et al., 2004a) was pulled up maximally in the primary traffic OA (PTOA) factor and the fractional expected change in the target was set to 0.4.

Diel profiles of PTOA factors from the unconstrained and constrained solutions are shown in Fig. S11. The constrained PTOA displayed more pronounced morning and evening rush-hours peaks than the unconstrained solution. The unconstrained PTOA showed higher concentrations

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230 suggesting that the use of the constraint on 1-NP led to a better separation of POA factors

231 (Srivastava et al., 2018a; Zhang et al., 2019). In addition, no notable change was observed

232 between the base and the constrained factor profiles and temporal evolutions (Figs. S12 and S13).

233 Details are presented in the SM.

234

235 **3.   Description of the factors obtained from the PMF-combined data analysis**

236 The PMF-combined data analysis allowed the deconvolution of 10 OA factors including 3 POA

237 (primary traffic OA (PTOA), biomass burning OA (BBOA), and oxidized BBOA (OBBOA)) and

238 7 SOA factors (2 biogenic-SOA, 4 anthropogenic-SOA and 1 highly processed/aged SOA) (Fig.

239 1). The identified OA factors have been classified in terms of oxidation state, sources and/or

240 precursors. Overall, aged (highly processed) SOA (SOA-5) was the main contributor (34%) to the

241 OA mass during the campaign. Oxidized biomass burning (OBBOA) (14%), biogenic SOA

242 (BSOA-1, marine-rich) (14%), anthropogenic SOA (ASOA-2, nitro-PAHs) (10%) and primary

243 traffic OA (PTOA) (8%) made significant contributions to the total OA mass.

244

245 As for PMF-ACSM (Fig. 2), the results obtained showed that about 75% of OA mass was

246 secondary in origin. Details on the PMF-ACSM analysis performed in the frame of the present

247 study are given in the SM (section S.C. Results from PMF-ACSM analysis, Figs. S14-S19).

248 Using the combined data matrix, the origin of 54% of the total SOA fraction was clearly

249 identified. Specifically, 28% of the total SOA fraction was found to be related to anthropogenic

250 SOA (ASOA-1, ASOA-2, ASOA-3 and ASOA-4) from combustion sources such as biomass

251 burning and traffic emissions.

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252   The identified OA sources, their chemical profiles and temporal evolutions are shown on Figs. 3

253   and 4. They are discussed individually together with their diel cycles (Fig. 5).

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255   **3.1.   POA factors**

256   **3.1.1. Primary traffic OA (PTOA)**

257   The PTOA factor accounted for 8% of the OA mass during the studied period (Fig. 1). It was

258   identified based on its high proportion of aliphatic hydrocarbons, especially m/z 27, 41, 55, 57,

259   69, and 71 (Aiken et al., 2009) together with a significant amount of EC (43% in this factor) and

260   1-nitropyrene (1-NP) (35% of species in this factor) (Fig. 3). These mass fragments are consistent

261   with the mass spectral characteristics found for the primary combustion sources (i.e., fossil fuel)

262   and have been commonly used in urban environment as a proxy of traffic emissions (Lanz et al.,

263   2007a; Mohr et al., 2009; Ulbrich et al., 2009; Zhang et al., 2019).

264   The use of 1-NP, known to be a good marker of diesel emissions (Keyte et al., 2016; Schulte

265   et al., 2015; Zielinska et al., 2004a; Zielinska et al., 2004b) to constraint this factor, clearly

266   improved its separation from other primary sources (see section 2.4.3). PTOA also showed a fair

267   correlation with BC_{ff} (r^2= 0.39; n= 774) (Fig. S20), thereby corroborating this factor link with

268   traffic emissions. In addition, the diel cycle of the resolved source exhibited two pronounced

269   peaks in agreement with the traffic rush hours in the morning and in the evening (Fig. 5).

270

271   **3.1.2. Biomass burning OA (BBOA)**

272   BBOA source profile included high contributions of m/z 60 and 73 (Fig. 3). Thee ions are typical

273   fragments of anhydrous sugars, such as levoglucosan, which are produced during cellulose

274   pyrolysis (Alfarra et al., 2007; Lanz et al., 2007b; Simoneit et al., 1999). Levoglucosan, a well-

275   known marker for biomass burning, was mainly present (67%) in this factor. In addition, this

276   factor included noticeable contributions of other species often emitted by wood combustion, such

277   as benzo[*a*]fluorenone (B[a]Fone), benzo[*b*]fluorenone (B[b]Fone), and 9-nitroanthracene (9-

278   NA) (Nalin et al., 2016).

279   Overall, BBOA contributed only 3% of the OA mass (Fig. 1). Slightly higher concentrations

280   were measured at the beginning of the PM pollution event, a period that was highly affected by

281   local emissions and notably by residential heating (Petit et al., 2017b; Srivastava et al., 2018a).

282   The diel cycle of BBOA illustrated significant increases from the late afternoon until the night

283   corresponding to residential heating (Fig. 5).

284

285   **3.1.3.   Oxidized BBOA (OBBOA)**

286   The source profile of this factor contained m/z, 43, 44, 45, 59, 60, 71 and 73, together with a

287   significant contribution of oxidized species like oxalate (38% of the OBBOA in mass

288   concentration) (Fig. 3). This source accounted for 14% of the OA mass for the study period (Fig.

289   1). This factor was found to be correlated with levoglucosan and potassium (K^+) (levoglucosan,

290    $r^2= 0.48$; K^+, $r^2= 0.46$; n= 92), both, tracers for biomass burning activities (Cachier et al., 1995;

291   Simoneit et al., 1999) (Fig. S21). The observed diel profile of this factor also illustrated the same

292   behaviour as BBOA with high concentrations during the night corresponding to wood burning

293   activities (Fig. 5). Therefore, this factor was considered as another biomass-burning source with

294   oxidized characteristics and named as OBBOA. In addition, the oxidized organic masses m/z, 45,

295   59, 71, and 73 are commonly found in aged biomass burning particles, formed via the

296   photochemical oxidation of organic acids followed by gas-to-particle partitioning (Zhang et al.,

297   2017), supporting the connection of this source with biomass burning activity.

298   To further investigate the evolution of OA factors, the triangle plot f_{44} vs. f_{43} (fraction of m/z

299   44 and m/z 43 in OA, respectively) was investigated as suggested by Ng et al. (2010). The f_{44} can

be considered as indicator of atmospheric ageing due to photochemical processes leading to the increase of f_{44} in the atmosphere while f_{43} is an indicator of the degree of hydrogenation and thus of primary combustion processes. The triangle plot is presented in Fig. 6.

Both, PTOA and BBOA factors, identified above, showed low oxidative properties (low f_{44}) with high hydrogenated ones (high f_{43}) (both located at the bottom right of the triangle plot) in agreement with previous studies (Sun et al., 2012; Zhang et al., 2015). Alternatively, the present factor showed similarities with oxidized primary OA (OPOA) resulting from the rapid oxidation in the gas phase of low volatility and/or semi-volatile organics (Grieshop et al., 2009), together with the characteristics of partially oxidized biomass burning with mid f_{60} values typical of primary BBOA (Figs. 6 and S22). Thus, this resolved source represents a good example of OPOA from wood burning probably formed between the emission and the introduction in ambient air, as already shown previously (Nalin et al., 2016). In addition, this factor could also be part of the burn-out phase of combustion when there is a lot of pyrolysis, followed by the formation of oxidized OA and humic-like substances (HuLIS). Finally, OBBOA seemed to be more oxidized at the end of the campaign due to enhanced atmospheric processing (Fig. S23).

3.2. SOA factors

As described previously, the f_{44} vs. f_{43} plot provides valuable information on the photochemical ageing of the evolved SOA components (Ng et al., 2010). All SOA components were found in the upper half part of the triangle plot (Fig. 6). The variability observed in f_{44} and f_{43} suggested the role of various sources, precursors, and different chemical pathways involved in their formation as discussed below.

3.2.1. Biogenic SOA-1 (marine-rich) (BSOA-1)

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324   This factor was identified based on high contributions of m/z 44 and methanesulfonic acid

325   (MSA, being fully present in this factor). MSA is a known secondary oxidation product of

326   dimethylsulfide (DMS), which is emitted by phytoplankton and several types of anaerobic

327   bacteria in the oceanic environment (Charlson et al., 1987; Chasteen and Bentley, 2004; Zorn et

328   al., 2008). Due to low signal-to-noise ratio from the ACSM measurements, typical MSA mass

329   fragments such as m/z 78 and 79 (Crippa et al., 2013b) were not present in the factor profile.

330   This factor accounted for 14% of the OA mass, with a high contribution during the final days

331   of the campaign (Figs. 1 and 4). These results were in agreement with the impact of long range

332   transport and ageing processes highlighted previously for the same pollution event during this

333   period together with high NO_3^- and SO_4^{2-} concentrations and high wind speed (Petit et al., 2017a;

334   Srivastava et al., 2018a) (Fig. S24). In addition, a phytoplankton bloom hotspot near the North

335   Sea in March 2015 in agreement with the origin of air masses at the end of the campaign (Fig.

336   S25) been previously reported, confirming the marine influence (Srivastava et al., 2018a).

337   This factors also included a significant contribution of oxalate (43% in this factor), an ultimate

338   by-product of photochemical oxidation processes. Secondary formation routes for oxalic acid

339   (quantified as oxalate) are thought to be driven by the photochemical decomposition of gaseous

340   anthropogenic (e.g., cycloalkanes) and biogenic organic compounds (Carlton et al., 2007; Carlton

341   et al., 2009; Hatakeyama et al., 1987; Kawamura et al., 1996), followed by partitioning onto the

342   condensed phase (Martinelango et al., 2007; Sullivan and Prather, 2007). Heterogeneous

343   formation, which includes in-cloud processing (Pun et al., 2000), also represents a formation

344   pathway of this oxidized species. Therefore, the observations suggest that BSOA-1 is principally

345   linked to marine SOA, but the significant impacts of other sources (anthropogenic/ biogenic)

346   should not be excluded. This possibility was further confirmed by the results obtained from the

347   Concentration-Weighted Trajectory (CWT) (Petit et al., 2017a) analysis showing a geographical

348 origin of this factor from the North Sea including substantial influence of air masses from the

349 continental Eastern Europe (Fig. S26). Note that, terrestrial sources of DMS (from soil and trees)

350 were reported recently (in the Amazon rain forest) by Jardine et al. (2015).

351

352 **3.2.2. Biogenic SOA-2 (isoprene-rich) (BSOA-2)**

353   The identification of this factor was based on oxygenated mass fragments (m/z 44 and m/z 43)

354 and the presence of two isoprene oxidation products (Carlton et al., 2009), i.e., α-MGA (60% in

355 this factor) and 2-MT (2-methylerythritol, 99% in this factor, as shown in Fig. 4. BSOA-2

356 accounted for 5% of the total OA mass (Fig. 1). Such low contributions during the late winter and

357 early spring periods is expected due to low biogenic emissions in this season. Finally, BSOA-2

358 was found to be significantly less oxidized compared to previous BSOA-1 (Fig. 6).

359

360 **3.2.3. Anthropogenic SOA-1 (nitro-PAHs) (ASOA-1)**

361   This factor was characterized by the presence of 2-nitrofluoranthene (2-NFlt, 100% in this

362 factor) and oxygenated mass fragments (m/z 44 and m/z 43) (Fig. 4). 2-NFlt is an exclusive

363 secondary oxidation product from the gas phase reaction between fluoranthene and NO_2 initiated

364 by OH (day-time) or NO_3 (night-time) radicals (Arey et al., 1986; Atkinson et al., 1987).

365 Therefore, this factor was considered to be associated with PAH SOA from anthropogenic

366 sources i.e., biomass burning and traffic.

367   ASOA-1 showed significant contributions to the OA mass (10%) (Fig. 1). The diel cycle

368 showed an increase of the concentrations from early night until early morning indicating the

369 predominance of night-time processes as previously shown by Srivastava et al. (2018a) (Fig. 5).

370 This factor is oxidized but also included a significant fraction of f_{43} (Fig. 6).

371

3.2.4. Anthropogenic SOA-2 (oxy-PAHs) (ASOA-2)

High proportions of dibenzo[b,d]pyran-6-one (6H-DPone, almost exclusively present in this factor) and oxygenated mass fragments (m/z 44 and m/z 43) were observed in this source profile (Fig. 4). 6H-DPone is a by-product from phenanthrene photooxidation and is considered to be a good marker of PAH SOA formation (Lee and Lane, 2010; Tomaz et al., 2017). This factor also included B[a]Fone and B[b]Fone (33% and 47% in this factor, respectively) that may originate from both primary and secondary processes (Albinet et al., 2007; Srivastava et al., 2018a; Tomaz et al., 2017) (Fig. 4). Thus, this factor was treated as another PAH SOA source accounting for 4% of the OA mass (Fig. 1).

ASOA-2 appeared slightly less oxidized than the other PAH SOA (ASOA-1) (Fig. 6), suggesting different chemical processes involved in the formation of nitro- and oxy-PAHs (Srivastava et al., 2018a). The diel cycle of ASOA-2 also illustrated a different pattern with noticeable morning and evening peaks (Fig. 5), which may suggest an influence from traffic, but a more detailed identification of the sources linked to this factor is difficult to obtain.

3.2.5. Anthropogenic SOA-3 (phenolic compounds oxidation) (ASOA-3)

The source profile of this factor incorporated high proportions of 4-methyl-5-nitrocatechol (4-Me5Nc) (100% in this factor) and 3-methyl-5-nitrocatechol (3-Me5Nc) (91% in this factor) together with high m/z 44 and m/z 43 (oxidized mass fragments) (Fig. 4). Nitrocatechols are by-products from the photooxidation of phenolic compounds (i.e., cresols, methoxy phenols) largely emitted by biomass burning (Bruns et al., 2016; Iinuma et al., 2010). In addition, this factor also included significant contributions of m/z 60, m/z 73 and levoglucosan (17% in this factor). The ASOA-3 factor followed a distinctive temporal evolution with higher concentrations at the beginning of the sampling campaign in agreement with the BBOA pattern (Figs. 3 and 4). The

17

396   diel cycle showed concentration peaks in the early evening concurrently with the wood burning

397   emissions (Fig. 5). Therefore, this factor illustrated the characteristics of anthropogenic SOA

398   linked to biomass burning emissions. This assignment was also supported by the f_{44} vs. f_{60} plot

399   (Fig. S22) showing very high f_{60} values comparable to the BBOA factor.

400   ASOA-3 showed a similar oxidation level to both previously identified anthropogenic SOA

401   factors (ASOA-1 and ASOA-2) (Fig. 6) but significantly less hydrogenated (low f_{43}). Finally,

402   ASOA-3 had a low contribution to the OA mass (3% on average) (Fig. 1).

403

404   **3.2.6. Anthropogenic SOA-4 (toluene oxidation) (ASOA-4)**

405   The source profile of this factor showed a high proportion of m/z 44, including 100%

406   contribution of DHOPA (Fig. 4). DHOPA is a SOA marker of toluene oxidation (Kleindienst et

407   al., 2004). Therefore, this factor seemed to be another anthropogenic SOA from combustion

408   sources notably biomass burning and traffic, as they both emit large quantities of toluene (Baudic

409   et al., 2016; VanderSchelden et al., 2017).

410   Small contributions of m/z 60 and levoglucosan (~10% in this factor) could also be observed

411   (Fig. 4). The diel cycle of ASOA-4 showed a pronounced peak at night concurrent with

412   residential heating activities (Fig. 5). Thus, ASOA-4 seemed another anthropogenic SOA factor

413   mainly linked to biomass burning emissions.

414   This factor was also more oxidized (high f_{44} content) with different f_{43} and f_{60} fractions than

415   the other biomass burning SOA (ASOA-3) (Figs. 6 and S22), showing that different chemical

416   processes were involved. Finally, the contribution of ASOA-4 to total OA was about 5% (Fig. 1).

417

418   **3.2.7. SOA-5 (aged SOA)**

419   High contributions of m/z 44 and m/z 43 were observed for this factor. This pattern is similar

420   to the more oxidized OA factors determined at other urban/suburban sites from AMS/ACSM

421   PMF analyses (Fig. 4) (Ng et al., 2010; Ulbrich et al., 2009). Interestingly, no organic markers

422   have been observed to be associated with this factor except a small contribution of α-MGA (30%

423   in this factor), an isoprene oxidation by-product. This factor was the predominant one over the

424   PM pollution event, accounting for about 34% of the OA mass (Fig. 1) and clearly very oxidized

425   (Fig. 6).

426   In addition, SOA-5 showed good correlations with secondary inorganic species ($r^2_{sulfate}$= 0.67;

427      $r^2_{nitrate}$= 0.81; $r^2_{ammonium}$= 0.83; n= 774) (Fig. S27) and a distinctive temporal variation, with very

428   high concentrations at the end of the campaign (Fig. 4). Its high oxidized properties (Fig. 6),

429   together with the impact of long range transport observed during this period, suggested that SOA-

430   5 may contained highly processed aerosol, as also supported by previous findings for the same

431   campaign (Petit et al., 2017a; Srivastava et al., 2018a).

432   A similar OOA factor has also been observed at other European sites in winter with the same

433   characteristics, i.e., high correlation with long-range transported secondary inorganic species

434   (Daellenbach et al., 2017; Lanz et al., 2007b), supporting the assignment of this source.

435

4. Comparison between PMF-ACSM and PMF-combined data outputs

437   Results from PMF-combined data were compared here to those of PMF-ACSM to investigate

438   the consistency and the benefits of the developed OA source apportionment methodology over

439   the conventional approaches. Briefly, four factors were identified from the PMF-ACSM analysis:

440   2 POA factors - i.e., HOA (hydrocarbon-like OA, 16%) and BBOA (biomass burning OA, 14%) -

441   and 2 SOA factors, i.e., LO-OOA (low oxidized- oxygenated OA, 15%) and MO-OOA (more

442   oxidized-OOA, 55%) (Fig. 2). These results notably highlighted the enhanced formation of SOA

443   during this PM pollution event as shown previously (Petit et al., 2017a).

444

445   **4.1. POA sources**

446   The primary traffic emissions and biomass burning-related OA factors from both PMF

447   analyses are presented in Fig. 7. The primary biomass burning factor from the PMF-combined

448   data analysis was considered to be the sum of both identified biomass burning-related factors:

449   BBOA and OBBOA (see details in section 3.1). Relatively good agreement was observed for this

450   comparison (r^2= 0.62, slope= 0.90, n= 774, y-axis= [BBOA + OBBOA]$_{combined}$, x-axis=

451   BBOA$_{ACSM}$), with diel cycles notably presenting maximum concentrations during the night (Fig.

452   S28). A good agreement was also noticed between the traffic OA factors (r^2= 0.75, slope= 0.68,

453   n= 774, y-axis= PTOA, x-axis= HOA). However, higher night time concentrations were noticed

454   for the PMF-ACSM HOA factor. This result could be attributed to the influence of biomass

455   burning PM on the HOA mass concentrations as suggested in section 3.1 and previously shown at

456   SIRTA during this time of the year (Petit et al., 2014; Srivastava et al., 2018a; Zhang et al.,

457   2019).

458   The PMF-combined data analysis seemed better able to resolve primary traffic OA than PMF-

459   ACSM, whereas HOA should only be considered as a proxy of road transport OA. Discrepancies

460   were observed for biomass burning emissions between both approaches at the end of the

461   campaign, a period highly affected by oxidized species as previously specified. OBBOA may

462   contain more secondary species than primary ones in this period, explaining the observed

463   discrepancies. Overall, the primary biomass burning source was well resolved by both

464   approaches, although the PMF-combined data analysis allowed the distinction of POA and

465 OPOA from wood combustion, which was not possible with the conventional PMF-ACSM

466 approach. In addition, the results obtained showed that about 80% of the BBOA was composed of

467 OBBOA suggesting that BBOA in the atmosphere was probably more oxidized in nature rather

468 being like the primary BBOA found in this study.

469

470 **4.2. SOA fractions**

471 The comparison of the total SOA estimates (total OOA factors) from both approaches is

472 discussed here (Fig. S29). The total SOA estimates from the PMF-combined data analysis was

473 the sum of the 7 OOA (Σ_7OOA) factors (BSOA-1, BSOA-2, ASOA-1, ASOA-2, ASOA-3, ASO4

474 and SOA-5), while only 2 OOA factors (MO-OOA and LO-OOA) were resolved using the PMF-

475 ACSM analysis. Overall, both approaches showed very good agreement (r^2= 0.96, slope= 1.10,

476 n= 774, y-axis= Σ_7OOA, x-axis= MO-OOA + LO-OOA) highlighting that the PMF performed on

477 the combined dataset has given valuable insights into the secondary sources with 7 sources

478 resolved instead of only 2. This result is discussed into details below.

479 Individual SOA sources from both approaches have been compared to provide comprehensive

480 information on the SOA formation processes/sources. No direct association was observed

481 between the individual SOA factors obtained from both approaches, except between the highly

482 oxidized OOA factors (MO-OOA, BSOA-1 and SOA-5; Table S4). MO-OOA was found to be

483 significantly correlated with both, BSOA-1 and SOA-5 (Table S4; r^2= 0.76-0.89, n= 774).

484 Further, the sum of BSOA-1 and SOA-5 was compared with MO-OOA, and the results showed a

485 very good agreement (r^2= 0.96, slope= 1.13, n= 774, y-axis= BSOA-1 + SOA-5, x-axis= MO-

486 OOA) with similar temporal evolutions (Fig. S29). Hence, MO-OOA was mainly composed of

487 two factors, BSOA-1 and SOA-5, identified from the PMF-combined data analysis. However, the

488 clear identification of the sources linked to MO-OOA is still difficult to achieve. As explained

21

489 previously, SOA-5 could not be identified using any molecular markers and was mainly

490 explained as being processed aerosols and long-range transport. In addition, BSOA-1 contained a

491 part of the marine SOA but with substantial influences from other biogenic or anthropogenic

492 sources that cannot be ruled out. This source profile also included nonspecific oxidized species

493 such as oxalate. Therefore, a detailed description of MO-OOA, and more generally of aged SOA,

494 is not yet possible to achieve since this SOA fraction is represented mainly by ultimate oxidation

495 by-products (i.e. oxalate) and highly processed PM.

496 Finally, no evident correlation was observed for LO-OOA with any of the SOA sources identified

497 by PMF-combined data analysis, confirming that LO-OOA may not stand for a single source,

498 precursor or specific atmospheric process.

499

500 **5. Conclusions**

501 In this study, an advanced approach has been developed to investigate the OA sources using

502 ME-2 algorithm applied to a combined dataset including ACSM OA matrix (30-min time

503 resolution) and organic molecular markers from PM_{10} filter-based chemical analyses (4-h time

504 resolution) in their original time resolutions. This new methodology allowed resolution of 10 OA

505 factors, including POA sources such as primary traffic OA (PTOA), biomass burning OA

506 (BBOA), and one uncommonly-resolved OPOA factor related to wood combustion (OBBOA), as

507 well as 7 SOA factors (2 biogenic-SOA, 4 anthropogenic-SOA and1-highly processed SOA). A

508 clear identification of 54% of the total SOA fraction has been achieved thanks to this new

509 approach. Specifically, 28% of the total SOA fraction from 4 different SOA factors, seemed to be

510 directly related to combustion sources (biomass burning and/or traffic emissions), notably the

511 oxidation processes of toluene and phenolic compounds.

512   Overall, good agreement for both, primary and secondary sources was observed between the

513   PMF combined data analysis and the conventional PMF-ACSM approach. An improvement in

514   the source apportionment of traffic emissions has been obtained with the clear identification of

515   the primary traffic OA while the PMF-ACSM elucidates a proxy (HOA) for this source. The

516   PMF-combined data analysis also indicated that OBBOA could represent more than 80% of the

517   primary biomass burning fraction, suggesting that wood combustion PM is mainly present in the

518   atmosphere as OPOA under the conditions during the study period.

519   For secondary sources, the comparison with PMF-ACSM highlighted the significant

520   advantage of the PMF-combined data analysis by resolving 7 SOA factors instead of 2 SOA

521   factors (MO-OOA, LO-OOA). Moreover, the results confirmed that MO-OOA was mainly

522   associated with ultimate oxidation by-products and highly processed aerosols, also possibly

523   accounting for a small fraction from marine SOA.

524   Finally, the use of the combined dataset provided valuable insights into the processes involved

525   in the SOA formation and their sources. It should then be promoted and further developed (e.g.,

526   using more molecular markers, such as organo-sulphates or organo-nitrates) to conduct future OA

527   source apportionment studies.

528

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Fig. 1. Average contributions (left) and temporal evolution (right) of the identified sources to OA fraction. PTOA: primary traffic OA; BBOA: biomass burning OA; OBBA: oxidized BBOA; BSOA-1: biogenic SOA-1 (marine-rich); BSOA-2: biogenic SOA-2 (isoprene-rich); ASOA-1: anthropogenic SOA-1 (nitro-PAHs); ASOA-2: anthropogenic SOA-2 (oxy-PAHs); ASOA-3: anthropogenic SOA-3 (phenolic compounds oxidation); ASOA-4: anthropogenic SOA-4 (toluene oxidation); SOA-5 (aged SOA).

Fig. 2. Average contributions (left) and temporal evolution (right) of the identified sources to OA mass concentrations from PMF-ACSM.

Fig. 3. Chemical profiles and temporal evolutions of OA factors identified at SIRTA. Chemical profiles: left part, ACSM mass fragments (log scale); right part, organic marker contributions. PTOA: primary traffic OA; BBOA: biomass burning OA; OBBOA: oxidized BBOA; BSOA-1: biogenic SOA-1 (marine-rich); BSOA-2: biogenic SOA-2 (isoprene-rich).

Fig. 4. Chemical profiles and temporal evolutions of OA factors identified at SIRTA (continued). Chemical profiles: left part, ACSM mass fragments (log scale); right part, organic marker contributions. ASOA-1: anthropogenic SOA-1 (nitro-PAHs); ASOA-2: anthropogenic SOA-2 (oxy-PAHs); ASOA-3: anthropogenic SOA-3 (phenolic compounds oxidation); ASOA-4: anthropogenic SOA-4 (toluene oxidation); SOA-5 (aged SOA).

Fig. 5. Diel profiles of anthropogenic OA factors resolved from the PMF-combined data analysis at Paris-SIRTA. Error bars represent ± 2 SD (standard deviation). PTOA: primary traffic OA; BBOA: biomass burning OA; OBBOA: oxidized BBOA; ASOA-1: anthropogenic SOA-1 (nitro-PAHs); ASOA-2: anthropogenic SOA-2 (oxy-PAHs); ASOA-3: anthropogenic SOA-3 (phenolic compounds oxidation); ASOA-4: anthropogenic SOA-4 (toluene oxidation).

Fig. 6. Triangle plot showing f_{44} vs. f_{43}. f_{44} and f_{43} represent the fraction of m/z 44 and m/z 43 in OA, respectively. The dots are coloured according to the sampling dates. PTOA: primary traffic emissions; BBOA: biomass burning OA; OBBOA: oxidized BBOA; BSOA-1: biogenic SOA-1 (marine-rich); BSOA-2: biogenic SOA-2 (isoprene-rich); ASOA-1: anthropogenic SOA-1 (nitro-

PAHs); ASOA-2: anthropogenic SOA-2 (oxy-PAHs); ASOA-3: anthropogenic SOA-3 (phenolic compounds oxidation); ASOA-4: anthropogenic SOA-4 (toluene oxidation); SOA-5 (aged SOA).

Fig. 7. Temporal evolutions of primary biomass burning- (BBOA$_{ACSM}$ vs [BBOA + OBBOA]$_{combined}$) and primary traffic emissions-related (HOA vs PTOA) POA factors identified using both PMF-ACSM and PMF- combined data analyses.

Legend:
- HOA (hydrocarbon-like OA)
- BBOA (biomass burning OA)
- LO-OOA (low oxidized oxygenated OA)
- MO-OOA (more oxidized oxygenated OA)