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1 Polyols and glucose particulate species as tracers of primary 2 biogenic organic aerosols at 28 French sites

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33 **Abstract.** A growing number of studies is using specific primary sugar species, such as sugar alcohols or primary
34 saccharides, as marker compounds to characterize and apportion primary biogenic organic aerosols (PBOA) in the
35 atmosphere. To better understand their annual cycles, as well as their spatio-temporal abundance in terms of
36 concentrations and sources, we conducted a large study focusing on three major atmospheric primary sugar
37 compounds (i.e., arabitol, mannitol and glucose) measured in various environmental conditions on about 5,300
38 filter samples collected at 28 sites in France. Our results show significant atmospheric concentrations of polyols
39 (defined here as the sum of arabitol and mannitol) and glucose at each sampling location, highlighting their
40 ubiquity. Results also confirm that polyols and glucose are mainly associated with the coarse rather than the fine
41 aerosol mode. At nearly all sites, atmospheric concentrations of polyols and glucose display a well-marked
42 seasonal pattern, with maximum concentrations from late spring to early autumn, followed by an abrupt decrease
43 in late autumn, and a minimum concentration during wintertime. Such seasonal patterns support biogenic
44 emissions associated with higher biological metabolic activities (e.g., sporulation, growth, etc.) during warmer
45 periods. Results from a previous comprehensive study using Positive Matrix Factorization (PMF) based on an
46 extended aerosol chemical composition dataset of up to 130 species for 16 of the same sample series has also been
47 used in the present work. The Polyols-to-PM_{PBOA} ratio is ~~about~~ 0.024 ± 0.010 on average for all sites, with no clear
48 distinction between traffic, urban or rural typology. Overall, even if the exact origin of the PBOA source is still
49 under investigation, it appears to be an important source of PM, especially during summertime. Results also show
50 that PBOA are significant sources of total OM in PM₁₀ (13 ± 4 % on a yearly average, and up to 40 % in some
51 environments in summer) at most of the investigated sites. The mean PBOA chemical profile is clearly dominated
52 by contribution from organic matter (OM) (78 ± 9 % of the mass of the PBOA PMF factor on average), and only a
53 minor contribution from dust class (3 ± 4 %), suggesting that ambient polyols are most likely associated with
54 biological particle emissions (e.g., active spore discharge) rather than soil dust resuspension.

55 **1. Introduction**

56 Airborne particles (or particulate matter, PM) are of major concern due to their multiple effects on climate and
57 adverse human health impacts (Boucher et al., 2013; Cho et al., 2005; Ntziachristos et al., 2007). The diversity of
58 PM impacts is closely linked to their complex and highly variable nature: size distribution, concentration and
59 chemical composition, or specific surface properties. PM consists of inorganic and elemental substances, and a
60 large fraction made of carbonaceous matter (organic carbon (OC) and elemental carbon (EC)) (Franke et al., 2017;
61 Putaud et al., 2004a; Yttri et al., 2007a). Substantial amounts of atmospheric organic matter (OM) remain
62 unidentified and uncharacterized at the molecular level. In most studies, a maximum of only 20 % of particulate
63 OM mass can generally be speciated and quantified (Alfarra et al., 2007; Fortenberry et al., 2018; Liang et al.,
64 2017; Nozière et al., 2015). This detailed composition of OM and its spatial and seasonal distribution can give
65 important insights on the adverse effects of PM. So far, the majority of air pollution studies have focused on
66 organic atmospheric particles associated with anthropogenic and secondary sources, whereas a significant fraction
67 of OM can also be associated with primary emissions from biogenic sources (Bauer et al., 2008a; Jaenicke, 2005;
68 Liang et al., 2016). Therefore, the characterization of primary OM biogenic sources at the molecular level is still
69 limited (Fuzzi et al., 2006; Liang et al., 2017; Zhu et al., 2015), and should be further investigated for a better
70 understanding of aerosol sources and formation processes.

71 Primary biogenic organic aerosols (PBOA) are emitted directly from the biosphere to the atmosphere where they
72 are ubiquitous and participate in many atmospheric processes (Elbert et al., 2007; Fröhlich-Nowoisky et al., 2016).
73 Additionally, their inhalation has long been associated with human respiratory impairments (e.g., asthma,
74 aspergillosis, etc.) (Després et al., 2012; Morris et al., 2011). PBOA comprise living and dead microorganisms
75 such as bacteria, fungi, viruses, bacterial and fungal spores, and microbial fragments, endotoxins, mycotoxins, or
76 pollens (Elbert et al., 2007; Jaenicke, 2005; Morris et al., 2011). In most semi-urban European sites, PBOA can
77 account for up to 25 % of the atmospheric aerosol mass, in the size range of 0.2 to 50 μm (Fröhlich-Nowoisky et
78 al., 2016; Jaenicke, 2005; Huffman et al., 2012; Manninen et al., 2014; Morris et al., 2011). However, their sources
79 and contribution to total airborne particles are still poorly documented, partly because of the difficulty to recognize
80 them by conventional microbiological methods (cell culture, microscopic examination, etc.) (Di Filippo et al., 2013;
81 Heald and Spracklen, 2009; Jia et al., 2010a).

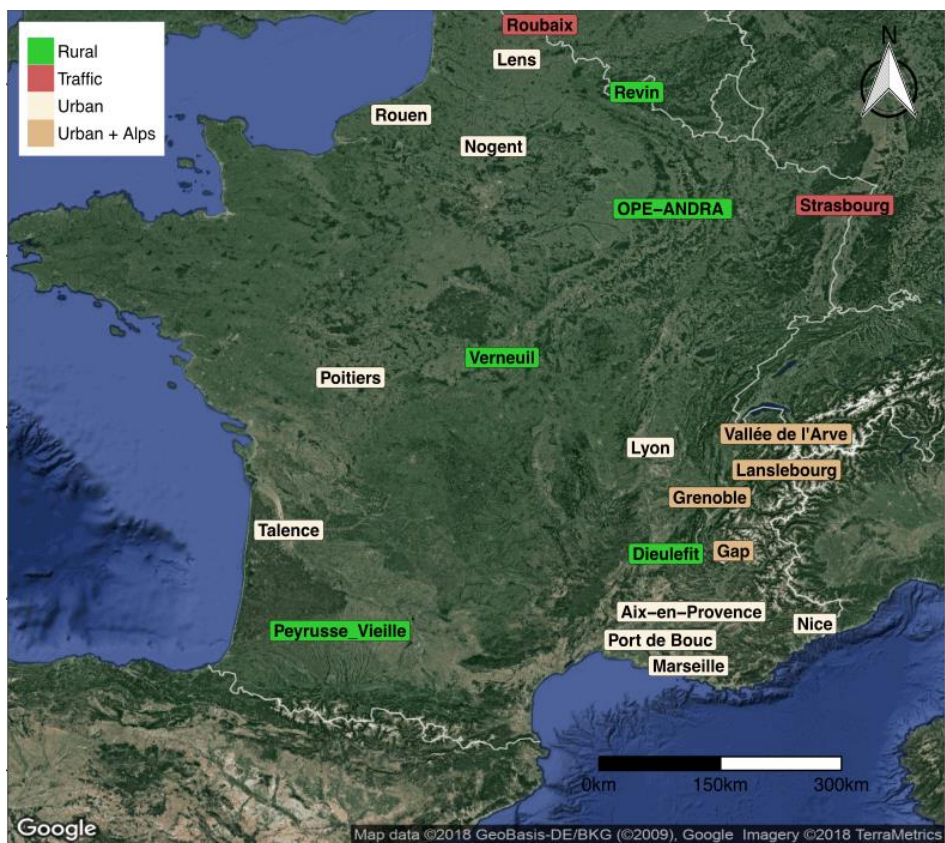
82 Several specific chemical components, such as primary sugar compounds (i.e., primary saccharides and sugar
83 alcohols) emitted persistently from biogenic sources, have long been suggested as powerful and unique biomarkers
84 in tracing sources, and abundances of PBOA as well (Bauer et al., 2008a; Medeiros et al., 2006; Simoneit et al.,
85 2004b; Zhang et al., 2010; Zhu et al., 2016). For instance, ambient concentrations of glucose have been used as
86 markers for plant materials (such as pollen, leaves, and their fragments) or soil emissions from several areas in the
87 world (Fu et al., 2012; Jia et al., 2010a, 2010b; Pietrogrande et al., 2014; Rathnayake et al., 2017). Many studies
88 indicated that glucose is the most abundant monosaccharide in vascular plants, where it serves as the common
89 energy material, and an important source of carbon for soil active microorganisms (such as bacteria or fungi) (Jia
90 et al., 2010a; Medeiros et al., 2006; Pietrogrande et al., 2014; Zhu et al., 2015). Additionally, sugar alcohols (also
91 called polyols) including arabitol and mannitol have been proposed as markers for airborne fungi, and are widely
92 used to quantify their contributions to PBOA mass (Bauer et al., 2008a, 2008b; Golly et al., 2018; Srivastava et
93 al., 2018; Zhang et al., 2010). These sugar alcohols have also been found to correlate very well with fluorescent
94 PBOA in the ultraviolet aerodynamic particle sizer (UV-APS) and wideband integrated bioaerosol sensor (WIBS-
95 3) online studies, particularly in rainy periods (Gosselin et al., 2016), favoring microbial sporulation (such as fungi
96 belonging to Ascomycota and Basidiomycota phyla) (China et al., 2016; Elbert et al., 2007; Jones and Harrison,
97 2004). Polyols are produced in large amounts by many fungi and bacteria, and several functions have been
98 described for these compounds, such as common energy storage materials, intracellular protectants against
99 stressful conditions (e.g., heat or drought), storage or transport of carbohydrates, quencher of oxygenated reactive
100 species, or regulators of intracellular pH by acting as a sink or source of protons (Jennings et al., 1998; Medeiros
101 et al., 2006; Vélèz et al., 2007). Hence, polyols, especially arabitol and mannitol, may represent a significant
102 fraction of the dry weight of fungi, and mannitol can contribute between 20 to 50 % of the mycelium dry weight
103 (Ruijter et al., 2003; Vélèz et al., 2007). However, polyols are also often identified in the lower plants (leaves,
104 pollens) and green algal lichens (Medeiros et al., 2006; Vélèz et al., 2007; Yang et al., 2012). The primary sugar
105 compounds (defined as polyols and primary saccharide species) are thought to be relatively stable in the
106 atmosphere (Wang et al., 2018), although studies investigating their atmospheric lifetime are quite limited. One
107 previous laboratory study has been conducted by the US-EPA to evaluate the stability of these chemicals on filter
108 material exposed to gaseous oxidants as well as in aqueous solutions (simulating clouds and fog droplet chemistry).
109 Findings of this former study have shown that primary sugar compounds remain quite stable up to 7 days (the

110 extent of the testing period), pointing out their suitability for use as tracers of atmospheric transport (Fraser, 2010).
111 With all of this information, the use of primary sugar compounds (such as mannitol, arabinol, glucose, etc.) as
112 suitable tracers of PBOA is generally acknowledged (Jia and Fraser, 2011; Zhu et al., 2015, 2016).
113 Although atmospheric concentrations of polyols, including arabinol and mannitol, as well as that of some primary
114 monosaccharides (e.g., glucose), have been previously quantified as part of several studies in various environments
115 including urban/suburban, rural, rainforest, mountain, and marine areas (Fu et al., 2012; Graham et al., 2003; Jia
116 et al., 2010a, 2010b; Liang et al., 2016; Pietrogrande et al., 2014; Simoneit, 2004a, 2004b; Verma et al., 2018;
117 Yttri et al., 2007b; Zhu et al., 2015), large datasets investigating their annual cycles and spatial distributions are
118 still limited. Such information could give important insights on environmental factors influencing their
119 atmospheric levels such as climate and biotope, and therefore help to elucidate patterns regarding their major
120 sources and atmospheric emission pathways. Even if numerous sources and emission mechanisms have been
121 widely proposed, including among others, metabolic active microbial wet emissions, entrainment of farmland or
122 natural soils and associated microbiota (Elbert et al., 2007; Fu et al., 2013; Gosselin et al., 2016; Jia et al., 2010a,
123 2010b; Medeiros et al., 2006; Pietrogrande et al., 2014; Simoneit et al., 2004a, 2004b; Verma et al., 2018; Yttri
124 et al., 2007b), the dominant atmospheric input processes have not been yet sufficiently elucidated.
125 In this context, the present study was designed to provide a large overview of the spatial and seasonal variations
126 of polyols and glucose mass concentrations, as well as their contribution to the aerosol organic mass fraction in
127 France. To do so, data was collected at many sites in different environments (rural, traffic, urban), in order to
128 represent various sampling conditions in terms of site typologies and meteorological conditions. Thanks to the
129 availability of results from an extended Positive Matrix Factorization (PMF) analysis performed for the
130 corresponding datasets, the overall contributions of the main polyols and glucose emission sources could also be
131 investigated in light of their spatial patterns. To the best of our knowledge, this is the first study providing such an
132 extended phenomenology of these compounds over multiple sites with different typologies.

133 **2. Material and methods**

134 **2.1 Aerosol sampling**

135 Ambient aerosol samples considered in the present work come from different research and monitoring programs,
136 conducted over the last 5 years in France (Figure 1). Each program includes at least one-year of field sampling,
137 providing a total number of 5,343 daily filter samples available for the sake of the present study. These sites offer
138 diverse conditions in terms of typologies (i.e., rural, traffic, urban sites, Alpine valley environments, etc.), local
139 climate and vegetation types and were selected in order to cover the complex and variable national environmental
140 conditions. These sites are assumed to represent typical environmental conditions in France, and our
141 observations/and general tendency could therefore be extrapolated to neighboring western European countries
142 presenting quite homogeneous environmental conditions.



143
 144 **Figure 1: Map of sampling site locations in France. Green: rural background, red: traffic, wheat: urban background**
 145 **and dark wheat: urban background in Alpine valley sites. The areas of Grenoble (Grenoble_LF, Grenoble_CB and**
 146 **Grenoble_VIF) and Vallée de L'Arve (Marnaz, Passy and Chamonix) include 3 sites each. The area of Marseille**
 147 **includes four sites: Marseille, Mallet, Meyreuil and Gardanne.**

148 The site of OPE-ANDRA is a specific monitoring observatory in a rural environment, without any village or
 149 industry within several kilometers (description available from: <http://www.andra.fr>). All other sites correspond to
 150 stations of regional air quality monitoring networks (AASQA). The availability of filter samples was variable from
 151 one site to the other one, depending on the sampling frequency (typically every third or sixth day). Filter collection
 152 was conducted within the PM₁₀ or the PM_{2.5} aerosol size fraction, depending on the investigated site (Table SI-1).
 153 Moreover, co-located and simultaneous PM₁₀ and PM_{2.5} samplings were conducted at OPE-ANDRA and Revin,
 154 allowing to investigate the distribution of primary sugar compounds between the fine and the coarse aerosol size
 155 fractions at these two sites.

156 Ambient aerosols were collected onto quartz fiber filters (Tissu-quartz PALL QAT-UP 2500 150 mm diameter),
 157 preheated at 500 °C for 4 h minimum before use. After collection, all filter samples were wrapped in aluminum
 158 foils, sealed in zipper plastic bags and stored at <4°C until further chemical analysis. Field blank filters were also
 159 collected, at least once a month, using the same handling procedure as for PM samples. More detailed information
 160 on the sampling periods, air sampler, number of filters and nature of PM samples are provided in Table SI-1 and
 161 Fig. SI-1.

162 **2.2 Chemical analyses**

163 PM samples were analyzed for various chemical species using sub-sampled fractions of the collection filters. In
 164 the frame of the present study, the carbonaceous matter (organic carbon (OC) and elementary carbon (EC)) was
 165 analyzed using a thermo-optical method on a Sunset Lab analyzer (Birch and Cary, 1996) as described by Aymoz

166 et al. (2007), using the EUSAAR2 temperature program (Cavalli et al., 2010), except for the five sites of Northern
167 France where the NIOSH870 protocol was employed (Birch and Cary, 1996). OM contents were then estimated
168 by multiplying the organic carbon mass concentrations by a fixed factor, with $OM = 1.8 \times OC$. This OM-to-OC
169 ratio value of 1.8 was chosen based on previous studies performed in France (Favez et al., 2010; Petit et al., 2015
170 and reference therein) and around the world. (e.g., Aiken et al., 2008; Li et al., 2018; Ruthenburg et al., 2014;
171 Vlachou et al., 2018), with a typical range of 1.2-2.4 values.

172 For the analysis of anhydrosugars, sugar alcohols, and primary saccharides, filter punches (typically of about 10
173 cm²) were first extracted into ultrapure water, then filtered using a 0.22 μm Acrodisc filter. Depending on the site,
174 analyses were conducted either by IGE (Institut des Géosciences de l'Environnement) or by LSCE (Laboratoire
175 des Sciences du Climat et de l'Environnement) (Table SI-1). At IGE, extraction was performed during 20 min in
176 a vortex shaker and analyses were achieved using ~~a~~ High-Performance Liquid Chromatography (HPLC) with
177 Pulsed Amperometric Detection. A first set of equipment was used until March 2016, consisting of a Dionex
178 DX500 equipped with three columns Metrosep (Carb 1-Guard + A Supp 15-150 + Carb 1-150), the analytical run
179 being isocratic with 70 mM sodium hydroxide eluent, followed by a gradient cleaning step with a 120 mM NaOH
180 eluent. This analytical technique enables to detect anhydrous saccharides (levoglucosan, mannosan, galactosan),
181 polyols (arabitol, sorbitol, mannitol), and glucose (Waked et al., 2014). A second set of equipment was used after
182 this date, with a Thermo-Fisher ICS 5000⁺ HPLC equipped with 4 mm diameter Metrosep Carb 2 × 150 mm
183 column and 50 mm pre-column. The analytical run is isocratic with 15 % of an eluent of sodium hydroxide
184 (200 mM) and sodium acetate (4 mM) and 85 % water, at 1 mL min⁻¹. This method allows for additional separation
185 and quantification of erythritol, xylitol, and threulose. At LSCE, extraction was performed during 45 min by
186 sonication and analyses were achieved using an ion chromatography (IC) instrument (DX600, Dionex) with Pulsed
187 Amperometric Detection (ICS3000, Dionex). A CarboPAC MA1 column has been used (4 × 250 mm, Dionex), the
188 analytical run being isocratic with 480 mM sodium hydroxide eluent. This analytical technique enables to detect
189 anhydrous saccharides (levoglucosan, mannosan, galactosan), polyols (arabitol, mannitol), and glucose.

190 Field blank filters were handled as real samples for quality assurance. The present data were corrected with field
191 blanks. The reproducibility of the analysis of primary sugar species (polyols, glucose), estimated from the analysis
192 of extracts of 10 punches from the same filters is generally in the range of 10-15 %.

193 Additional chemical analyses were conducted for most of the sites, allowing to quantify up to 130 different
194 chemical species (Calas et al., 2018). 30- 35 chemical species were then selected in order to achieve PMF analyses
195 as discussed hereafter.

196 **2.3 Statistical analysis**

197 Species concentration measurements were first analyzed for normality using Shapiro-Wilk's method with the
198 statistical program *R studio interface* (version 3.4.1). Since data were generally not distributed normally, we used
199 non-parametric statistical methods. The strength of the relationship between species concentrations was
200 investigated using the non-parametric Spearman rank correlation method. Multiple mean comparison analyses
201 were performed with the Kruskal-Wallis test method. Statistical significance was set at $p < 0.05$.

202 Positive Matrix Factorization for the source apportionment of the PM was previously performed at several sites of
203 this study, as part of the [SOURCES](#) (Favez et al., 2016; Salameh et al., in prep.) and [DECOMBIO](#) (Chevrier, 2017)
204 projects. We used the US EPA PMF 5.0 software (US EPA, 2015), following the general recommendation

205 guidelines of the European Joint Research Centre (JRC) (Belis et al., 2014). Briefly, the SOURCES program aimed
206 at performing source apportionment at 15 sites using a harmonized methodology, i.e., using the same chemical
207 species, uncertainties, constraints, and criteria for factor identification. The PMF conducted within SOURCES
208 project uses about 30 different species (Table SI-6), including carbonaceous fraction (OC, EC), ions (Cl^- , NO_3^- ,
209 SO_4^{2-} , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}), organic markers (polyols i.e., sum of arabitol, mannitol and sorbitol; levoglucosan;
210 mannosan) and metals (Al, As, Ba, Cd, Co, Cs, Cu, Fe, La, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, V, Zn). The
211 PMF conducted within the DECOMBIO project, for the sites of Marnaz, Chamonix, and Passy, used aethalometer
212 (AE 33) measurements instead of EC (Chevrier, 2016). This complementary measure gives the total black carbon
213 (BC), thus enabling the deconvolution of BC concentrations into its two main constituents: wood-burning BC
214 (BC_{wb}) and fossil-fuel BC (BC_{ff}) (Sandradewi et al., 2008). For graphical simplicity, BC_{wb} and BC_{ff} were summed
215 up and labeled as EC in the following Figures. PMF modelling was performed separately for each site. Statistical
216 significance was validated with bootstrap higher than 80 % for each factor. Detailed methodology and results about
217 these studies are given in their respective papers (Chevrier, 2017; Favez et al., 2016; Salameh et al., in prep.). It
218 should be noted that glucose was not included in the final solution for any of these PMF, since it generally produced
219 statistical instability of the solutions (this point is further discussed in Sect. 3.2).

220 The PMF analysis took advantage of the ME-2 algorithm to add constraints to different chemical profiles (see
221 Tables SI-3 and SI-4 for details). Mainly soft constraints were applied in order to add some prior knowledge about
222 the emission sources and “clean” the different profiles without forcing the model toward an explicit solution. In
223 particular, the polyol concentrations were “pulled up maximally”, while levoglucosan and mannosan were set to
224 zero, and EC was “pulled down maximally” in the PBOA factor. This was achieved to avoid mixing with the
225 biomass burning factor as well as possible influences of unrealistic high contributions of EC to PBOA. Other
226 constraints were added parsimoniously to other factors, targeting specific proxies of sources (Table SI-4).

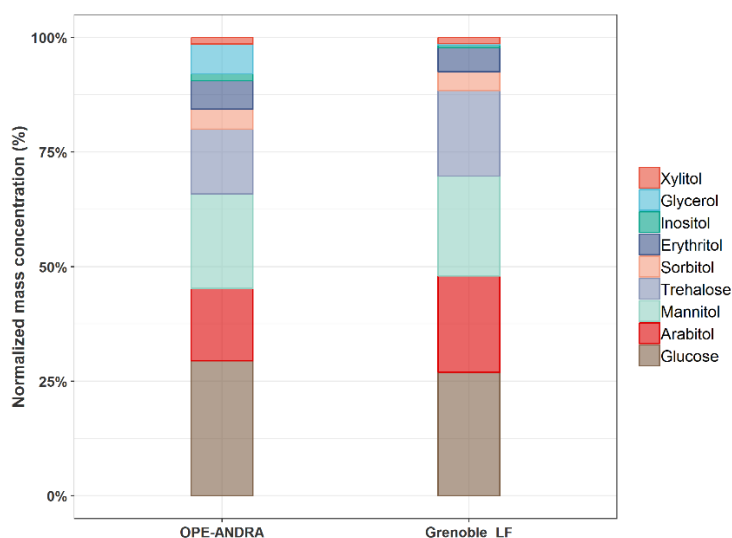
227 As for the general results of this large PMF study, we identified some well-known sources for almost all the sites
228 (biomass-burning, road traffic, secondary inorganics, dust and sea salt). Two other less-common factors were
229 identified for all sites: secondary biogenic aerosols (probably from marine origin), traced mainly by the presence
230 of MSA, and PBOA, traced by the presence of more than 90% of the polyols total mass in the factor. Table SI-5
231 and Fig. SI-4 present more detailed description of the chemical tracers in each factor, together with their yearly
232 average contribution for each site, respectively. Hereafter, only the PBOA chemical profile will be extensively
233 investigated. The uncertainties of this PBOA factor are discussed below and its stability is presented in Fig. SI-5.
234 Bootstrap analysis based on 100 resampling runs evidenced the very high stability of this PBOA factor since the
235 PBOA initial constrained factor was mapped to PBOA bootstrap factor (BF) more than 99% of the time.

236 **3. Results and discussion**

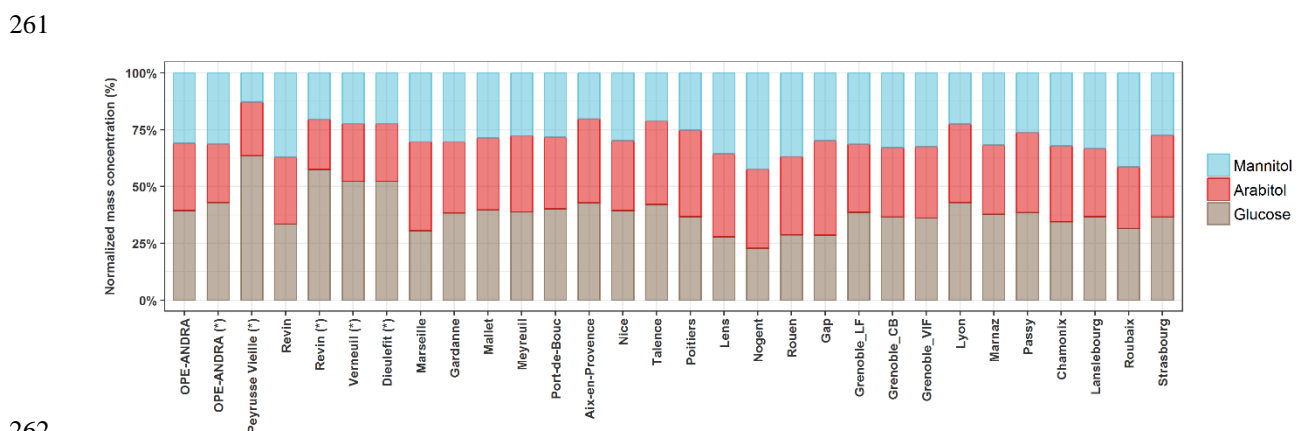
237 **3.1 Relative distribution between sugar alcohols and glucose**

238 Figure 2 presents an overview of the relative mass concentration distributions of individual chemical species
239 quantified at two sites with very different characteristics, an urban site in Grenoble and the rural site of OPE-
240 ANDRA. Data are presented for the warmer season (e.g., during summer and fall), when concentrations were at
241 their maximum (see Sect. 3.4). Glucose is the most abundant species measured (average $37.6 \pm 26.4 \text{ ng m}^{-3}$),
242 accounting on average for 25 % of primary sugar compounds (SC) total mass at both sites. Mannitol

243 (37.3±24.6 ng m⁻³) and arabitol (32.0±22.2 ng m⁻³), are the second and third most abundant species, accounting
 244 respectively for 25 and 23 % of SC mass. Trehalose is relatively abundant in samples from these two sites
 245 (20.1±16.2 ng m⁻³), accounting for 14 % of SC mass, but in general its concentration is frequently below the limit
 246 of quantification for samples from other sites in France. The other identified polyols (i.e., erythritol, inositol,
 247 glycerol, sorbitol, and xylitol) present lower concentration levels (4.9±2.1 ng m⁻³), corresponding altogether to
 248 13 % of SC total mass.
 249 Such ambient mass concentration distribution patterns are similar (but with variable intensities) to those previously
 250 reported for aerosol samples collected at various locations around the world. For example, Verma et al. (2018)
 251 found that glucose, and arabitol together with mannitol, contributed to 16.7 and 48.1 %, respectively, of total
 252 primary sugar compounds in aerosols from Chichijima Island. Similarly, Yttri et al. (2007b) showed that glucose
 253 and the pair arabitol-mannitol were the main contributors of total primary monosaccharides and sugar alcohols in
 254 aerosols collected from four various background sites in Norway. In addition, Carvalho et al. (2003) reported that
 255 arabitol, mannitol and glucose are the most dominant primary sugar compounds in aerosols from rural background
 256 and boreal forest sites in Germany and Finland, respectively.



257
 258 **Figure 2: Overview of relative mass distributions of individual primary sugar alcohols and saccharide compounds**
 259 **quantified in PM₁₀ samples at two sites over summer and autumn periods (June to November) corresponding to**
 260 **maximal atmospheric concentrations of sugar alcohols/saccharide compounds.**

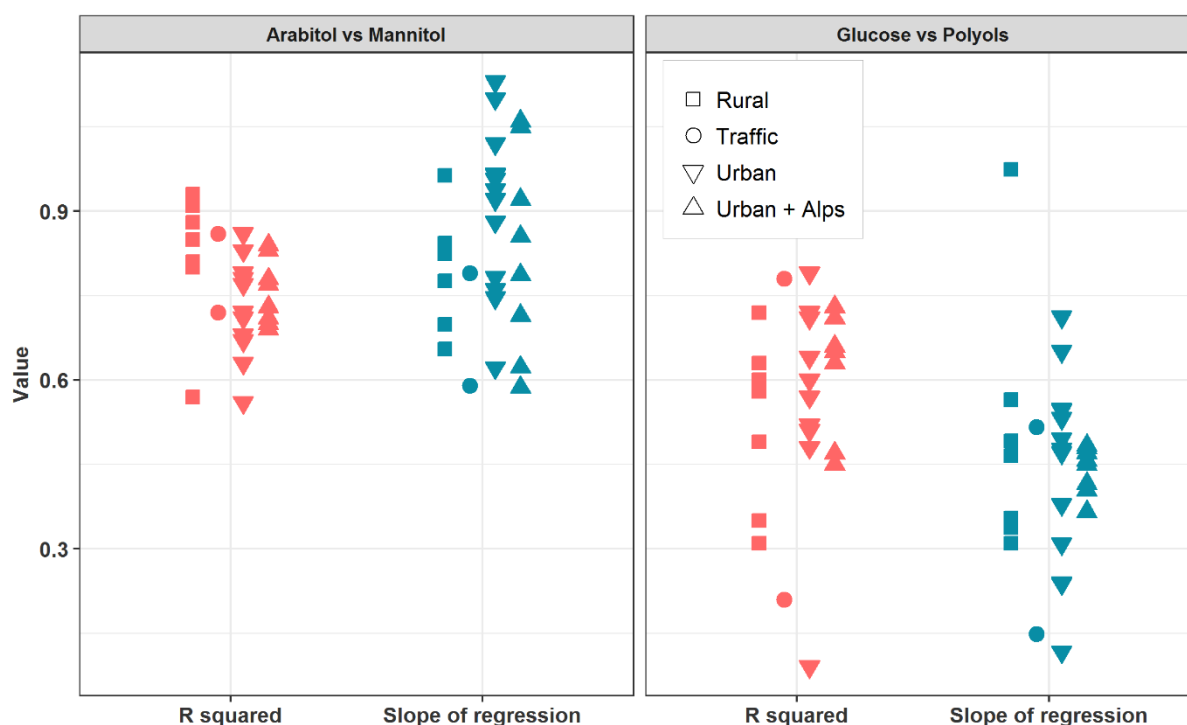


262
 263 **Figure 3: Average mass concentration distributions of arabitol, mannitol, and glucose. Symbol (*) indicates PM_{2.5}**
 264 **aerosol samples. Only data for warmer season (June to November), corresponding to maximal atmospheric**
 265 **concentration of polyols and glucose are shown.**

266 Although various primary sugar alcohols and saccharides have been detected and quantified for most of the
267 investigated sites, the following study focuses only on the three major and ubiquitous species, namely arabitol,
268 mannitol and glucose. Figure 3 presents their average relative contributions at all sites, for the warmer period,
269 displaying very similar features at a first glance. However, discrepancies could be observed from site to site, as
270 discussed in following sections.

271 **3.2 Relationships between selected primary sugar compounds**

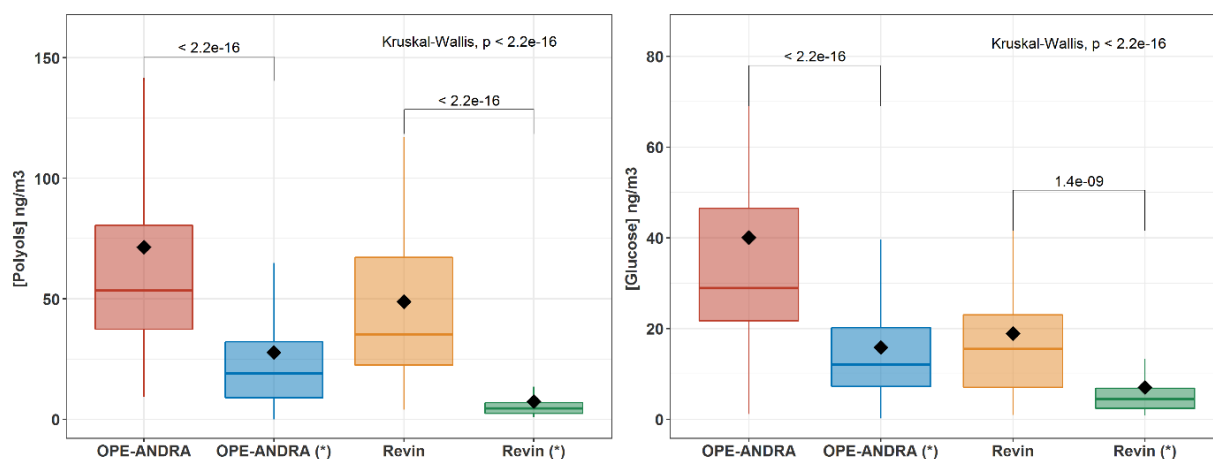
272 Figure 4 summarizes linear correlations obtained between arabitol and mannitol concentrations at each site during
273 the warmer period. Medium to very high coefficients of determination could be observed ($0.58 \leq R^2 \leq 0.93$; $30 \leq$
274 $n \leq 143$ or $45 \leq n \leq 341$ for $PM_{2.5}$ and PM_{10} series, respectively), with slopes in a rather narrow range (between
275 0.59 and 1.10), and quite low intercepts (always below 9 ng m^{-3}). Such covariations indicate that both species are
276 most probably co-emitted, by one or several type(s) of sources, at each site during the summer-autumn period.
277 These observations are in agreement with previous studies also showing strong covariations between arabitol and
278 mannitol (Kang et al., 2018; Verma et al., 2018; Zhu et al., 2015). Therefore, it seemed reasonable to consider both
279 species together, so that their concentrations are summed up and labelled as "polyols" in the following sections.
280 Conversely, linear correlations between glucose and polyols concentrations are generally weaker
281 ($0.10 < R^2 \leq 0.78$), with slopes varying over a much larger range (between 0.12 and 0.94), and variable intercepts
282 (between -5.6 and 16.4 ng m^{-3}). This suggests that glucose concentrations might follow a different pattern
283 compared to that of polyols, either due to different emission sources, or different chemical stability in the
284 atmosphere. It is therefore reasonable to keep glucose as a separate chemical species in the following discussion.
285 It should be emphasized that the variability in the slope of the regressions between the chemical concentrations is
286 most probably related to the emissions and atmospheric processing. Particularly in the case of mannitol and
287 arabitol, they may be influenced by biogenic or biotope characteristics. Nevertheless, no evident relationship
288 between the slope values and the typology or the geographical location of the sites could be observed (Figure 4).



289
 290 **Figure 4: Linear regression analysis between selected primary sugar compounds mass concentrations (i.e., arabitol,**
 291 **mannitol and glucose) during summer and autumn seasons (June to November), for all the sites considered in this study.**

292 **3.3 Relative distributions between PM₁₀ and PM_{2.5}**

293 Figure 5 shows the average PM₁₀ and PM_{2.5} concentrations of polyols and glucose at OPE-ANDRA and Revin
 294 during the summer and autumn seasons. The polyols mass concentrations ranged from 7.5±10.9 to 27.8±33.3 ng m⁻³
 295 in PM_{2.5}, and from 48.9±38.2 to 73.5±61.8 ng m⁻³ in PM₁₀, in Revin and OPE-ANDRA sites, respectively. PM₁₀-
 296 to-PM_{2.5} ratios were then on average of about 3 to 5. Similar size distribution patterns, with variable intensity, were
 297 observed for glucose (Fig. 5). These results indicate that polyols and glucose are mainly associated with the coarse
 298 PM fraction. This observation is in good agreement with several previous investigations where polyols (especially
 299 arabitol and mannitol), together with glucose, were prevalent in the coarse fraction (Fu et al., 2012; Fuzzi et al.,
 300 2007; Pio et al., 2008; Yttri et al., 2007b). However, Carvalho et al. (2003) reported different size distributions for
 301 polyols and glucose, with variable fine or coarse mode maxima depending upon sampling location. For instance,
 302 maximum atmospheric concentrations of mannitol were associated to fine and coarse aerosols from boreal forest
 303 (Finland) and rural background sites (Germany), respectively. The authors hypothesized that these observations
 304 are due to different assemblages of dominant fungal biota (with variable aerodynamic characteristics) at different
 305 sites. Some other previous studies showed aerodynamic diameters typically ranging from 2 to 10 μm, even though
 306 a few airborne bacterial/fungal spores could exceed that size (Bauer et al., 2008a; Elbert et al., 2007; Huffman et
 307 al., 2012; Zhang et al., 2015).



308
 309 **Figure 5: Box plots of mass concentrations of polyols (left) and glucose (right) in PM₁₀ and PM_{2.5} (with symbol (*)**
 310 **samples). Black markers inside each boxplot indicate the mean concentration value, while the top, middle and bottom**
 311 **lines of the box represent the 75th, median and 25th percentile, respectively. The whiskers at the top and bottom of the**
 312 **box extend from the 95th to the 5th percentile. Number of samples were N = 123 for OPE-ANDRA and N = 87 for Revin,**
 313 **respectively. Statistical differences between average mass concentrations were analyzed with the Kruskal-Wallis**
 314 **methods (p < 0.05).**

315 Hence, although if the precise mechanisms of atmospheric emission of particulate polyols and glucose are not fully
 316 resolved, our observations are in good agreement with ambient mass concentrations of polyols and glucose being
 317 likely associated with biological particles, as already suggested elsewhere (Fu et al., 2012; Verma et al., 2018;
 318 Zhang et al., 2015). These species could enter into the atmosphere through either natural or anthropogenic
 319 resuspension of surface soils and associated bacterial/fungal spores (containing polyols and primary sugar
 320 compounds), or via a direct input resulting from microbial activities (e.g., sporulation). Another hypothesis would
 321 be the abrasion of leaves and the subsequent release of microbial organisms and plant debris (Fu et al., 2012;
 322 Medeiros et al., 2006; Simoneit et al., 2004b).

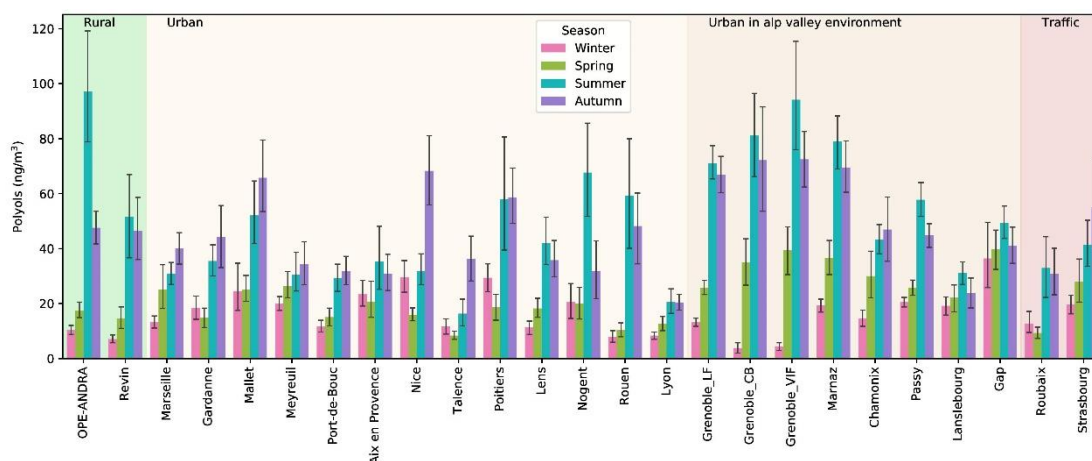
323 3.4 Spatial and seasonal distribution of atmospheric concentrations

324 3.4.1 Spatial and seasonal patterns of polyol concentrations

325 As illustrated in Fig. 6, significant concentrations of polyols were measured at each investigated site, evidencing
 326 the ubiquity of these organic compounds. The annual average concentration levels of polyols measured in PM₁₀
 327 aerosols at all sites ($33.2 \pm 33.5 \text{ ng m}^{-3}$; see Table SI-2) are within the range previously reported for urban and rural
 328 sites across Europe (Burshtein et al., 2011; Di Filippo et al., 2013; Pietrogrande et al., 2014; Yttri et al., 2007b,
 329 2011). Additionally, polyols mass concentrations clearly exhibit seasonal trends, with variable intensity according
 330 to the sampling sites. On a seasonal average, polyols are more abundant in summer ($46.8 \pm 43.6 \text{ ng m}^{-3}$) and autumn
 331 ($43.0 \pm 36.7 \text{ ng m}^{-3}$), followed by spring ($19.0 \pm 13.6 \text{ ng m}^{-3}$) and winter ($16.2 \pm 11.5 \text{ ng m}^{-3}$). The average
 332 concentrations of polyols are at least 2 to 3 times higher during summer or autumn months than during the cold
 333 months, with a ratio that can be as high as 8 to 10.

334 Previous studies also reported similar seasonal variation pattern for urban and rural aerosol samples collected at
 335 various locations. For example, Pashynska et al. (2002) measured higher atmospheric polyol (arabitol, mannitol)
 336 contents during late summer and autumn, in Belgium. Several other studies reported higher concentrations of
 337 polyols in summer than spring and winter time, in aerosols collected from Texas, USA and Jeju Island, respectively

338 (Fu et al., 2012; Jia et al., 2010a, 2010b). More recently, Liang et al. (2016) and Verma et al. (2018) also reported
 339 similar seasonal distributions for aerosols sampled in Beijing, China and north-western Pacific, respectively.
 340 The higher atmospheric polyols concentrations observed are likely due to the increased contribution from
 341 metabolically active microbial derived sources (fungi, bacteria, green algal lichens) as a result of external stressors
 342 such as heat, drought and relative moisture. Indeed, fungal and prokaryotic cells activities, including their growth
 343 and sporulation, are promoted by high temperature and humid conditions occurring in summer and autumn (China
 344 et al., 2016; Elbert et al., 2007b; Jones and Harrison, 2004; Rathnayake et al., 2017).
 345 As also evidenced from Fig. 6, atmospheric polyols concentrations do not present any significant seasonal
 346 differences related to the site typology (rural, traffic, urban sites with/without Alpine influences), or latitude. There
 347 is some tendency toward higher concentrations in summer in Alpine environments, but some other sites (like the
 348 rural site of OPE-ANDRA, in the North-East of France) can reach the same levels of concentrations. We tested
 349 several types of hierarchical classifications, including variables like monthly or seasonal mean polyols
 350 concentrations, the ratio arabitol-to-mannitol, or linear regression parameters (slope, R square) but none of them
 351 led to a simple clustering of the sites that would explain the variability of the concentrations.

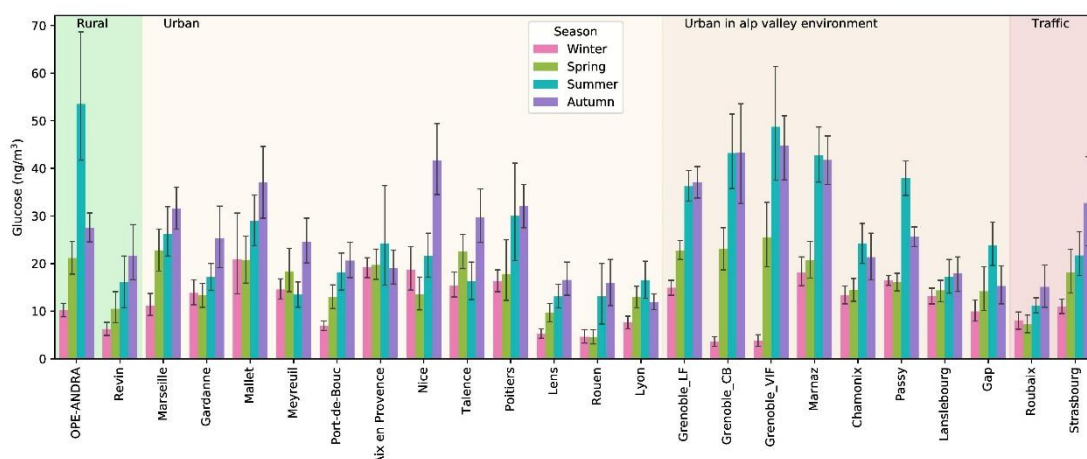


352
 353 **Figure 6: Spatial and seasonal distributions of atmospheric polyol average concentrations (ng m^{-3}) for various types of**
 354 **sites in France. Error bars correspond to standard deviations calculated with seasonal concentrations. Years of PM**
 355 **sampling campaigns are not concurrent at all sites (see Fig. SI-1). The seasons were defined as follows: Winter =**
 356 **December to February, Spring = March to May, Summer = June to August, and Autumn = September to November.**

357 3.4.2 Spatial and seasonal patterns of glucose concentrations

358 The annual average concentrations of glucose measured in PM_{10} aerosols at all sites ($20.4 \pm 15.6 \text{ ng m}^{-3}$; see Table
 359 SI-2) are comparable to those previously reported for various sites across Europe (Alves et al., 2006; Theodosi et
 360 al., 2018; Yttri et al., 2007b, 2011). Likewise polyols, the atmospheric concentrations of glucose also display
 361 seasonal and site-to-site variations (Fig. 7). The ambient seasonal mean concentrations (with standard deviations)
 362 of glucose are maximum in summer ($25.0 \pm 24.2 \text{ ng m}^{-3}$) and autumn ($24.6 \pm 19.8 \text{ ng m}^{-3}$), followed by spring
 363 ($15.8 \pm 12.4 \text{ ng m}^{-3}$) and winter ($12.6 \pm 10.2 \text{ ng m}^{-3}$). The summer / winter ratio for glucose seems generally lower
 364 than that of polyols, with higher ratios in the Alpine areas than in other parts of France. However, as for polyols,
 365 it remains difficult to classify the sites according to any criteria linked to site typology or latitude.
 366 The seasonal trend of glucose concentrations in the present work is similar to that recently observed for aerosols
 367 (PM_{10} or total suspended particles) collected at various environmental background (suburban, urban and coastal)

368 sites around the world (Liang et al., 2016; Srithawirat and Brimblecombe, 2015; Verma et al., 2018). On average,
 369 a wide range of daily glucose concentrations (expressed as min-max, mean) in PM₁₀ (0.1-297.2 ng m⁻³,
 370 20.4±15.6 ng m⁻³) were observed in the present study. These values are comparable to those in PM₁₀ (8.4-93.0,
 371 47.0 ng m⁻³) reported from an urban site in Norway (Yttri et al., 2007b). More recently, Liang et al. (2016) also
 372 reported similar concentrations in PM₁₀ (3.1-343.6, 46.2±27.5 ng m⁻³) from Beijing (China).
 373 The sources and formation processes of glucose in the atmosphere are not currently well known and are rarely
 374 discussed. Glucose is an important carbon source for soil metabolic active microbiota, and it is commonly present
 375 in vascular plants. Additionally, cellulose (a linear polymer made of glucose subunits linked by β-1,4 bonds) is
 376 one of the most important form of organic compounds in terrestrial ecosystems and a major plant structural
 377 polymer (Boex-Fontvieille et al., 2014). It can also be quite abundant in the atmosphere (Puxbaum and Tenze-
 378 Kunit, 2003). Hence, it is hypothesized that ambient glucose could be formed through active microbial (i.e.,
 379 bacteria, fungi, etc.) enzymatic hydrolysis of cellulose in plant debris. Consistent with these observations, glucose
 380 could be released into the atmosphere from both vascular plant materials (e.g., leaves, fruits, pollens, etc.) growing
 381 in spring and decomposing in autumn/summer, and soil microbiota, as already suggested elsewhere (Di Filippo et
 382 al., 2013; Jia et al., 2010a; Medeiros et al., 2006; Verma et al., 2018; Zhu et al., 2015).



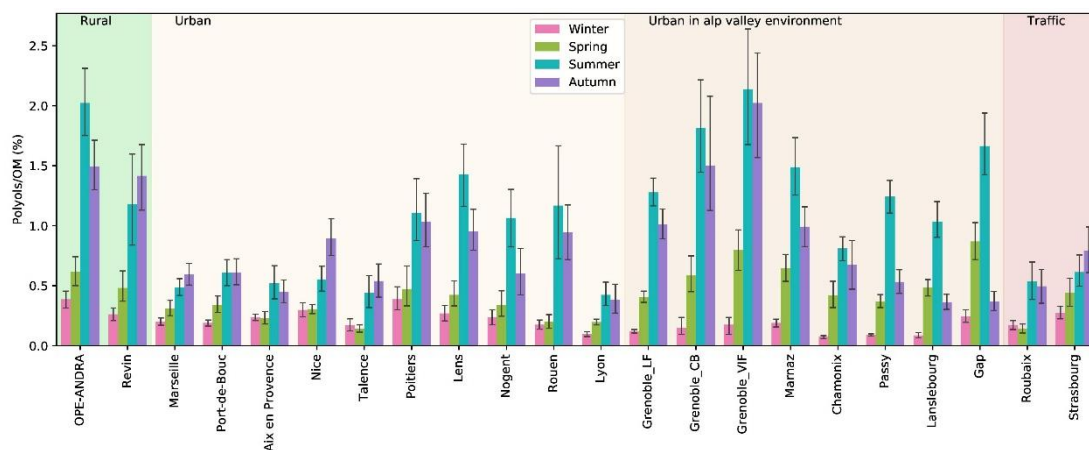
383
 384 **Figure 7: Spatial and seasonal distributions of atmospheric glucose levels (ng m⁻³) for various types of sites in France**
 385 **(except the site of Nogent, which presented too many missing values. Error bars correspond to standard deviations**
 386 **calculated with seasonal concentrations.**

387 3.4.3 Relative contributions to aerosol organic matter concentrations

388 The average contribution of polyols to the OM content of PM clearly displayed a seasonal behavior, as shown in
 389 Fig. 8. Here again, contributions are 2 to 10 times higher during summer and autumn compared to winter and
 390 spring, consistent with the assumption of higher emissions during these periods. The seasonal mean contribution
 391 of polyols to OM fluctuates from site to site, and accounts for 0.1 to 2.1 % of overall OM for these French sites
 392 (Fig. 8). Similarly, the seasonal mean concentrations of polyols together with glucose represent between 0.2 to
 393 3.1 % of total OM at these sites (Fig. SI-2). However, on a daily basis (Samake et al., in prep.), atmospheric polyols
 394 mass concentrations can represent up to 6.3 % of total OM in PM₁₀, indicating that polyols can be amongst the
 395 major molecular species identified in aerosol organic matter (Fig. SI-3). Again, we could not find any simple way
 396 to group the sites according to their characteristics (typology or latitude, or climatic region), in order to better

397 understand the drivers behind the variability of this mass fraction. Further studies are currently conducted using
398 multi criterion examinations.

399 The seasonal polyols-to-OM distribution patterns in this study are comparable to those found for different urban
400 or rural sites in Europe (around 0.2 to 2.5 % of OM) (Pashynska et al., 2002; Yttri et al., 2007b). Zhu et al. (2015)
401 also reported similar seasonal polyols-to-OM contribution trend for aerosols sampled at Cape Hedo (coastal site,
402 Japan).



403
404 **Figure 8: Spatial and seasonal distributions of mean contributions (in %) of polyols to the organic matter content of**
405 **PM for various types of sites in France. Daily time-series of organic carbon (OC) were not available for the following**
406 **sites: Gardanne, Mallet, and Meyreuil. Error bars correspond to standard deviations calculated with seasonal**
407 **concentrations.**

408 3.5 Primary biogenic factor in PMF studies

409 The sum of polyols (arabitol + mannitol) represents only a small fraction of the total OM. However, as proxies of
410 PBOA, they are most probably emitted with other chemical species. Emission from biological particles is a
411 complex topic since it may include a wide variety of compounds, both organic and inorganic (Elbert et al., 2007;
412 Zhang et al., 2015). Moreover, it is not clear if polyols are mainly emitted directly in the atmosphere or are linked
413 to other materials, for example with soil dust during resuspension processes. To investigate the relationship
414 between polyols and other molecular tracers of emission sources, it would have been possible to perform simple
415 correlation analysis with individual chemical species. This approach has the disadvantage of being a one-to-one
416 relation and thus highly sensitive to the dynamics of all PM emission sources, not only the one we are interested
417 in. Alternatively, another way is to use a PMF approach, also based on correlations but including much more
418 information on the temporal variations of the different sources influencing the PM chemistry at a given receptor
419 site.

420 As mentioned in Sect. 2.3, the PMF results used in this study include sites of different typologies (rural, traffic,
421 urban sites in Alpine valley environments, etc.) for 16 different locations spread over France and part of the current
422 dataset. At each site, the PMF studies allowed to identify a PBOA factor, characterized by the presence of more
423 than 90 % of the total polyols content (sum of arabitol, mannitol and sorbitol), as presented in table SI-5 and
424 Fig. SI-6. Moreover, the sensitivity of this factor to random noise in the data was investigated thanks to randomly
425 re-sampling the input matrix of observation. In PMF analysis, this is done via the bootstrap method (Paatero et al.,
426 2014) in the constrained run. The PBOA factor was always mapped to itself for 13 of the sites and quasi-always
427 (97%) for the last three ones. It means that the PBOA factor does have a very high statistical stability since it never

428 swaps with another factor (see Fig. SI-5). Hence, the chemical composition of this factor may be informative to
429 investigate the PBOA source components (Table SI-6), and to evaluate the importance of PBOA emissions in
430 terms of OM mass apportionment.

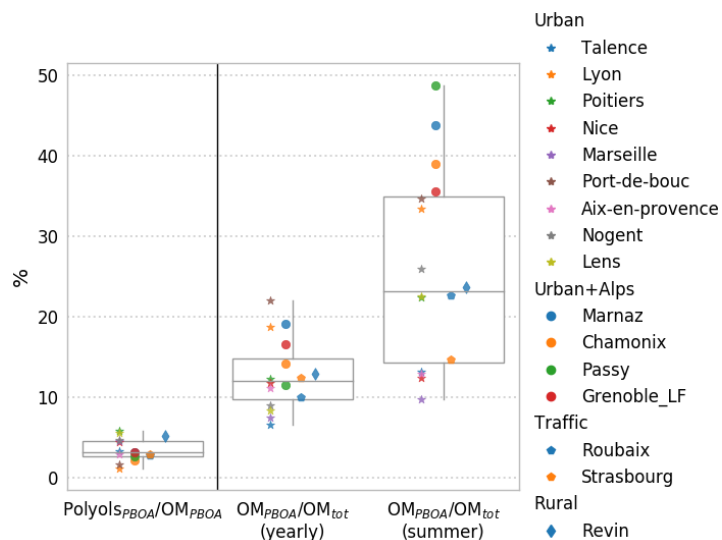
431 **3.5.1. Contributions of PBOA to OM and polyols to PBOA**

432 Altogether, the results from the 16 sites highlight the importance of the PBOA source contribution to total OM. As
433 shown in Fig. 9, the OM apportioned by the PBOA factor represents a significant fraction of the total OM mass
434 on a yearly average (range 6–28 %; average 13 ± 6 %). When considering only the summer period (June-July-
435 August), this contribution is even larger and can exceed 40 % of the total OM at sites in the Alpine area (Marnaz,
436 Passy, Chamonix, Grenoble_LF) which are partially protected from large regional influences due to the local
437 topography. This result may be nuanced, in particular during summer, since some extent of mixing between PBOA
438 and Biogenic Secondary Organic Aerosols (BSOA) cannot be entirely excluded. However, several evidences tend
439 in favor of a non-significant mixing between BSOA and PBOA. First, the ratio of polyols-to- OC_{PBOA} shows a low
440 variability from site to site, while it is unlikely that such a secondary process led to the same amount of OC for all
441 sites since they present different meteorology, sunshine duration, etc. Second, the bootstrap analysis does not show
442 any “swap” between factors for the PBOA profile for all sites, indicative of a well-defined factor (see Fig. SI-5).
443 Finally, the OC_{PBOA} -to-polyols ratio in this work (about 16) is in the range of ratio expected for fungal spores (12
444 -27, when arabitol and mannitol are considered together) (Bauer et al., 2008a; Yttri et al., 2011).

445 Interestingly, some previous work using the same samples from the sites in the Arve valley (Passy, Chamonix)
446 showed that about 90 % of the OM is from modern origin (using ^{14}C measurements) during summer, with no
447 apparent correlation between this modern carbon and polyols concentrations (Bonvalot et al., 2016). Hence, despite
448 being an important contributing source, PBOA is not the major biogenic source in this type of environment.

449 Interestingly, opposite to the case of the Alpine valleys where this proportion is the highest, the ratios OM_{PBOA} -to-
450 OM_{total} are amongst the lowest for coastal environments (Talence, Marseille, Nice), a possible indication that the
451 marine environment is not a large emitter for these species. Recently, much lower concentrations of polyols in
452 aerosols from marine environments than those in terrestrially influenced sites were also reported off the coast of
453 Japan, also suggesting a higher contribution from terrestrial sources (Kang et al., 2018).

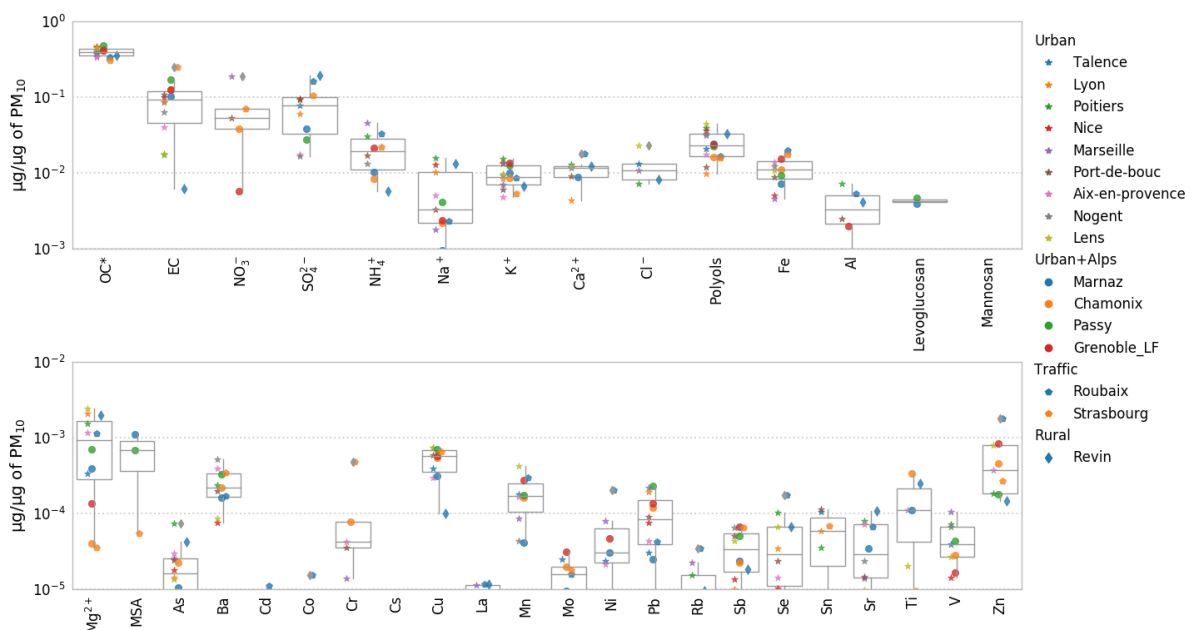
454 As illustrated in Fig. 9, polyols represent only a small fraction of the OM apportioned in the PBOA factor (1.2 %–
455 6.0 %; average 3.0 ± 1.5 %) for the 16 studied sites. This variability is indeed rather small, considering the wide
456 range of sites and the diversity of other potential sources (on average 8 to 10 PMF factors were obtained for the
457 different sites). Indeed, this narrow range of the polyols fraction to the OM_{PBOA} highlights the stability of the
458 chemical profile of this source over a large regional scale. It indicates also that, if polyols are good proxies of the
459 PBOA sources, a large amount of other organic species are co-emitted, that still remain unknown.



460
 461 **Figure 9: Mass contribution of polyols to OM in the PBOA factor, and relative contributions of the OM_{PBOA} factor to**
 462 **the total OM in PM for the 16 studied sites where PMF model was run, over the year and summertime only. Stars and**
 463 **circle refer to urban sites without/and with Alpine valley influence, respectively. Pentagon corresponds to traffic sites**
 464 **and diamond to rural sites.**

465 3.5.2 PBOA profile constituents and emission process

466 Figure 10 shows the contribution (in μg of species per μg of PM in the PBOA factor profile) of each chemical
 467 species included in the averaged PBOA factor from the 16 PMF studies. The principal contributors are OC and
 468 EC, and significant fractions of crustal material also appear (Na^+ , K^+ , Ca^{2+} , Al, Ba, Cu, Fe, Mn, Ti, Zn) as well as
 469 secondary elements such as nitrate and sulfate. However, EC appears to be highly variable both within and between
 470 sites under consideration. The reader may refer to figure SI-7 for an estimation of the EC mass uncertainties in the
 471 different sites. On average, the PBOA factor does not comprise a large fraction of metals and trace elements, most
 472 of them being below $1 \text{ pg } \mu\text{g}^{-1}$. Here again, the low variability of the PBOA chemical profile encountered across
 473 a large array of sites is remarkable.



474
 475 **Figure 10: PMF chemical profile of the PBOA factor in the DECOMBIO and SOURCES programs expressed as a**
 476 **fraction of the PM mass. Values lower than a few $\text{pg } \mu\text{g}^{-1}$ are not displayed on purpose. For each boxplot, the top, middle**

477 and bottom lines represent the 75th, median and 25th percentile, respectively. The whiskers at the top and bottom of the
478 box extend from the maximum to the minimum. OC* corresponds to the bulk organic carbon fraction minus the carbon
479 in the characterized organic species.

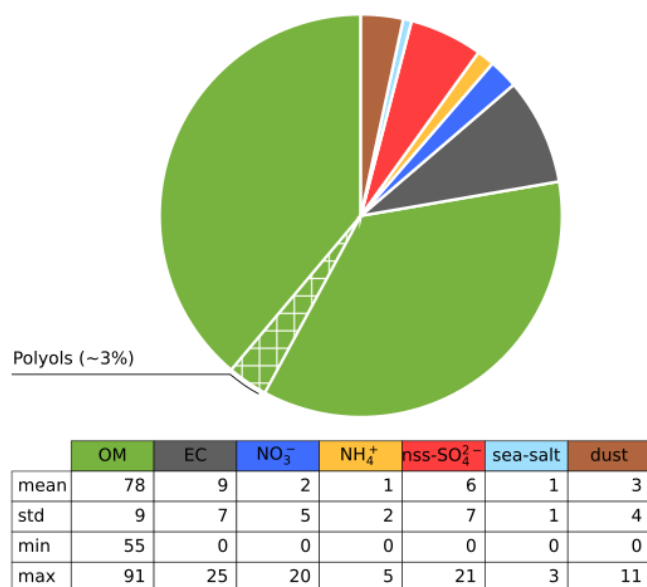
480 The contribution from some crustal material could agree with the coarse mode distributions of polyols (Sect. 3.3)
481 and could be indicative of an emission process with the entrainment of spores with soil dust resuspension. To
482 investigate the importance of mineral dust in the PBOA factor, we clustered the chemical components of PM from
483 PBOA into 7 classes: OM ($= 1.8 \times \text{OC}$), EC, NO_3^- , NH_4^+ , non-sea-salt sulfate (nss- SO_4), sea-salt, and dust. nss-
484 SO_4^{2-} is calculated from the measured SO_4^{2-} minus the sea-salt fraction of SO_4^{2-} ($\text{nssSO}_4^{2-} = \text{SO}_4^{2-} - \text{ssSO}_4^{2-}$
485 where $\text{ssSO}_4^{2-} = 0.252 \times \text{Na}^+$) according to Seinfeld and Pandis (1997). The sea-salt fraction is calculated
486 according to Putaud et al. (2010): $\text{sea} - \text{salt} = \text{Cl}^- + 1.47 \times \text{Na}^+$. Finally the dust fraction is estimated thanks
487 to Putaud et al. (2004b) as: $\text{dust} = (\text{nss} - \text{Ca}^{2+}) \times 5.6$ with nss- Ca^{2+} stands for non-sea salt Ca^{2+} and is
488 computed thanks to $\text{nss} - \text{Ca}^{2+} = \text{Ca}^{2+} - \text{Na}^+ / 26$. We note that the conversion coefficient provided by Putaud
489 et al. (2004b) may be influenced by an extreme value and then gives only a low estimate of dust resuspension.

490 Figure 11 presents the normalized average contributions of these 7 classes to the PBOA mass for the 16 sites with
491 PMF modelling. It clearly reveals that the PBOA factor is dominated by contributions from OM (78±9 %),
492 followed by EC (9±7 %), and only a minor contribution from the dust class (3±4 %).

493 The large value for the contribution of EC is driven by two high values obtained at the sites of Strasbourg (that
494 reaches 25%) and Chamonix (18%) both influenced by direct and indirect traffic emissions. However, 6 other sites
495 present no EC in PBOA. Moreover, the uncertainties of EC in the PBOA profile of Strasbourg and Chamonix is
496 rather high (between 5 to 30% of PM mass at Strasbourg, see SI-7). On a yearly average, EC apportioned by this
497 factor (0 to 400 ng m⁻³ depending on the site) is close to the rural EC background in France of about 300 ng m⁻³
498 (Golly et al., 2018).

499 This result on the general chemical profile of the PBOA factor, with a low crustal fraction, tends to infirm the
500 hypothesis of an emission process associating PBOA material with mineral dust resuspension. Indeed, our findings
501 rather suggest that a main part of PBOA (and polyols) is most likely associated with biological particle direct
502 emissions. It leaves only a minor fraction that could be linked to the mechanical resuspension of PBOA with crustal
503 elements. Some minor fraction of EC in this factor could come from resuspended EC-containing dust particles
504 being accumulated in topsoil as demonstrated in previous works (Forbes et al., 2006; Hammes et al., 2007; Zhan
505 et al., 2016). Hence, the origin of the larger fraction of the contribution of EC remains unknown. Our conclusions
506 are in good agreement with those made by Jia and Fraser (2011), based on the concentrations of these chemicals
507 in different types of samples: i.e., size-fractionated (equivalent to $\text{PM}_{2.5}$ and PM_{10}) soil, plant, fungi, atmospheric
508 $\text{PM}_{2.5}$ and PM_{10} . They found that the ambient concentrations of primary saccharide compounds at the suburban
509 site of Higley (USA) are typically dominated by contributions of biological materials rather than resuspension of
510 soil dust particles and associated microbiota.

511



512
 513 **Figure 11: Average contribution (%) of species in the PBOA factor for the sites in SOURCES and DECOMBIO. The**
 514 **hatched area represents the proportion of the OM apportioned by the polyols (see text for reconstruction method).**

515 **4. Conclusion**

516 The contribution of primary biogenic organic aerosols to PM is barely documented in the scientific literature. The
 517 present study aimed at providing a large overview of the spatial and temporal evolution of concentrations and
 518 contributions to aerosol organic matter of dominant primary sugar alcohols and saccharide compounds, for a large
 519 selection of environmental conditions in France. With 28 sites and more than 5,340 samples, it is to our knowledge
 520 the most comprehensive dataset for these compounds. The main results obtained indicate that:

- 521 • among the identified polyols, arabitol together with mannitol are the major species by mass, with lesser
 522 amounts of others polyols (e.g., erythritol, inositol, glycerol, sorbitol, and xylitol). Glucose is the
 523 dominant primary monosaccharide and its relative abundance is comparable to the sum of arabitol and
 524 mannitol;
- 525 • the two main polyols (arabitol and mannitol) together with glucose are mainly present within the coarse
 526 aerosol mode;
- 527 • at nearly all sites, ambient levels of the main polyols and glucose displayed clear seasonal variation cycles,
 528 with a gradual increase from spring and maximum in summer and autumn aerosols, followed by a sudden
 529 decrease in late autumn, and a winter minimum;
- 530 • atmospheric concentrations of the main polyols and glucose fluctuate according to site and season, and
 531 account each for between 0.1 to 2.1 % of OM on a seasonal average basis at these French sites;
- 532 • ambient mass concentrations of arabitol and mannitol are comparable. Meanwhile, they display very good
 533 temporal covariation, with ratios varying between sites. Conversely, linear correlations between the main
 534 polyols and glucose concentrations are much lower, suggesting different atmospheric sources, or
 535 atmospheric processes;

- 536 • arabitol and mannitol are efficient organic markers for PBOA. PMF studies of the yearly series from 16
537 sites give contributions of the primary biogenic emission (traced with the main polyols) to the total OM
538 around $13\pm 6\%$ on a yearly average and $26\pm 12\%$ during summer, thereby showing that PBOA is an
539 important source of total OM in PM_{10} for all sites across France. Furthermore, the average PBOA
540 chemical source profile is made out of a very large fraction of OM ($78\pm 9\%$ of the total PBOA mass on
541 average), suggesting it is mainly related to direct biogenic emissions from biological particles.
542 Noteworthy, the presence of BSOA within the PBOA factor, particularly during summer could not be
543 fully ruled out and further works using additional organic tracers (such as 3-methylbutanecarboxylic acid,
544 pinic acid, and/or cellulose) are still needed to solve this issue. Additionally, the low crustal fraction
545 indicates that this factor is weakly linked to soil dust resuspension associated with biological material;
- 546 • however, the PBOA source remains chemically poorly characterized as the main polyols represent only
547 a small fraction of its total OM mass ($3.0\pm 1.5\%$ on average);
- 548 • despite comparable high concentrations in the atmosphere, the sources and processes leading to glucose
549 concentrations and seasonal evolutions are still elusive. Indeed, the different PMF performed with glucose
550 in input variable do not lead to a statistically stable solution;

551 Further investigations of the emission pathways and chemical characterization of the PBOA source associated with
552 polyols are on-going, which may improve our understanding of its dynamic at various geographical scales, for a
553 potential implementation in emission models in the future.

554

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568

569 **Author contributions:** JLJ was the supervisor for the PhD for AS, FC, SW, and for the post-doc of DS. He
570 directed all the personnel who performed the analysis at IGE. He was coordinator or principal investigator (PI) of
571 the programs that generated the data for 18 of the 28 sites in this study (OPE-ANDRA, Part'Aera, CAMERA,
572 SRN 2013, 3 Villes PACA, DECOMBIO, QAMECS) and co-PI for programs for 5 other sites. He is the
573 coordinator for the CNRS LEFE-EC2CO CAREMBIOS program that is funding the work of AS. GU was the co-
574 supervisor for the PhD of AS and SW. OF is the coordinator of the CARA program, (co-)funding and supervising
575 the filter sampling and chemical analyses at 12 of the 28 sites. EP, OF, and VR supervised the PhD of DMO who

576 investigated the 5 sites in northern France. Finally, JLB was the coordinator (program Lanslebourg) or partner of
577 several programs whose data were used in this study (OPE-ANDRA, Part'Aera, 3 Villes PACA, DECOMBIO),
578 and OF was the coordinator of the SOURCES program, which includes the work of DS as a post-doctoral fellow
579 under the supervision of JLJ to gather and prepare most of the datasets used in the present studies.

580 All authors from the ANDRA (#5) and AASQA (#6 to 13) are representatives for each network that conducted the
581 sample collection and the general supervision of the sampling sites.

582 FC and DS ran the PMF analysis. AS, SW and JLJ processed the data and wrote up the manuscript. All authors
583 reviewed and commented on the manuscript.

584 **Competing interests:** The authors declare that they have no conflict of interest.

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586 References

587 Aiken, A. C., DeCarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr,
588 C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M.
589 R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and
590 Jimenez, J. L.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution
591 time-of-flight aerosol mass spectrometry, *Environ. Sci. Technol.*, 42(12), 4478–4485, 2008.

592 Alfarra, M. R., Prevot, A. S. H., Szidat, S., Sandradewi, J., Weimer, S., Lanz, V. A., Schreiber, D., Mohr, M., and
593 Baltensperger, U.: Identification of the mass spectral signature of organic aerosols from wood burning emissions,
594 *Environ. Sci. Technol.*, 41(16), 5770–5777, 2007.

595 Alves, C., Pio, C., Carvalho, A., and Santos, C.: Atmospheric carbonaceous aerosols over grasslands of central
596 Europe and a Boreal forest, *Chemosphere*, 63(1), 153–164, 2006.

597 Aymoz, G., Jaffrezo, J. L., Chapuis, D., Cozic, J., and Maenhaut, W.: Seasonal variation of PM 10 main
598 constituents in two valleys of the French Alps. I: EC/OC fractions, *Atmos. Chem. Phys.*, 7(3), 661–675, 2007.

599 Bauer, H., Claeys, M., Vermeylen, R., Schueller, E., Weinke, G., Berger, A., and Puxbaum, H.: Arabitol and
600 mannitol as tracers for the quantification of airborne fungal spores, *Atmos. Environ.*, 42(3), 588–593, 2008a.

601 Bauer, H., Schueller, E., Weinke, G., Berger, A., Hitzinger, R., Marr, I. L., and Puxbaum, H.: Significant
602 contributions of fungal spores to the organic carbon and to the aerosol mass balance of the urban atmospheric
603 aerosol, *Atmos. Environ.*, 42(22), 5542–5549, 2008b.

604 Belis, C. A., Favez, O., Harrison, R. M., Larsen, B. R., Amato, F., El Haddad, I., Hopke, P. K., Nava, S., Paatero,
605 P., Prévôt, A., Quass, U., Vecchi, R., Viana, M., European Commission, Joint Research Centre, and Institute for
606 Environment and Sustainability: European guide on air pollution source apportionment with receptor models,
607 Publications office, Luxembourg. [online] Available from: <http://dx.publications.europa.eu/10.2788/9307>, 2014.

608 Birch, M. E. and Cary, R. A.: Elemental carbon-based method for monitoring occupational exposures to particulate
609 diesel exhaust, *Aerosol Sci. Technol.*, 25(3), 221–241, 1996.

610 Boex-Fontvieille, E., Davanture, M., Jossier, M., Zivy, M., Hodges, M., and Tcherkez, G.: Photosynthetic activity
611 influences cellulose biosynthesis and phosphorylation of proteins involved therein in Arabidopsis leaves, *J. Exp.*
612 *Bot.*, 65(17), 4997–5010, 2014.

613 Bonvalot, L., Tuna, T., Fagault, Y., Jaffrezo, J.-L., Jacob, V., Chevrier, F., and Bard, E.: Estimating contributions
614 from biomass burning, fossil fuel combustion, and biogenic carbon to carbonaceous aerosols in the Valley of
615 Chamonix: a dual approach based on radiocarbon and levoglucosan, *Atmos. Chem. Phys.*, 16(21), 13753–13772,
616 2016.

- 617 Boucher, O., Randall, D., Artaxo, P., Bretherton, C., Feingold, G., Forster, P., Kerminen, V.-M., Kondo, Y., Liao,
618 H., and Lohmann, U.: Clouds and aerosols, in *Climate change 2013: the physical science basis. Contribution of*
619 *Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, pp. 571–
620 657, Cambridge University Press., 2013.
- 621 Burshtein, N., Lang-Yona, N., and Rudich, Y.: Ergosterol, arabitol and mannitol as tracers for biogenic aerosols
622 in the eastern Mediterranean, *Atmos. Chem. Phys.*, 11(2), 829–839, 2011.
- 623 Calas, A., Uzu, G., Kelly, F. J., Houdier, S., Martins, J. M. F., Thomas, F., Molton, F., Charron, A., Dunster, C.,
624 Oliete, A., Jacob, V., Besombes, J.-L., Chevrier, F., and Jaffrezo, J.-L.: Comparison between five acellular
625 oxidative potential measurement assays performed with detailed chemistry on PM10 samples from the city of
626 Chamonix (France), *Atmos. Chem. Phys.*, 18(11), 7863–7875, 2018.
- 627 Carvalho, A., Pio, C., and Santos, C.: Water-soluble hydroxylated organic compounds in German and Finnish
628 aerosols, *Atmos. Environ.*, 37(13), 1775–1783, 2003.
- 629 Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J.-P.: Toward a standardised thermal-optical protocol
630 for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, *Atmospheric Meas. Tech.*, 3(1),
631 79–89, 2010.
- 632 Chevrier, F.: Chauffage au bois et qualité de l'air en Vallée de l'Arve : définition d'un système de surveillance et
633 impact d'une politique de rénovation du parc des appareils anciens, PhD thesis, Université Grenoble Alpes, 23
634 November. [online] Available from: <https://tel.archives-ouvertes.fr/tel-01527559/document>, 2017.
- 635 China, S., Wang, B., Weis, J., Rizzo, L., Brito, J., Cirino, G. G., Kovarik, L., Artaxo, P., Gilles, M. K., and Laskin,
636 A.: Rupturing of biological spores as a source of secondary particles in amazonia, *Environ. Sci. Technol.*, 50(22),
637 12179–12186, 2016.
- 638 Cho, A. K., Sioutas, C., Miguel, A. H., Kumagai, Y., Schmitz, D. A., Singh, M., Eiguren-Fernandez, A., and
639 Froines, J. R.: Redox activity of airborne particulate matter at different sites in the Los Angeles Basin, *Environ.*
640 *Res.*, 99(1), 40–47, 2005.
- 641 Després, V. R., Alex Huffman, J., Burrows, S. M., Hoose, C., Safatov, A. S., Buryak, G., Fröhlich-Nowoisky, J.,
642 Elbert, W., Andreae, M. O., Pöschl, U., and Jaenicke, R.: Primary biological aerosol particles in the atmosphere:
643 a review, *Tellus B: Chem.Phys.Meteorol.*, 64:1, 15598, 2012.
- 644 Di Filippo, P., Pomata, D., Riccardi, C., Buiarelli, F., and Perrino, C.: Fungal contribution to size-segregated
645 aerosol measured through biomarkers, *Atmos. Environ.*, 64, 132–140, 2013.
- 646 Elbert, W., Taylor, P. E., Andreae, M. O., and Pöschl, U.: Contribution of fungi to primary biogenic aerosols in
647 the atmosphere: wet and dry discharged spores, carbohydrates, and inorganic ions, *Atmos. Chem. Phys.*, 7(17),
648 4569–4588, 2007.
- 649 Favez, O., Haddad, I. E., Piot, C., Boreave, A., Abidi, E., and Marchand, N.: Inter-comparison of source
650 apportionment models for the estimation of wood burning aerosols during wintertime in an Alpine city (Grenoble,
651 France), *Atmos. Chem. Phys.*, 20, 2010.
- 652 Favez, O., Salameh, D., and Jaffrezo, J.-L.: Traitement harmonisé de jeux de données multi-sites pour l'étude de
653 sources de PM par Positive Matrix Factorization (PMF) | LCSQA. [online] Available from:
654 https://www.lcsqa.org/system/files/rapport/lcsqa2016-traitement_harmonise_etude_sources_pmf.pdf, 2016.
- 655 Forbes, M. S., Raison, R. J., and Skjemstad, J. O.: Formation, transformation and transport of black carbon
656 (charcoal) in terrestrial and aquatic ecosystems, *Sci. Total Environ.*, 370(1), 190–206,
657 doi:10.1016/j.scitotenv.2006.06.007, 2006.
- 658 Fortenberry, C. F., Walker, M. J., Zhang, Y., Mitroo, D., Brune, W. H., and Williams, B. J.: Bulk and molecular-
659 level characterization of laboratory-aged biomass burning organic aerosol from oak leaf and heartwood fuels,
660 *Atmospheric Chem. Phys.*, 18(3), 2199–2224, 2018.

661 Franke, V., Zieger, P., Wideqvist, U., Acosta Navarro, J. C., Leck, C., Tunved, P., Rosati, B., Gysel, M., Salter,
662 M. E., and Ström, J.: Chemical composition and source analysis of carbonaceous aerosol particles at a mountaintop
663 site in central Sweden, *Tellus B Chem. Phys. Meteorol.*, 69(1), 1353387, 2017.

664 Fraser, M. P.: Final Report | Using carbohydrates as molecular markers to determine the contribution of agricultural
665 soil to ambient fine and coarse PM | Research Project Database | Grantee Research Project |ORD| USEPA, [\[online\]](#),
666 2010.

667 Fröhlich-Nowoisky, J., Kampf, C. J., Weber, B., Huffman, J. A., Pöhlker, C., Andreae, M. O., Lang-Yona, N.,
668 Burrows, S. M., Gunthe, S. S., Elbert, W., Su, H., Hoor, P., Thines, E., Hoffmann, T., Després, V. R., and Pöschl,
669 U.: Bioaerosols in the Earth system: Climate, health, and ecosystem interactions, *Atmospheric Res.*, 182, 346–
670 376, 2016.

671 Fu, P., Kawamura, K., Kobayashi, M., and Simoneit, B. R. T.: Seasonal variations of sugars in atmospheric
672 particulate matter from Gosan, Jeju Island: Significant contributions of airborne pollen and Asian dust in spring,
673 *Atmos. Environ.*, 55, 234–239, 2012.

674 Fu, P. Q., Kawamura, K., Chen, J., Charrière, B., and Sempéré, R.: Organic molecular composition of marine
675 aerosols over the Arctic Ocean in summer: contributions of primary emission and secondary aerosol formation,
676 *Biogeosciences*, 10(2), 653–667, 2013.

677 Fuzzi, S., Andreae, M. O., Huebert, B. J., Kulmala, M., Bond, T. C., Boy, M., Doherty, S. J., Guenther, A.,
678 Kanakidou, M., and Kawamura, K.: Critical assessment of the current state of scientific knowledge, terminology,
679 and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change, *Atmos.*
680 *Chem. Phys.*, 6(7), 2017–2038, 2006.

681 Fuzzi, S., Decesari, S., Facchini, M. C., Cavalli, F., Emblico, L., Mircea, M., Andreae, M. O., Trebs, I., Hoffer,
682 A., Guyon, P., Artaxo, P., Rizzo, L. V., Lara, L. L., Pauliquevis, T., Maenhaut, W., Raes, N., Chi, X., Mayol-
683 Bracero, O. L., Soto-García, L. L., Claeys, M., Kourchev, I., Rissler, J., Swietlicki, E., Tagliavini, E., Schkolnik,
684 G., Falkovich, A. H., Rudich, Y., Fisch, G., and Gatti, L. V.: Overview of the inorganic and organic composition
685 of size-segregated aerosol in Rondônia, Brazil, from the biomass-burning period to the onset of the wet season, *J.*
686 *Geophys. Res.*, 112, D01201, 2007.

687 Golly, B., Waked, A., Weber, S., Samake, A., Jacob, V., Conil, S., Rangonio, J., Chrétien, E., Vagnot, M., Robic,
688 P., Besombes, J.-L., and Jaffrezo, J. L.: Organic markers and OC source apportionment for seasonal variations of
689 PM_{2.5} at 5 rural sites in France, *Atmos. Environ.*, 198, 142–157, 2018..

690 Gosselin, M. I., Rathnayake, C. M., Crawford, I., Pöhlker, C., Fröhlich-Nowoisky, J., Schmer, B., Després, V. R.,
691 Engling, G., Gallagher, M., Stone, E., Pöschl, U., and Huffman, J. A.: Fluorescent bioaerosol particle, molecular
692 tracer, and fungal spore concentrations during dry and rainy periods in a semi-arid forest, *Atmos. Chem. Phys.*,
693 16(23), 15165–15184, 2016.

694 Graham, B., Guyon, P., Taylor, P. E., Artaxo, P., Maenhaut, W., Glovsky, M. M., Flagan, R. C., and Andreae, M.
695 O.: Organic compounds present in the natural Amazonian aerosol: Characterization by gas chromatography-mass
696 spectrometry: Organic compounds in Amazonian aerosols., *J. Geophys. Res. Atmospheres*, 108(D24), 4766, 2003.

697 Hammes, K., Schmidt Michael W. I., Smernik Ronald J., Currie Lloyd A., Ball William P., nguyen Thanh H.,
698 Louchouart Patrick, Houel Stephane, Gustafsson Örjan, Elmquist Marie, Cornelissen Gerard, Skjemstad Jan O.,
699 Masiello Caroline A., Song Jianzhong, Peng Ping'an, Mitra Siddhartha, Dunn Joshua C., Hatcher Patrick G.,
700 Hockaday William C., Smith Dwight M., Hartkopf-Fröder Christoph, Böhmer Axel, Luer Burkhard, Huebert Barry
701 J., Amelung Wulf, Brodowski Sonja, Huang Lin, Zhang Wendy, Gschwend Philip M., Flores-Cervantes D. Xanat,
702 Largeau Claude, Rouzaud Jean-Noël, Rumpel Cornelia, Guggenberger Georg, Kaiser Klaus, Rodionov Andrei,
703 Gonzalez-Vila Francisco J., Gonzalez-Perez José A., de la Rosa José M., Manning David A. C., López-Capel
704 Elisa, and Ding Luyi: Comparison of quantification methods to measure fire-derived (black/elemental) carbon in
705 soils and sediments using reference materials from soil, water, sediment and the atmosphere, *Glob. Biogeochem.*
706 *Cycles*, 21(3), GB3016, 2007.

707 Heald, C. L. and Spracklen, D. V.: Atmospheric budget of primary biological aerosol particles from fungal spores,
708 *Geophys. Res. Lett.*, 36(9), L09806, 2009.

709 Huffman, J. A., Sinha, B., Garland, R. M., Snee-Pollmann, A., Gunthe, S. S., Artaxo, P., Martin, S. T., Andreae,
710 M. O., and Pöschl, U.: Size distributions and temporal variations of biological aerosol particles in the Amazon
711 rainforest characterized by microscopy and real-time UV-APS fluorescence techniques during AMAZE-08,
712 *Atmos. Chem. Phys.*, 12(24), 11997–12019, 2012.

713 Jaenicke, R.: Abundance of cellular material and proteins in the atmosphere, *Science*, 308(5718), 73–73,
714 doi:10.1126/science.1106335, 2005.

715 Jennings, D. B., Ehrenshaft, M., Pharr, D. M., and Williamson, J. D.: Roles for mannitol and mannitol
716 dehydrogenase in active oxygen-mediated plant defense, *Proc. Natl. Acad. Sci.*, 95(25), 51129–51133, 1998.

717 Jia, Y. and Fraser, M.: Characterization of Saccharides in Size-fractionated Ambient Particulate Matter and
718 Aerosol Sources: The contribution of primary biological aerosol particles (PBAPs) and soil to ambient particulate
719 matter, *Environ. Sci. Technol.*, 45(3), 930–936, 2011.

720

721 Jia, Y., Bhat, S., and Fraser, M. P.: Characterization of saccharides and other organic compounds in fine particles
722 and the use of saccharides to track primary biologically derived carbon sources, *Atmos. Environ.*, 44(5), 724–732,
723 2010a.

724 Jia, Y., Clements, A. L., and Fraser, M. P.: Saccharide composition in atmospheric particulate matter in the
725 southwest US and estimates of source contributions, *J. Aerosol Sci.*, 41(1), 62–73, 2010b.

726 Jones, A. M. and Harrison, R. M.: The effects of meteorological factors on atmospheric bioaerosol
727 concentrations—a review, *Sci. Total Environ.*, 326(1), 151–180, 2004.

728 Kang, M., Fu, P., Kawamura, K., Yang, F., Zhang, H., Zang, Z., Ren, H., Ren, L., Zhao, Y., Sun, Y., and Wang,
729 Z.: Characterization of biogenic primary and secondary organic aerosols in the marine atmosphere over the East
730 China Sea, *Atmos. Chem. Phys. Discuss.*, 1–45, 2018.

731 Li, Y.-C., Shu, M., Ho, S. S. H., Yu, J.-Z., Yuan, Z.-B., Wang, X.-X., Zhao, X.-Q., and Liu, Z.-F.: Effects of
732 chemical composition of PM_{2.5} on visibility in a semi-rural city of Sichuan basin, *Aerosol Air Qual. Res.*, 18(4),
733 957–968, 2018.

734 Liang, L., Engling, G., Du, Z., Cheng, Y., Duan, F., Liu, X., and He, K.: Seasonal variations and source estimation
735 of saccharides in atmospheric particulate matter in Beijing, China, *Chemosphere*, 150, 365–377, 2016.

736 Liang, L., Engling, G., Du, Z., Duan, F., Cheng, Y., Liu, X., and He, K.: Contribution of fungal spores to organic
737 carbon in ambient aerosols in Beijing, China, *Atmospheric Pollut. Res.*, 8(2), 351–358, 2017.

738 Manninen, H. E., Bäck, J., Sihto-Nissilä, S.-L., Huffman, J. A., Pessi, A.-M., Hiltunen, V., Aalto, P. P., Hidalgo
739 Fernández, P. J., Hari, P., Saarto, A., and others: Patterns in airborne pollen and other primary biological aerosol
740 particles (PBAP), and their contribution to aerosol mass and number in a boreal forest, *Boreal Environ. Res.*, 383–
741 405, 2014.

742 Medeiros, P. M., Conte, M. H., Weber, J. C., and Simoneit, B. R. T.: Sugars as source indicators of biogenic
743 organic carbon in aerosols collected above the Howland Experimental Forest, Maine, *Atmos. Environ.*, 40(9),
744 1694–1705, 2006.

745 Morris, C. E., Sands, D. C., Bardin, M., Jaenicke, R., Vogel, B., Leyronas, C., Ariya, P. A., and Psenner, R.:
746 Microbiology and atmospheric processes: research challenges concerning the impact of airborne micro-organisms
747 on the atmosphere and climate, *Biogeosciences*, 8(1), 17–25, doi:10.5194/bg-8-17-2011, 2011.

748 Nozière, B., Kalberer, M., Claeys, M., Allan, J., D’Anna, B., Decesari, S., Finessi, E., Glasius, M., Grgić, I.,
749 Hamilton, J. F., Hoffmann, T., Iinuma, Y., Jaoui, M., Kahnt, A., Kampf, C. J., Kourtchev, I., Maenhaut, W.,
750 Marsden, N., Saarikoski, S., Schnelle-Kreis, J., Surratt, J. D., Szidat, S., Szmigielski, R., and Wisthaler, A.: The
751 molecular identification of organic compounds in the atmosphere: state of the art and challenges, *Chem. Rev.*,
752 115(10), 3919–3983, doi:10.1021/cr5003485, 2015.

753 Ntziachristos, L., Froines, J. R., Cho, A. K., and Sioutas, C.: Relationship between redox activity and chemical
754 speciation of size-fractionated particulate matter, *Part. Fibre Toxicol.*, 4(1), 5, doi:10.1186/1743-8977-4-5, 2007.

755 Paatero, P., Eberly, S., Brown, S. G. and Norris, G. A.: Methods for estimating uncertainty in factor analytic
756 solutions, *Atmos. Meas. Tech.*, 7(3), 781–797, 2014.

757 Pashynska, V., Vermeulen, R., Vas, G., Maenhaut, W., and Claeys, M.: Development of a gas chromatographic/ion
758 trap mass spectrometric method for the determination of levoglucosan and saccharidic compounds in atmospheric
759 aerosols. Application to urban aerosols, *J. Mass Spectrom.*, 37(12), 1249–1257, doi:10.1002/jms.391, 2002.

760 Petit, J.-E., Favez, O., Sciare, J., Crenn, V., Sarda-Estève, R., Bonnaire, N., Močnik, G., Dupont, J.-C., Haeffelin,
761 M., and Leoz-Garziandia, E.: Two years of near real-time chemical composition of submicron aerosols in the
762 region of Paris using an Aerosol Chemical Speciation Monitor (ACSM) and a multi-wavelength Aethalometer,
763 *Atmos. Chem. Phys.*, 15(6), 2985–3005, 2015.

764 Pietrogrande, M. C., Bacco, D., Visentin, M., Ferrari, S., and Casali, P.: Polar organic marker compounds in
765 atmospheric aerosol in the Po Valley during the Supersito campaigns — Part 2: Seasonal variations of sugars,
766 *Atmos. Environ.*, 97, 215–225, 2014.

767 Pio, C. A., Legrand, M., Alves, C. A., Oliveira, T., Afonso, J., Caseiro, A., Puxbaum, H., Sanchez-Ochoa, A., and
768 Gelencsér, A.: Chemical composition of atmospheric aerosols during the 2003 summer intense forest fire period,
769 *Atmos. Environ.*, 42(32), 7530–7543, doi:10.1016/j.atmosenv.2008.05.032, 2008.

770 Putaud, J.-P., Raes, F., Van Dingenen, R., Brüggemann, E., Facchini, M.-C., Decesari, S., Fuzzi, S., Gehrig, R.,
771 Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Querol, X., Rodriguez, S., Schneider,
772 J., Spindler, G., Brink, H. ten, Tørseth, K., and Wiedensohler, A.: A European aerosol phenomenology 2: chemical
773 characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, *Atmos. Environ.*,
774 38(16), 2579–2595, 2004a.

775 Putaud, J.-P., Dingenen, R. V., Dell’Acqua, A., Raes, F., Matta, E., Decesari, S., Facchini, M. C., and Fuzzi, S.:
776 Size-segregated aerosol mass closure and chemical composition in Monte Cimone (I) during MINATROC, *Atmos.*
777 *Chem. Phys.*, 4(4), 889–902, 2004b.

778 Putaud, J.-P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R.,
779 Hansson, H. C., Harrison, R. M., Herrmann, H., Hitznerberger, R., Hüglin, C., Jones, A. M., Kasper-Giebl, A.,
780 Kiss, G., Koussa, A., Kuhlbusch, T. A. J., Löschau, G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J.,
781 Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J.,
782 Spindler, G., ten Brink, H., Tursic, J., Viana, M., Wiedensohler, A., and Raes, F.: A European aerosol
783 phenomenology – 3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside
784 sites across Europe, *Atmos. Environ.*, 44(10), 1308–1320, 2010.

785 Puxbaum, H. and Tenze-Kunit, M.: Size distribution and seasonal variation of atmospheric cellulose, *Atmos.*
786 *Environ.*, 37(26), 3693–3699, 2003.

787 Rathnayake, C. M., Metwali, N., Jayarathne, T., Kettler, J., Huang, Y., Thorne, P. S., O’Shaughnessy, P. T., and
788 Stone, E. A.: Influence of rain on the abundance of bioaerosols in fine and coarse particles, *Atmos. Chem. Phys.*,
789 17(3), 2459–2475, 2017.

790 Ruijter, G. J. G., Bax, M., Patel, H., Flitter, S. J., Vondervoort, P. J. I. van de, Vries, R. P. de, vanKuyk, P. A., and
791 Visser, J.: Mannitol is required for stress tolerance in aspergillus niger aonidiospores, *Eukaryot. Cell*, 2(4), 690–
792 698, doi:10.1128/EC.2.4.690-698.2003, 2003.

793 Ruthenburg, T. C., Perlin, P. C., Liu, V., McDade, C. E., and Dillner, A. M.: Determination of organic matter and
794 organic matter to organic carbon ratios by infrared spectroscopy with application to selected sites in the IMPROVE
795 network, *Atmos. Environ.*, 86, 47–57, 2014.

796 Salameh, D., Weber, S., Favez, O., Riffault, V., Perdrix, E., Albinet, A., Jacob, V., Alleman, L., Waked, A.,
797 Olievera, D. M., Chevrier, F., Guillaud, G., Meshba, B., Rocq, B., Hulin, A., Le Meur, S., Chrétien, E. and Jaffrezo,
798 J. L.: A harmonized PM source apportionment at 15 different sites in France using a constrained PMF approach
799 (2018), *Atmosphere*, in prep.

800 Samake, A., Jaffrezo, J. L., Favez, O., Weber, S., Jacob, V., Albinet, A., Alleman, L., Waked, A., Golly, B.,
801 Salameh, D., Chevrier, F., Oliveira, D., Besombes, J.-L., Martins, J. M. F., Conil, S., Atmo Aura, Air PACA, Atmo
802 HdF, Atmo NA, Atmo Normandie, Lig'Air, Atmo Grand-Est, and Uzu, G.: Polyols and glucose in atmospheric
803 PM10: regional variations and factor influencing the concentrations., *Atmos. Chem. Phys.*, in prep.

804 Sandradewi, J., Prévôt, A. S. H., Szidat, S., Perron, N., Alfarra, M. R., Lanz, V. A., Weingartner, E., and
805 Baltensperger, U.: Using aerosol light absorption measurements for the quantitative determination of wood
806 burning and traffic emission contributions to particulate matter, *Environ. Sci. Technol.*, 42(9), 3316–3323, 2008.

807 Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 1
808 edition., Wiley-Interscience, New York., 1997.

809 [Simoneit, B. R. T., Elias, V. O., Kobayashi, M., Kawamura, K., Rushdi, A. I., Medeiros, P. M., Rogge, W. F., and](#)
810 [Didyk, B. M.: Sugars dominant water-soluble organic compounds in soils and characterization as tracers in](#)
811 [atmospheric particulate matter, *Environ. Sci. Technol.*, 38\(22\), 5939–5949, 2004b.](#)

812 [Simoneit, B. R. T., Kobayashi, M., Mochida, M., Kawamura, K., Lee, M., Lim, H. J., Turpin, B. J., and Komazaki,](#)
813 [Y.: Composition and major sources of organic compounds of aerosol particulate matter sampled during the](#)
814 [ACE-Asia campaign, *J. Geophys. Res.*, 109 \(D19\): D19S10, 2004a.](#)

815 [Simoneit, B. R. T., Elias, V. O., Kobayashi, M., Kawamura, K., Rushdi, A. I., Medeiros, P. M., Rogge, W. F., and](#)
816 [Didyk, B. M.: Sugars dominant water soluble organic compounds in soils and characterization as tracers in](#)
817 [atmospheric particulate matter, *Environ. Sci. Technol.*, 38\(22\), 5939–5949, 2004b.](#)

818 Srithawirat, T. and Brimblecombe, P.: Seasonal variation of saccharides and furfural in atmospheric aerosols at a
819 semi-urban site, *Aerosol Air Qual. Res.*, 15, 2277–2290, 2015.

820 Srivastava, D., Tomaz, S., Favez, O., Lanzafame, G. M., Golly, B., Besombes, J.-L., Alleman, L. Y., Jaffrezo, J.-
821 L., Jacob, V., Perraudin, E., Villenave, E., and Albinet, A.: Speciation of organic fraction does matter for source
822 apportionment. Part 1: A one-year campaign in Grenoble (France), *Sci. Total Environ.*, 624, 1598–1611, 2018.

823 Theodosi, C., Panagiotopoulos, C., Nouara, A., Zarnpas, P., Nicolaou, P., Violaki, K., Kanakidou, M., Sempéré,
824 R., and Mihalopoulos, N.: Sugars in atmospheric aerosols over the Eastern Mediterranean, *Prog. Oceanogr.*, 163,
825 70–81, 2018.

826 US EPA, O.: Positive Matrix Factorization Model for environmental data analyses, US EPA [online] Available
827 from: <https://www.epa.gov/air-research/positive-matrix-factorization-model-environmental-data-analyses>
828 (Accessed 7 September 2017), 2015.

829 Véléz, H., Glassbrook, N. J., and Daub, M. E.: Mannitol metabolism in the phytopathogenic fungus *Alternaria*
830 *alternata*, *Fungal Genet. Biol.*, 44(4), 258–268, 2007.

831 Verma, S. K., Kawamura, K., Chen, J., and Fu, P.: Thirteen years of observations on primary sugars and sugar
832 alcohols over remote Chichijima Island in the western North Pacific, *Atmos. Chem. Phys.*, 18(1), 81–101, 2018.

833 Vlachou, A., Daellenbach, K. R., Bozzetti, C., Chazau, B., Salazar, G. A., Szidat, S., Jaffrezo, J.-L., Hueglin, C.,
834 Baltensperger, U., Haddad, I. E., and Prévôt, A. S. H.: Advanced source apportionment of carbonaceous aerosols
835 by coupling offline AMS and radiocarbon size-segregated measurements over a nearly 2-year period, *Atmos.*
836 *Chem. Phys.*, 18(9), 6187–6206, doi:10.5194/acp-18-6187-2018, 2018.

837 Waked, A., Favez, O., Alleman, L. Y., Piot, C., Petit, J.-E., Delaunay, T., Verlinden, E., Golly, B., Besombes, J.-
838 L., Jaffrezo, J.-L., and Leoz-Garziandia, E.: Source apportionment of PM10 in a north-western Europe regional
839 urban background site (Lens, France) using positive matrix factorization and including primary biogenic
840 emissions, *Atmos. Chem. Phys.*, 14(7), 3325–3346, 2014.

841 Yang, Y., Chan, C., Tao, J., Lin, M., Engling, G., Zhang, Z., Zhang, T., and Su, L.: Observation of elevated fungal
842 tracers due to biomass burning in the Sichuan Basin at Chengdu City, China, *Sci. Total Environ.*, 431, 68–77,
843 2012.

844 Yttri, K. E., Aas, W., Bjerke, A., Cape, J. N., Cavalli, F., Ceburnis, D., Dye, C., Emblico, L., Facchini, M. C.,
845 Forster, C., Hanssen, J. E., Hansson, H. C., Jennings, S. G., Maenhaut, W., Putaud, J. P., and Tørseth, K.: Elemental
846 and organic carbon in PM10: a one year measurement campaign within the European Monitoring and Evaluation
847 Programme EMEP, *Atmos. Chem. Phys.*, 15, 2007a.

848 Yttri, K. E., Dye, C., and Kiss, G.: Ambient aerosol concentrations of sugars and sugar-alcohols at four different
849 sites in Norway, *Atmos. Chem. Phys.*, 7(16), 4267–4279, 2007b.

850 Yttri, K. E., Simpson, D., Stenström, K., Puxbaum, H. and Svendby, T.: Source apportionment of the carbonaceous
851 aerosol in Norway – quantitative estimates based on 14C, thermal-optical and organic tracer analysis, *Atmos.*
852 *Chem. Phys. Discuss.*, 11(3), 7375–7422, 2011.

853 Wang, X., Shen, Z., Liu, F., Lu, D., Tao, J., Lei, Y., Zhang, Q., Zeng, Y., Xu, H., Wu, Y., Zhang, R., and Cao, J.:
854 Saccharides in summer and winter PM2.5 over Xi'an, Northwestern China: Sources, and yearly variations of
855 biomass burning contribution to PM2.5, *Atmospheric Res.*, 214, 410–417, 2018.

856 Zhan, C., Zhang, J., Cao, J., Han, Y., Wang, P., Zheng, J., Yao, R., Liu, H., Li, H., and Xiao, W.: Characteristics
857 and sources of black carbon in atmospheric dustfall particles from Huangshi, China, *Aerosol Air Qual. Res.*, 16(9),
858 2096–2106, doi:10.4209/aaqr.2015.09.0562, 2016.

859 Zhang, T., Engling, G., Chan, C.-Y., Zhang, Y.-N., Zhang, Z.-S., Lin, M., Sang, X.-F., Li, Y. D., and Li, Y.-S.:
860 Contribution of fungal spores to particulate matter in a tropical rainforest, *Environ. Res. Lett.*, 5(2), 24010, 2010.

861 Zhang, Z., Engling, G., Zhang, L., Kawamura, K., Yang, Y., Tao, J., Zhang, R., Chan, C., and Li, Y.: Significant
862 influence of fungi on coarse carbonaceous and potassium aerosols in a tropical rainforest, *Environ. Res. Lett.*,
863 10(3), 34015, 2015.

864 Zhu, C., Kawamura, K., and Kunwar, B.: Organic tracers of primary biological aerosol particles at subtropical
865 Okinawa Island in the western North Pacific Rim: Organic biomarkers in the North Pacific, *J. Geophys. Res.*
866 *Atmospheres*, 120(11), 5504–5523, 2015.

867 Zhu, C., Kawamura, K., Fukuda, Y., Mochida, M., and Iwamoto, Y.: Fungal spores overwhelm biogenic organic
868 aerosols in a midlatitudinal forest, *Atmos. Chem. Phys.*, 16(11), 7497–7506, 2016.

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