Atmospheric
Chemistry
and Physics
Discussions

Polyols and glucose particulate species as tracers of primary biogenic organic aerosols at 28 french sites

Abdoulaye Samake[1], Jean-Luc Jaffrezo[1], Olivier Favez[2], Samuël Weber[1], Véronique Jacob[1], Alexandre Albinet[2], Véronique Riffault[3], Esperanza Perdrix[3], Antoine Waked[1*], Benjamin Golly[1], Dalia Salameh[1†], Florie Chevrier[1], Diogo Miguel Oliveira[2,3], Jean-Luc Besombes[4], Jean M.F Martins[1], Sébastien Conil[5], Géraldine Guillaud[6], Boualem Meshba[7], Benoit Rocq[8], Pierre-Yves Robic[9], Agnès Hulin[10], Sébastien Le Meur[11], Maxence Descheemaecker[12], Eve Chretien[13], and Gaëlle Uzu[1].

[1]Univ. Grenoble Alpes, CNRS, IRD, INP-G, IGE (UMR 5001), F-38000 Grenoble, France.
[2]INERIS, Parc Technologique Alata, BP 2, 60550 Verneuil-en-Halatte, France
[3]IMT Lille Douai, Univ. Lille, SAGE – Département Sciences de l'Atmosphère et Génie de l'Environnement, F-59000 Lille, France
[4]Univ. Savoie Mont-Blanc, LCME, F-73000 Chambéry, France
[5]ANDRA DRD/GES Observatoire Pérenne de l'Environnement, F-55290 Bure, France
[6]Atmo AuRA, F-38400 Grenoble, France
[7]Air PACA, F-03040, France
[8]Atmo Hauts de France, F-59000, France
[9]Atmo Occitanie, F-31330 Toulouse, France
[10]Atmo Nouvelle Aquitaine, F-33000, France
[11]Atmo Normandie, F-76000, France
[12]Lig'Air, F-45590 Saint-Cyr-en-Val, France
[13] Atmo Grand Est, F-16034 Strasbourg, France
*Now at IMT Lille Douai, Univ. Lille, SAGE – Département Sciences de l'Atmosphère et Génie de l'Environnement, F-59000 Lille, France
†Now at Airport pollution control authority (ACNUSA), 75007 Paris, France

Corresponding author(s): A Samaké (abdoulaye.samake2@univ-grenoble-alpes.fr) and JL Jaffrezo (Jean-luc.Jaffrezo@univ-grenoble-alpes.fr)

Atmospheric
Chemistry
and Physics
Discussions

Abstract. A growing number of studies are using specific primary sugar species, such as sugar alcohols or primary saccharides, as marker compounds to characterize and apportion primary biogenic organic aerosols (PBOA) in the atmosphere. To better understand their annual cycles, as well as their spatio-temporal abundance in terms of concentrations and sources, we conducted a large study focusing on three major atmospheric primary sugar compounds (i.e. arabitol, mannitol and glucose) measured in various environmental conditions on about 5,300 filter samples collected at 28 sites in France. Our results show significant atmospheric concentrations of polyols (defined here as the sum of arabitol and mannitol) and glucose at each sampling location, highlighting their ubiquity. Results also confirm that polyols and glucose are mainly associated with the coarse rather than the fine aerosol mode. At nearly all sites, atmospheric concentrations of polyols and glucose display a well-marked seasonal pattern, with maximum concentrations from late spring to early autumn, followed by an abrupt decrease in late autumn, and a minimum concentration during wintertime. Such seasonal patterns support biogenic emissions associated with higher biological metabolic activities (e.g. sporulation, growth, etc.) during warmer periods. Results from a previous comprehensive study using Positive Matrix Factorization (PMF) based on an extended aerosol chemical composition dataset of up to 130 species for 16 of the same sample series has also been used in the present work. Results show that PBOA are significant sources of total OM in PM_{10} (13±4 % on a yearly average, and up to 40 % in some environments in summer) at most of the investigated sites. The mean PBOA chemical profile is clearly dominated by OM (78±9 % of the mass of the PBOA PMF factor on average), suggesting that ambient polyols are most likely associated with biological particle emissions (e.g. active spore discharge) rather than soil dust resuspension.

1. Introduction

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

Primary biogenic organic aerosols (PBOA) are emitted directly from the biosphere to the atmosphere where they are ubiquitous and participate in many atmospheric processes (Elbert et al., 2007; Fröhlich-Nowoisky et al., 2016). Additionally, their inhalation has long been associated with human respiratory impairments (e.g. asthma, aspergillosis, etc.) (Després et al., 2012; Morris et al., 2011). PBOA comprises living and dead microorganisms

Atmospheric
Chemistry
and Physics
Discussions

71   such as bacteria, fungi, viruses, bacterial and fungal spores, and microbial fragments, endotoxins, mycotoxins, or

72   pollens (Elbert et al., 2007; Jaenicke, 2005; Morris et al., 2011). It can account for an average of 25 % of the

73   atmospheric aerosol mass (Fröhlich-Nowoisky et al., 2016; Jaenicke, 2005; Manninen et al., 2014; Morris et al.,

74   2011). However, their sources and contribution to total airborne particles are still poorly documented, partly

75   because of the difficulty to recognize them by conventional microbiological methods (cells culture, or microscopic

76   examination) (Di Filippo et al., 2013; Heald and Spracklen, 2009; Jia et al., 2010a).

77   Several specific chemical components, such as primary sugar compounds (i.e. primary saccharides and sugar

78   alcohols) emitted persistently from biogenic sources, have long been suggested as powerful and unique biomarkers

79   in tracing sources, abundances, as well as atmospheric transport pathways of PBOA. For instance, ambient

80   concentrations of glucose have been used as markers for plant materials (such as pollen, leaves, and their

81   fragments) or soil emissions from several areas in the world (Fu et al., 2012; Jia et al., 2010a, 2010b; Pietrogrande

82   et al., 2014; Rathnayake et al., 2017). Many studies indicated that glucose is the most abundant monosaccharide

83   in vascular plants, where it serves as the common energy materials, and an important source of carbon for soil

84   active microorganisms (such as bacteria or fungi) (Jia et al., 2010a; Medeiros et al., 2006; Pietrogrande et al.,

85   2014; Zhu et al., 2015). Additionally, sugar alcohols (also called polyols) including arabitol and mannitol have

86   been proposed as markers for airborne fungi, and are widely used to quantify their contributions to PM mass (Bauer

87   et al., 2008a, 2008b; Golly et al., 2018; Srivastava et al., 2018; Zhang et al., 2010). These sugar alcohols also

88   correlate very well with a factor identified as PBOA in AMS off-line studies (Vlachou et al., 2018b). Polyols are

89   produced in large amounts by many fungi and bacteria, and several functions have been described for these

90   compounds, such as common energy storage materials, intracellular protectants against stressful conditions (e.g.

91   heat or drought), storage or transport of carbohydrates, quencher of oxygenated reactive species, or regulators of

92   intracellular pH by acting as a sink or source of protons (Jennings et al., 1998; Medeiros et al., 2006; Vélëz et al.,

93   2007). Hence, polyols, especially arabitol and mannitol, may represent a significant fraction of the dry weight of

94   fungi, and mannitol can contribute between 20 to 50 % of the mycelium dry weight (Ruijter et al., 2003; Vélëz et

95   al., 2007). However, polyols are also often identified in the lower plants (leaves, pollens) and green algal lichens

96   (Medeiros et al., 2006; Vélëz et al., 2007; Yang et al., 2012).

97   Although atmospheric concentrations of polyols, including arabitol and mannitol, as well as that of some primary

98   monosaccharides (e.g. glucose), have been previously quantified as part of several studies in various environments

99   including urban/suburban, rural, rainforest, mountain, and marine areas (Fu et al., 2012; Graham et al., 2003; Jia

100 et al., 2010a, 2010b; Liang et al., 2016; Pietrogrande et al., 2014; Simoneit, 2004; Verma et al., 2018; Yttri et al.,

101 2007; Zhu et al., 2015), large sets of data investigating their annual cycles and spatial distributions are still limited.

102 Such information could give important insights on environmental factors influencing their atmospheric levels such

103 as climate and biotope, and therefore help to elucidate patterns regarding their major sources and atmospheric

104 emission pathways. Even if numerous sources and emission mechanisms have been widely proposed, including

105 among others, metabolic active microbial wet emissions, entrainment of farmland or natural soils and associated

106 microbiota (Elbert et al., 2007; Fu et al., 2013; Gosselin et al., 2016; Jia et al., 2010a, 2010b; Medeiros et al., 2006;

107 Pietrogrande et al., 2014; Simoneit et al., 2004; Verma et al., 2018; Yttri et al., 2007), the dominant atmospheric

108 input processes have not been yet sufficiently elucidated.

109   In this context, the present study was designed to provide a large overview of the spatial and seasonal variations

110   of polyols and glucose mass concentrations, as well as their contribution to the aerosol organic mass fraction, in

111   France. To do so, data was collected at many sites in different environments (rural, traffic, urban), in order to

112   represent various sampling conditions in terms of site typologies and meteorological conditions. Thanks to the

113   availability of results from an extended Positive Matrix Factorization (PMF) analysis performed for the

114   corresponding datasets, the overall contributions of the main polyols and glucose emission sources could also be

115   investigated in light of their spatial patterns. To the best of our knowledge, this is the first study providing such an

116   extended phenomenology of these compounds over multiple sites with different typologies.

117   **2. Material and methods**

118   **2.1 Aerosol sampling**

119   Ambient aerosol samples considered in the present work come from different research and monitoring programs,

120   conducted over the last 5 years in France (Figure 1). Each program includes at least one-year of field sampling,

121   providing a total number of 5,343 daily filter samples available for the sake of the present study. These sites offer

122   diverse conditions in terms of typologies (i.e. rural, traffic, urban sites, Alpine valley environments, etc.), local

123   climate and vegetation types and were selected in order to cover the complex and variable national environmental

124   conditions. These sites are assumed to represent typical environmental conditions in France, and our

125   observations/and general tendency could therefore be extrapolated to neighboring western European countries

126   presenting quite homogeneous environmental conditions.
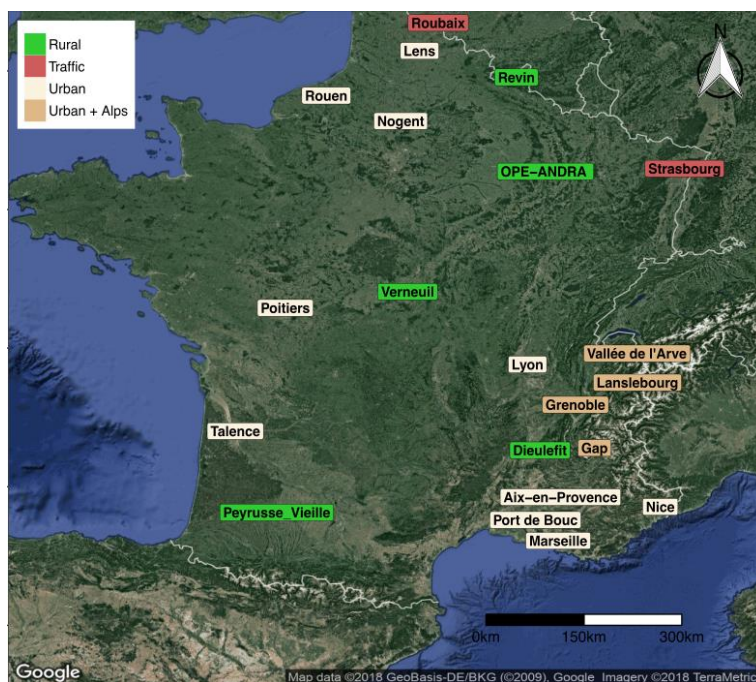
127

128   **Figure 1: Map of sampling site locations in France. Green: rural, red: traffic, wheat: urban and dark wheat: Urban in**

129   **Alps valley environment sites. Stations of Grenoble (Grenoble_LF, Grenoble_CB and Grenoble_VIF) and Vallée de**

Atmospheric
Chemistry
and Physics
Discussions

130 **L'Arve (Marnaz, Passy and Chamonix) include each 3 sites. Station of Marseille includes four sites: Marseille, Mallet,**
131 **Meyreuil and Gardanne.**

132 The site of OPE-ANDRA is a specific monitoring observatory in a very rural environment (description available
133 from: http://www.andra.fr). All other sites correspond to stations of regional air quality monitoring networks
134 (AASQA). The availability of filter samples was variable from one site to the other one, depending on the sampling
135 frequency (typically every third or sixth day). Filter collection was conducted within the PM_{10} or the $PM_{2.5}$ aerosol
136 size fraction, depending on the investigated site (Table S1). Moreover, co-located and simultaneous PM_{10} and
137 $PM_{2.5}$ samplings were conducted at OPE-ANDRA and Revin, allowing to investigate the distribution of primary
138 sugar compounds between the fine and the coarse aerosol size fractions at these two sites.

139 Ambient aerosols were collected onto quartz fiber filters (Tissu-quartz PALL QAT-UP 2500 150 mm diameter),
140 preheated at 500 °C for 4 h minimum before use. After collection, all filter samples were wrapped in aluminum
141 foils, sealed in zipper plastic bags and stored at <4°C until further chemical analysis. Field blank filters were also
142 collected, at least once a month, using the same handling procedure than for PM samples. More detailed
143 information on the sampling periods, air sampler, number of filters and nature of PM samples are provided in
144 Table S1 and Fig. S1.

145 **2.2 Chemical analyses**

146 PM samples were analyzed for various chemical species using sub-sampled fractions of the collection filters. In
147 the frame of the present study, the carbonaceous matter (organic carbon (OC) and elementary carbon (EC)) was
148 analyzed using a thermo-optical method on a Sunset Lab analyzer (Birch and Cary, 1996) as described by Aymoz
149 et al. (2007), using the EUSAAR2 temperature program (Cavalli et al., 2010), except for the five sites of Northern
150 France where the NIOSH870 protocol was employed (Birch and Cary, 1996). Particulate organic matter (OM)
151 contents were then estimated by multiplying the organic carbon mass concentrations by a fixed factor, with $OM =$
152 $1.8 \times OC$ (Li et al., 2018; Ruthenburg et al., 2014; Vlachou et al., 2018a).

153 For the analysis of anhydrosugars, sugar alcohols, and primary saccharides, filter punches (typically of about 10
154 cm²) were first extracted into ultrapure water, then filtered using a 0.22 μm Acrodisc filter. Depending on the site,
155 analyses were conducted either by IGE (Institut des Géosciences de l'Environnement) or by LSCE (Laboratoire
156 des Sciences du Climat et de l'Environnement) (Table S1). At IGE, extraction was performed during 20 min in a
157 vortex shaker and analyses were achieved using an HPLC with Pulsed Amperometric Detection. A first set of
158 equipment was used until March 2016, consisting of a Dionex DX500 equipped with three columns Metrosep
159 (Carb 1-Guard + A Supp 15-150 + Carb 1-150), the analytical run being isocratic with 70 mM sodium hydroxide
160 eluent, followed by a gradient cleaning step with a 120 mM NaOH eluent. This analytical technique enables to
161 detect anhydrous saccharides (levoglucosan, mannosan, galactosan), polyols (arabitol, sorbitol, mannitol), and
162 glucose (Waked et al., 2014). A second set of equipment was used after this date, with a Thermo-Fisher ICS 5000[+]
163 HPLC equipped with 4 mm diameter Metrosep Carb 2 × 150 mm column and 50 mm pre-column. The analytical
164 run is isocratic with 15 % of an eluent of sodium hydroxide (200 mM) and sodium acetate (4 mM) and 85 % water,
165 at 1 mL min^{-1}. This method allows for additional separation and quantification of erythritol, xylitol, and threalose.
166 At LSCE, extraction was performed during 45 min by sonication and analyses were achieved using an IC (DX600,
167 Dionex) with Pulsed Amperometric Detection (ICS3000, Dionex). A CarboPAC MA1 columns has be used
168 (4 × 250 mm, Dionex), the analytical run being isocratic with 480 mM sodium hydroxide eluent. This analytical

Atmospheric
Chemistry
and Physics
Discussions

169 technique enable to detect anhydrous saccharides (levoglucosan, mannosan, galactosan), polyols (arabitol,

170 mannitol), and glucose.

171 Field blank filters were handled as real samples for quality assurance. The present data were corrected with field

172 blanks. The reproducibility of the analysis of primary sugar species (polyols, glucose), estimated from the analysis

173 of extracts of 10 punches from the same filters are generally in the range of 10-15 %.

174 Additional chemical analyses were conducted for most of the sites, allowing to quantify up to 130 different

175 chemical species (Table S1) in order to achieve PMF analyses, as will be presented in a forthcoming paper

176 (Salameh et al., in prep.).

177 **2.3 Statistical analysis**

178 Species concentration measurements were first analyzed for normality using Shapiro-Wilk's method with the

179 statistical program *R studio interface* (version 3.4.1). Since data were generally not distributed normally, we used

180 non-parametric statistical methods. The strength of the relationship between species concentrations was

181 investigated using the non-parametric Spearman rank correlation method. Multiple mean comparison analyses

182 were performed with the Kruskall-Wallis test method. Statistical significance was set at $p < 0.05$.

183 Positive Matrix Factorization for the source apportionment of the PM was previously performed at several sites of

184 this study, as part of the SOURCES (Favez et al., 2016; Salameh et al., in prep.) and DECOMBIO (Chevrier, 2017)

185 projects. We used the US EPA PMF 5.0 software (US EPA, 2015) , following the general recommendation

186 guidelines of the JRC (Belis et al., 2014). Briefly, the SOURCES program aimed at performing source

187 apportionment at 15 sites using a harmonized methodology, i.e. using the same chemical species, uncertainties,

188 constraints, and criteria for factor identification. The PMF conducted within SOURCES project uses about 30

189 different species, including carbonaceous fraction (OC, EC), ions (Cl^-, NO_3^- SO_4^{2-}, NH_4^+ K^+, Mg^{2+}, Ca^{2+}), organic

190 markers (polyols i.e. sum of arabitol, mannitol and sorbitol; levoglucosan; mannosan) and metals (Al, As, Ba, Cd,

191 Co, Cs, Cu, Fe, La, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, V, Zn). The PMF conducted within the DECOMBIO

192 project, for the sites of Marnaz, Chamonix, and Passy, used in addition to the 30 different species, aethalometer

193 (AE 33) measurements for the separation between BC_{wb} and BC_{ff} (black carbon from wood burning and fossil fuel,

194 respectively). For simplicity, BC_{wb} and BC_{ff} were summed up and labeled as EC in the present study. PMF

195 modelling was performed separately for each site. Statistical significance was validated with bootstrap higher than

196 80 % for each factor. Detailed methodology and results about these studies are given in their respective papers

197 (Chevrier, 2017; Favez et al., 2016; Salameh et al., in prep.). It should be noted that glucose was not included in

198 the final solution for any of these PMF, since it generally produced statistical instability of the solutions (this point

199 is further discussed in Sect. 3.2).

200 Also, the PMF in the SOURCES project took advantage of the possibility to add constraints in the solution

201 chemical profiles. In the PBOA profiles that are systematically obtained when polyols are included in the initial

202 datasets, we "pulled up maximally" their concentrations, while levoglucosan and mannosan were set to zero and

203 EC was "pulled down" maximally. It means that the PMF model tried to enrich the polyols mass in the PBOA

204 factor and deplete EC. Other constraints were added parsimoniously, targeting specific proxies of sources and are

205 further discussed in the respective papers.

Atmospheric
Chemistry
and Physics
Discussions

3. Results and discussion

3.1 Relative distribution between sugar alcohols and glucose

Figure 2 presents an overview of the relative mass concentration distributions of individual chemical species quantified at two sites with very different characteristics, an urban site in Grenoble and the rural site of OPE-ANDRA. Data are presented for the warmer season (e.g. during summer and fall), when concentrations were at their maximum (see Sect. 3.4). Glucose is the most abundant species measured (range 3.2–297.2 ng m^{-3}; average 37.6±26.4 ng m^{-3}), accounting on average for 25 % of primary sugar compound (SC) total mass at both sites. Mannitol (1.4–199.1 ng m^{-3}; 37.3±24.6 ng m^{-3}) and arabitol (0.2–133.9 ng m^{-3}; 32.0±22.2 ng m^{-3},) are the second and third most abundant species, accounting respectively for 25 and 23 % of SC mass. Threalose is relatively abundant in samples from these two sites (4.3–104.1 ng m^{-3}; 20.1±16.2 ng m^{-3}), accounting for 14 % of SC mass, but in general its concentration is frequently below the limit of quantification for samples from other sites in France (Fig. SI-3). The other identified polyols (i.e. erythritol, inositol, glycerol, sorbitol, and xylitol) present lower concentration levels (0.01–33.8 ng m^{-3}, 4.9±2.1 ng m^{-3}), corresponding altogether to 13 % of SC total mass.

Such ambient mass concentration distribution patterns are similar (but with variable intensities) to those previously reported for aerosol samples collected at various locations around the world. For example, Verma et al. (2018) found that glucose, and arabitol together with mannitol, contributed to 16.7 and 48.1 %, respectively, of total primary sugar compounds in aerosols from Chichijima Island. Similarly, Yttri et al. (2007) showed that glucose and the pair arabitol-mannitol were the main contributors of total primary monosaccharides and sugar alcohols in aerosols collected from four various background sites in Norway. In addition, Carvalho et al. (2003) reported that arabitol, mannitol and glucose as the most dominant primary sugar compounds in aerosols from rural background and boreal forest sites in Germany and Finland, respectively.
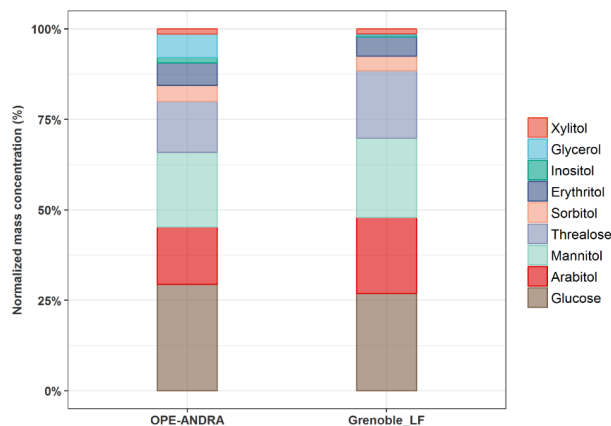
Figure 2: Overview of relative mass distributions of individual primary sugar alcohols and saccharide compounds quantified in PM$_{10}$ samples at two sites over summer and autumn periods (June to November) corresponding to maximal atmospheric concentrations of sugar alcohols/saccharide compounds.

Atmospheric
Chemistry
and Physics
Discussions

232
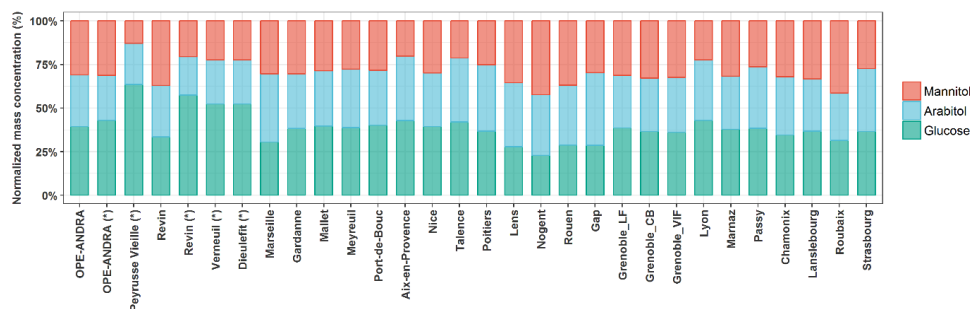
Figure 3: Mass concentration distributions of arabitol, mannitol, and glucose. Symbol (*) indicates PM$_{2.5}$ aerosol
samples. Only data for warmer season (e.g. during summer and fall), corresponding to maximal atmospheric
**concentration of polyols and glucose are shown.**

236

Although various primary sugar alcohols and saccharides have been detected and quantified for most of the

investigated sites, the following study focuses only on the three major and ubiquitous species, namely arabitol,

mannitol and glucose. Figure 3 presents their average relative contributions at all sites, for the warmer period,

displaying very similar features at a first glance. However, discrepancies could be observed from site to site, as

discussed in following sections.

3.2 Relationships between selected primary sugar compounds

Figure 4 summarizes linear correlations obtained between arabitol and mannitol concentrations at each site during

the warmer period. Medium to very high correlation coefficients could be observed ($0.58 \leq R^2 \leq 0.93$; $30 \leq n \leq$

143 or $45 \leq n \leq 341$ for PM$_{2.5}$ and PM$_{10}$ series, respectively), with slopes in a rather narrow range (between 0.59

and 1.10), and quite low intercepts (always below 9 ng m^{-3}). Such covariations indicate that both species are most

probably co-emitted, by one or several type(s) of sources, at each site during the summer-autumn period. These

observations are in agreement with previous studies also showing strong covariations between arabitol and

mannitol (Kang et al., 2018; Verma et al., 2018; Zhu et al., 2015). Therefore, it seemed reasonable to consider both

species together, so that their concentrations are summed up and labelled as "polyols" in the following sections.

Conversely, linear correlations between glucose and polyols concentrations are generally weaker

($0.10 < R^2 \leq 0.78$), with slopes varying over a much larger range (between 0.12 and 0.94), and variable intercepts

(between -5.6 and 16.4 ng m^{-3}). This suggests that glucose concentrations might follow a different pattern

compared to that of polyols, either due to different emission sources, or different chemical stability in the

atmosphere. It is therefore reasonable to keep glucose as a separate chemical species in the following discussion.

Also, this distinct behavior is most probably one reason why we were not able to obtain stable solutions when

including glucose in the PMF studies described in Sect. 3.5.

It should be emphasized that the slope of the regressions between the chemical concentrations are most probably

related to the emissions and atmospheric processing. Particularly in the case of mannitol and arabitol, they may be

influenced by biogenic or biotope characteristics. Nevertheless, no evident relationship between the slope values

and the typology or the geographical location of the sites could be observed (Fig. 4).

Atmospheric
Chemistry
and Physics
Discussions

262
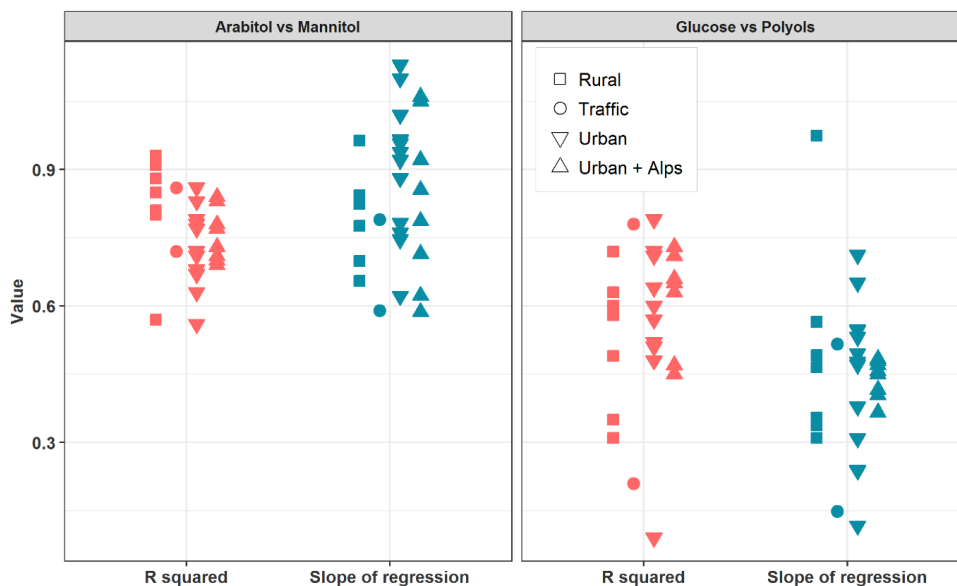
Figure 4: Linear regression analysis between selected primary sugar compounds mass concentrations (i.e. arabitol, mannitol and glucose) during summer and autumn seasons, for all the sites considered in this study.

265   **3.3 Relative distributions between PM$_{10}$ and PM$_{2.5}$**

266   Figure 5 shows the average PM$_{10}$ and PM$_{2.5}$ concentrations of polyols and glucose at OPE-ANDRA and Revin

267   during the summer and autumn seasons. The polyols mass concentrations ranged from 7.5±10.9 to 27.8±33.3 ng m$^-$

268   ^{3} in PM$_{2.5}$, and from 48.9±38.2 to 73.5±61.8 ng m^{-3} in PM$_{10}$, in Revin and OPE-ANDRA sites, respectively. PM$_{10}$-

269   to-PM$_{2.5}$ were then on average of about 3 to 5. Similar size distribution patterns, with variable intensity, were

270   observed for glucose (Fig. 5). These results indicate that polyols and glucose are mainly associated with the coarse

271   PM fraction. This observation is in good agreement with several previous investigations where polyols (especially

272   arabitol and mannitol), together with glucose, were prevalent in the coarse fraction (Fu et al., 2012; Fuzzi et al.,

273   2007; Pio et al., 2008; Yttri et al., 2007). However, Carvalho et al. (2003) reported different size distributions for

274   polyols and glucose, with variable fine or coarse mode maxima depending upon sampling location. For instance,

275   maximum atmospheric concentrations of mannitol were associated to fine and coarse aerosols from boreal forest

276   (Finland) and rural background sites (Germany), respectively. The authors hypothesized that these observations

277   are due to different assemblages of dominant fungal biota (with variable aerodynamic characteristics) at different

278   sites. Some other previous studies showed aerodynamic diameters typically ranging from 2 to 10 µm, even though

279   a few airborne bacterial/fungal spores could exceed that size (Bauer et al., 2008a; Elbert et al., 2007; Huffman et

280   al., 2012; Zhang et al., 2015).

Atmospheric
Chemistry
and Physics
Discussions

281
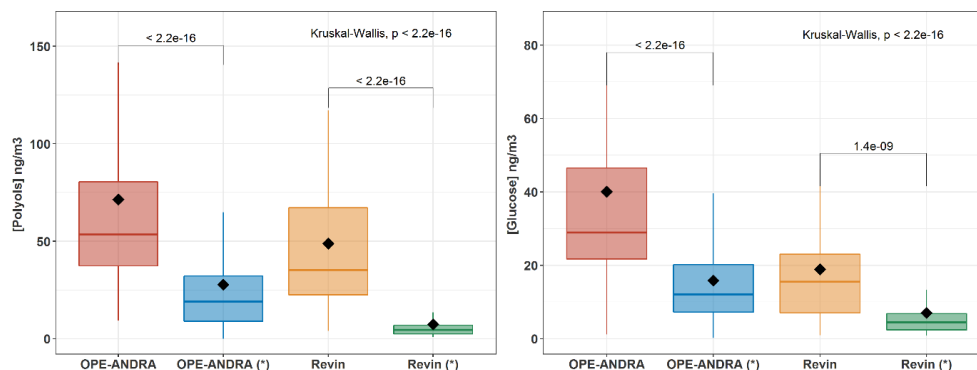
**Figure 5: Box plots of mass concentrations of polyols (left) and glucose (right) in PM$_{10}$ and PM$_{2.5}$ (with symbol (*)
samples). Black markers inside each boxplot indicate the mean concentration value, while the top, middle and bottom
lines of the box represent the 75th, median and 25th percentile, respectively. The whiskers at the top and bottom of the
box extend from the 95th to the 5th percentile. Statistical differences between average mass concentrations were analyzed
with the Kruskall-Wallis methods (p < 0.05).**

287 Hence, although if the precise mechanisms of atmospheric emission of particulate polyols and glucose are not fully

288 resolved, our observations are in good agreement with ambient mass concentrations of polyols and glucose being

289 likely associated with biological particles, as already suggested elsewhere (Fu et al., 2012; Verma et al., 2018;

290 Zhang et al., 2015). These species could enter the atmospheric compartment through either natural or

291 anthropogenic resuspension of surface soils and associated bacterial/fungal spores (containing polyols and primary

292 sugar compounds), or via a direct input resulting from microbial activities (e.g. sporulation). Another hypothesis

293 would be the abrasion of leaves and the subsequent release of microbial organisms and plant debris (Fu et al.,

294 2012; Medeiros et al., 2006; Simoneit et al., 2004).

3.4 Spatial and seasonal distribution of atmospheric concentrations

**3.4.1 Spatial and seasonal patterns of polyol concentrations**

297 As illustrated in Fig. 6, significant concentrations of polyols were measured at each investigated site, evidencing

298 the ubiquity of these organic compounds. Polyols mass concentrations clearly exhibit seasonal trends, with variable

299 intensity according to the sampling sites. On a seasonal average, polyols are more abundant in summer

300 (46.8±43.6 ng m^{-3}) and autumn (43.0±36.7 ng m^{-3}), followed by spring (19.0±13.6 ng m^{-3}) and winter

301 (16.2±11.5 ng m^{-3}). The average concentrations of polyols are then at least 2 to 3 times higher during summer or

302 autumn months than during the cold months, with a ratio that can be as high as 8 to 10.

303 Previous studies also reported similar seasonal variation pattern for urban and rural aerosol samples collected at

304 various locations. For example, Pashynska et al. (2002) measured higher atmospheric polyol (arabitol, mannitol)

305 contents during late summer and autumn, in Belgium. Several other studies reported higher concentrations of

306 polyols in summer than spring and winter time, in aerosols collected from Texas, USA and Jeju Island, respectively

307 (Fu et al., 2012; Jia et al., 2010a, 2010b). More recently, Liang et al. (2016) and Verma et al. (2018) also reported

308 similar seasonal distributions for aerosols sampled at Beijing, China and north-western Pacific, respectively.

309 The higher atmospheric polyols concentrations observed are likely due to the increased contribution from

310 metabolically active microbial derived sources (fungi, bacteria, green algal lichens) as a result of external stressors

Atmospheric
Chemistry
and Physics
Discussions

311   such as heat, drought and relative moisture. Indeed, fungal and prokaryotic cells activities, including their growth

312   and sporulation, are promoted by high temperature and humid conditions occurring in summer and autumn (China

313   et al., 2016; Elbert et al., 2007; Jones and Harrison, 2004; Rathnayake et al., 2017).

314   As also evidenced from Fig. 6, atmospheric polyols concentrations do not present any significant seasonal

315   differences related to the site typology (rural, traffic, urban sites with/without Alpine influences), or latitude. There

316   is some tendency toward higher concentrations in summer in Alpine environments, but some other sites (like the

317   rural site of OPE-ANDRA, in the North-East of France) can reach the same levels of concentrations. We tested

318   several types of hierarchical classifications, including variables like monthly or seasonal mean polyols

319   concentrations, the ratio arabitol-to-mannitol, or linear regression parameters (slope, R square) but none of them

320   led to a simple clustering of the sites that would explain the variability of the concentrations.

321
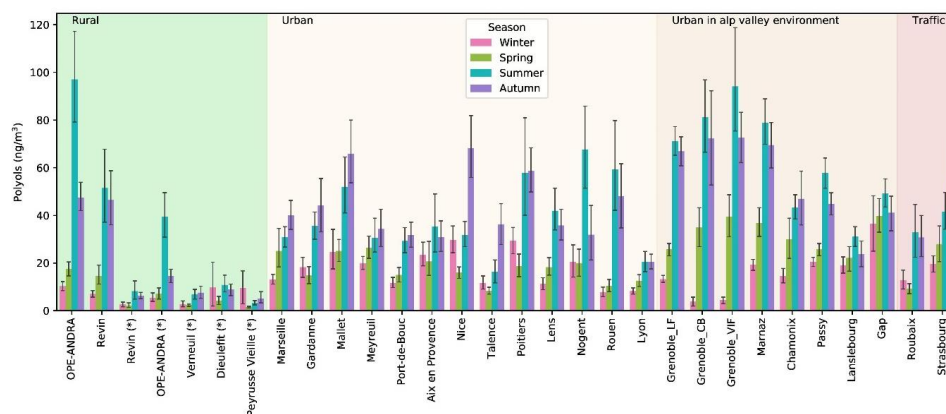
Figure 6: Spatial and seasonal distributions of atmospheric polyol average concentrations (ng m⁻³) for various types of sites in France. Error bars correspond to standard deviations calculated with seasonal concentrations. Symbol (*) indicates PM₂.₅ aerosol samples.

3.4.2 Spatial and seasonal patterns of glucose concentrations

326   Likewise polyols, the atmospheric concentrations of glucose also display seasonal and site-to-site variations

327   (Fig. 7). Except for Peyrusse-Vieille and Dieulefit, both rural sites with PM$_{2.5}$ sampling, ambient seasonal mean

328   concentrations (with standard deviations) of glucose are maximum in summer (25.0±24.2 ng m⁻³) and autumn

329   (24.6±19.8 ng m⁻³), followed by spring (15.8±12.4 ng m⁻³) and winter (12.6±10.2 ng m⁻³). The summer / winter

330   ratio for glucose seems generally lower than that of polyols, with higher ratios in the Alpine areas than in other

331   parts of France. However, as for polyols, it remains difficult to classify the sites according to any criteria linked to

332   site typology or latitude.

333   The seasonal trend of glucose concentrations in the present work is similar to that recently observed for aerosols

334   (PM$_{10}$ or total suspended particles) collected at various environmental background (suburban, urban and coastal)

335   sites around the world (Liang et al., 2016; Srithawirat and Brimblecombe, 2015; Verma et al., 2018). On average,

336   a wide range of daily glucose concentrations (expressed as min-max, mean) in PM$_{2.5}$ (0.02-162.0 ng m⁻³,

337   10.5±15.1 ng m⁻³) and PM$_{10}$ (0.1-297.2 ng m⁻³, 20.6±18.7 ng m⁻³) were observed in the present study. These values

338   are comparable to those in PM$_{2.5}$ (4.3-12.0, 7.2 ng m⁻³) and PM$_{10}$ (8.4-93.0, 47.0 ng m⁻³) reported from an urban

11

Atmospheric
Chemistry
and Physics
Discussions

339   site in Belgium (Yttri et al., 2007). More recently, Liang et al. (2016) also reported similar concentrations in $PM_{2.5}$

340   (7.1-202.8, 22.1±15.7 ng m^{-3}) and PM_{10} (3.1-343.6, 46.2±27.5 ng m^{-3}) from Beijing (China).

341   The sources and formation processes of glucose in the atmosphere are not currently well known and are rarely

342   discussed. Glucose is an important carbon source for soil metabolic active microbiota, and it is commonly present

343   in vascular plants. Additionally, cellulose (a linear polymer made of glucose subunits linked by β-1,4 bonds) is

344   one of the most important form of organic compounds in terrestrial ecosystems and a major plant structural

345   polymer (Boex-Fontvieille et al., 2014). It can also be quite abundant in the atmosphere (Puxbaum and Tenze-

346   Kunit, 2003). Hence, it is hypothesized that ambient glucose could be formed through active microbial (i.e.

347   bacteria, fungi etc.) enzymatic hydrolysis of cellulose in plant debris. Consistent with these observations, glucose

348   could be released into the atmosphere from both vascular plant materials (e.g. leaves, fruits, pollens, etc.) growing

349   in spring and decomposing in autumn/summer, and soil microbiota, as already suggested elsewhere (Di Filippo et

350   al., 2013; Jia et al., 2010a; Medeiros et al., 2006; Verma et al., 2018; Zhu et al., 2015).
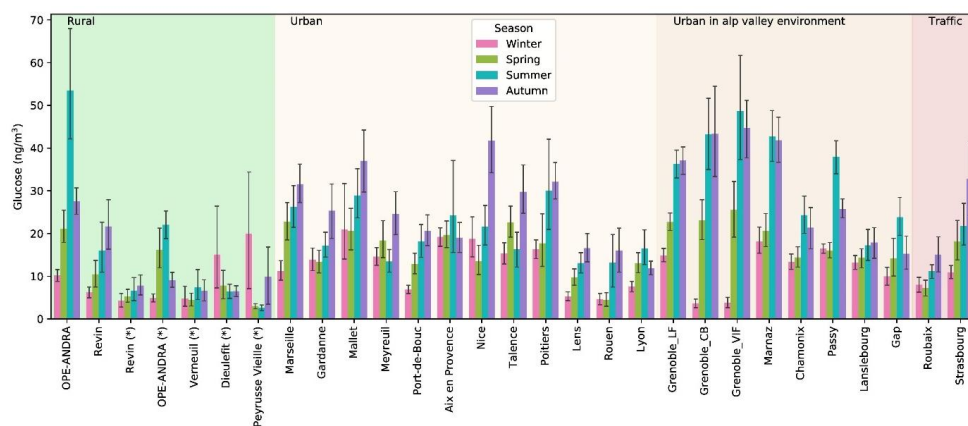

351

352   **Figure 7: Spatial and seasonal distributions of atmospheric glucose levels (ng m^{-3}) for various types of sites in France**
353   **(except the site of Nogent, which presented too many missing values. Error bars correspond to standard deviations**
354   **calculated with seasonal concentrations.**

355   **3.4.3 Relative contributions to aerosol organic matter concentrations**

356   The average contribution of polyols to the organic matter content (OM) of PM clearly displayed a seasonal

357   behavior, as shown in Fig. 8. Here again, contributions are 2 to 10 times higher during summer and autumn

358   compared to winter and spring, consistent with the assumption of higher emissions during these periods. The

359   seasonal mean contribution of polyols to OM fluctuates from site to site, and accounts for 0.1 to 2.1 % of overall

360   OM for these French sites (Fig. 8). Similarly, the seasonal mean concentrations of polyols together with glucose

361   represent between 0.2 to 3.1 % of total OM at these sites (Fig. S4). However, on a daily basis (Samake et al., in

362   prep.), atmospheric polyols mass concentrations can represent up to 6.3 % of total OM in PM_{10}, indicating that

363   polyols can be amongst the major molecular species identified in aerosol organic matter (Fig. S5). Again, we could

364   not find any simple way to group the sites according to their characteristics (typology or latitude, or climatic

365   region), in order to better understand the drivers behind the variability of this mass fraction. Further studies are

366   currently conducted using multi criterion examinations.

367 The seasonal polyols-to-OM distribution patterns in this study are comparable to those found for different urban

368 or rural sites in Europe (around 0.2 to 2.5 % of OM) (Pashynska et al., 2002; Yttri et al., 2007). Zhu et al. (2015)

369 also reported similar seasonal polyols-to-OM contribution trend for aerosols sampled at Cape Hedo (coastal site,

370 Japan).

371
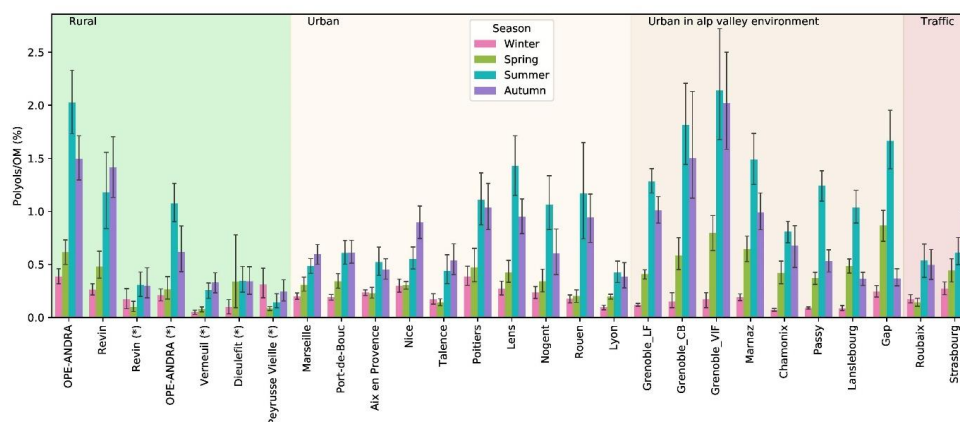
Figure 8: Spatial and seasonal distributions of mean contributions (in %) of polyols to the organic matter content of PM for various types of sites in France. Daily time-series of organic carbon (OC) were not available for the following sites: Gardanne, Mallet, and Meyreuil. Error bars correspond to standard deviations calculated with seasonal concentrations.

3.5 Primary biogenic factor in PMF studies

377 The sum of polyols (arabitol + mannitol) represent only a small fraction of the total OM. However, as proxies of

378 PBOA, they are most probably emitted with other chemical species. Emission from biological particles is a

379 complex topic since it may include a wide variety of compounds, both organic and inorganic (Elbert et al., 2007;

380 Zhang et al., 2015). Moreover, it is not clear if polyols are mainly emitted directly in the atmosphere or are linked

381 to other materials, for example with soil dust during resuspension processes. To investigate the relationship

382 between polyols and other species, it would have been possible to perform simple correlation analysis with

383 individual chemical species. This approach has the disadvantage of being a one-to-one relation and thus highly

384 sensitive to the dynamics of all PM emission sources, not only the one we are interested in. Alternatively, another

385 way is to use a PMF approach, also based on correlations but including much more information on the temporal

386 variations of the different sources influencing the PM chemistry at a given receptor site.

387 As mentioned in Sect. 2.3, the PMF results used in this study come from two different programs (SOURCES and

388 DECOMBIO) (Chevrier, 2017; Favez et al., 2016; Salameh et al., in prep.) and include sites of different typologies

389 (rural, traffic, urban sites in Alpine valley environments, etc.) for 16 different locations spread over France and

390 part of the current dataset. At each site, the PMF studies allowed to identify a PBOA factor, characterized by the

391 presence of more than 90 % of the total polyols content (sum of arabitol, mannitol and sorbitol), as presented in

392 Fig. S2. Hence, the chemical composition of this factor may be informative to investigate the PBOA source

393 components (Table S2), and to evaluate the importance of PBOA emissions in term of OM mass apportionment.

13

3.5.1. Contributions of PBOA to OM and polyols to PBOA

Altogether, the results from these 16 sites highlight the importance of the PBOA source contribution to total OM. As shown in Fig. 9, the OM apportioned by the PBOA factor represents a significant fraction of the total OM mass on a yearly average (range 6–28 %; average 13±6 %). When considering only the summer period (June-July-August), this contribution is even larger and can exceed 40 % of the total OM at sites in the Alpine area (Marnaz, Passy, Chamonix, Grenoble_LF) which are partially protected from large regional influences due to the local topography. Interestingly, some previous work using the same samples from the sites in the Arve valley (Passy, Chamonix) showed that about 90 % of the OM is from modern origin (using ^{14}C measurements) during summer, with no apparent correlation between this modern carbon and polyols concentrations (Bonvalot et al., 2016). Hence, despite being an important contributing source, PBOA is not the major biogenic source in this type of environment. Tracers of secondary biogenic formation processes (like pinic acid or 3-MBTCA) were measured in these series.

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

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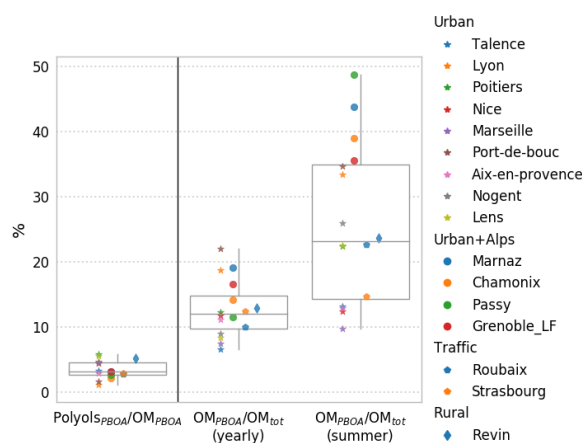

Figure 9: Mass contribution of polyols to OM in the PBOA factor, and relative contributions of the OM$_{PBOA}$ factor to the total OM in PM for the 16 studied sites where PMF model was run, over the year and summertime only. Stars and circle refer to urban sites without/and with Alpine valley influence,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

Atmospheric
Chemistry
and Physics
Discussions

3.5.2 PBOA profile constituents and emission process

Figure 10 shows the contribution (in µg of species per µg of PM in the PBOA factor profile) of each chemical

species included in the averaged PBOA factor from the 16 PMF studies. The principal contributors are OC and

EC, and significant fractions of crustal material also appear (Na^+, K^+, Ca^{2+}, Al, Ba, Cu, Fe, Mn, Ti, Zn) as well as

secondary elements such as nitrate and sulfate. On average, the PBOA factor does not comprise a large fraction of

metals and trace elements, most of them being below 1 pg µg^{-1}. Here again, the low variability of the PBOA

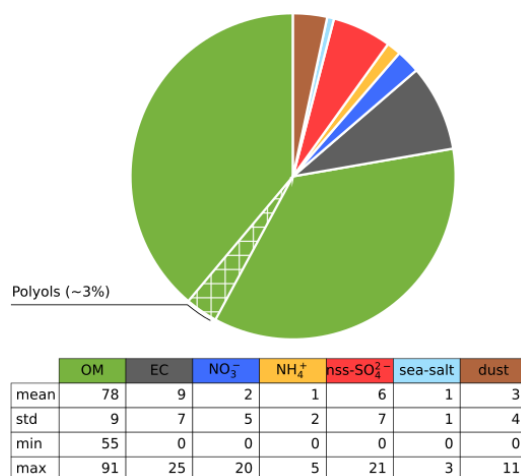chemical profile encountered across a large array of sites is remarkable.
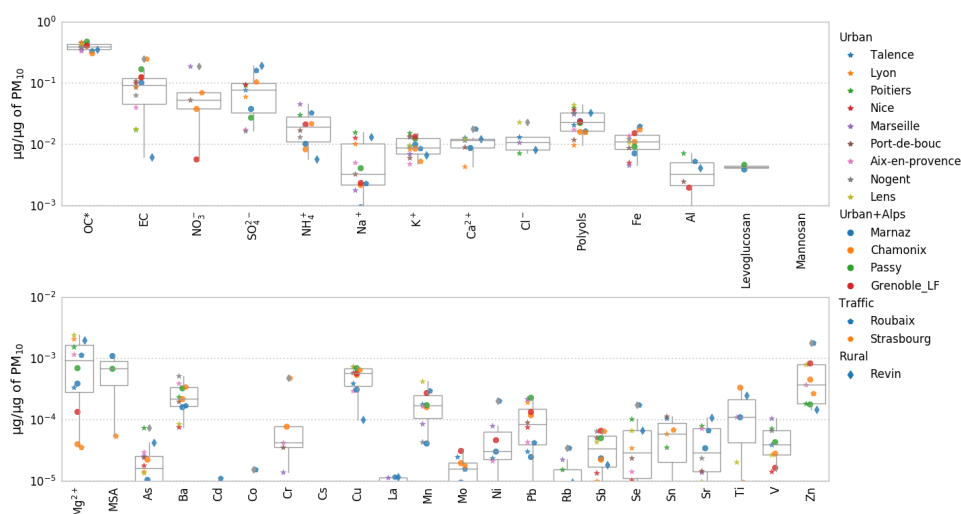
Figure 10: PMF chemical profile of the PBOA factor in the DECOMBIO and SOURCES programs expressed as a fraction of the PM mass. Values lower than a few pg µg^{-1} are not displayed on purpose. For each boxplot, the top, middle and bottom lines represent the 75th, median and 25th percentile, respectively. The whiskers at the top and bottom of the box extend from the maximum to the minimum.

The contribution from some crustal material could agree with the coarse mode distributions of polyols (Sect. 3.3)

and could be indicative of an emission process with the entrainment of spores with soil dust resuspension. To

investigate the importance of mineral dust in the PBOA factor, we clustered the chemical components of PM from

PBOA into 7 classes: OM (= $1.8 \times OC$), EC, NO_3^-, NH_4^+, non-sea-salt sulfate (nss-SO$_4$), sea-salt, and dust. nss-

SO$_4^{2-}$ is calculated from the measured SO$_4^{2-}$ minus the sea-salt fraction of SO$_4^{2-}$ ($nssSO_4^{2-} = SO_4^{2-} - ssSO_4^{2-}$

where $ssSO_4^{2-} = 0.252 \times Na^+$) according to Seinfeld and Pandis (1997). The sea-salt fraction is calculated

according to Putaud et al. (2010): $sea - salt = Cl^- + 1.47 \times Na^+$. Finally the dust fraction is estimated from

Putaud et al. (2004b) as: $dust = (nss - Ca^{2+}) \times 5.6$ with nss-Ca^{2+} stands for non-sea salt Ca^{2+} and is computed

thanks to $nss - Ca^{2+} = Ca^{2+} - Na^+/26$.

Figure 11 presents the normalized average contributions of these 7 classes to the PBOA mass for the 16 sites with

PMF modelling. It clearly revealed that the PBOA factor is dominated by OM (78±9 %), followed by EC (9±7 %),

and only a minor fraction of the dust class (3±4 %). This result tends to infirm the hypothesis associating PBOA

to mineral dust resuspension. Indeed, our findings rather suggest that a main part of PBOA (and polyols) are most

likely associated with biological particle direct emissions. It leaves only a minor fraction that could be linked to

the mechanical resuspension of PBOA with crustal elements and long-term deposited EC particles, being

449 accumulated in topsoil. Previous works indicate that a large proportion of produced EC ends up in soil, where it

450 can reside for thousands of years, being relatively resistant to biological and chemical degradation (Forbes et al.,

451 2006; Hammes et al., 2007; Zhan et al., 2016).

452

	OM	EC	NO_3^-	NH_4^+	nss-SO_4^{2-}	sea-salt	dust
mean	78	9	2	1	6	1	3
std	9	7	5	2	7	1	4
min	55	0	0	0	0	0	0
max	91	25	20	5	21	3	11

453

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

456 **4. Conclusion**

457 The contribution of primary biogenic organic aerosols to PM is barely documented in the scientific literature. The

458 present study aimed at providing a large overview of the spatial and temporal evolution of concentrations and

459 contributions to aerosol organic matter of dominant primary sugar alcohols and saccharide compounds, for a large

460 selection of environmental conditions in France. With 28 sites and more than 5,340 samples, it is to our knowledge

461 the most comprehensive dataset for these compounds. The main results obtained indicate that:

462 • among the identified polyols, arabitol together with mannitol are the major species by mass, with lesser
463 amounts of others polyols (e.g., erythritol, inositol, glycerol, sorbitol, and xylitol). Glucose is the
464 dominant primary monosaccharide and its relative abundance is comparable to the sum of arabitol and
465 mannitol;

466 • the two main polyols (arabitol and mannitol) together with glucose are mainly present within the coarse
467 aerosol mode;

468 • at nearly all sites, ambient levels of the main polyols and glucose displayed clear seasonal variation cycles,
469 with a gradual increase from spring and maximum in summer and autumn aerosols, followed by a sudden
470 decrease in late autumn, and a winter minimum;

471 • atmospheric concentrations of the main polyols and glucose fluctuate according to site and season, and
472 account each for between 0.1 to 2.1 % of OM on a seasonal average basis at these French sites;

Atmospheric
Chemistry
and Physics
Discussions

473 • ambient mass concentrations of arabitol and mannitol are comparable. Meanwhile, they display very good
474 temporal covariation, with ratios varying between sites. Conversely, linear correlations between the main
475 polyols and glucose concentrations are much lower, suggesting different atmospheric sources, or
476 atmospheric processes;

477 • Arabitol and mannitol are efficient organic markers for PBOA. PMF studies of the yearly series from 16
478 sites give contributions of the primary biogenic emission (traced with the main polyols) to the total OM
479 around 13±6 % on a yearly average and 26±12 % during summer, thereby showing that PBOA is an
480 important source of total OM in PM_{10} for all sites across France. Furthermore, the average PBOA
481 chemical source profile is made out of a very large fraction of OM (78±9 % of the total PBOA mass on
482 average), suggesting it is mainly related to direct biogenic emissions from biological particles. The low
483 crustal fraction indicates that this factor is weakly linked to soil dust resuspension associated with
484 biological material;

485 • however, the PBOA source remains chemically poorly characterized as the main polyols represent only
486 a small fraction of its total OM mass (3.0±1.5 % on average);

487 • despite comparable high concentrations in the atmosphere, the sources and processes leading to glucose
488 concentrations and seasonal evolutions are still elusive. Indeed, the different PMF performed with glucose
489 in input variable do not lead to statistically stable solution;

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

493

506

507 **Author contributions:** JLJ was the supervisor for the PhD for AS, FC, SW, and for the post-doc of DS. He
508 directed all the personnel who performed the analysis at IGE. He was coordinator or PI for the programs that
509 generated the data for 18 of the 28 sites in this study (OPE-ANDRA, Part'Aera, CAMERA, SRN 2013, 3 Villes
510 PACA, DECOMBIO, QAMECS) and co-PI for programs for 5 other sites. He is the coordinator for the CNRS
511 LEFE-EC2CO CAREMBIOS program that is funding the work of AS. GU was the co-supervisor for the PhD of

Atmospheric
Chemistry
and Physics
Discussions

524   **References**

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

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

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

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

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

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

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

544   Bonvalot, L., Tuna, T., Fagault, Y., Jaffrezo, J.-L., Jacob, V., Chevrier, F., and Bard, E.: Estimating contributions
545   from biomass burning, fossil fuel combustion, and biogenic carbon to carbonaceous aerosols in the Valley of
546   Chamonix: a dual approach based on radiocarbon and levoglucosan, Atmos. Chem. Phys., 16(21), 13753–13772,
547   2016.

548   Boucher, O., Randall, D., Artaxo, P., Bretherton, C., Feingold, G., Forster, P., Kerminen, V.-M., Kondo, Y., Liao,
549   H., and Lohmann, U.: Clouds and aerosols, in Climate change 2013: the physical science basis. Contribution of
550   Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, pp. 571–
551   657, Cambridge University Press., 2013.

552   Carvalho, A., Pio, C., and Santos, C.: Water-soluble hydroxylated organic compounds in German and Finnish
553   aerosols, Atmos. Environ., 37(13), 1775–1783, 2003.

554   Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J.-P.: Toward a standardised thermal-optical protocol
555   for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, Atmospheric Meas. Tech., 3(1),
556   79–89, 2010.

557   Chevrier, F.: Chauffage au bois et qualité de l'air en Vallée de l'Arve : définition d'un système de surveillance et
558   impact d'une politique de rénovation du parc des appareils anciens, PhD thesis, Université Grenoble Alpes, 23
559   November. [online] Available from: https://tel.archives-ouvertes.fr/tel-01527559/document, 2017.

560   China, S., Wang, B., Weis, J., Rizzo, L., Brito, J., Cirino, G. G., Kovarik, L., Artaxo, P., Gilles, M. K., and Laskin,
561   A.: Rupturing of biological spores as a source of secondary particles in amazonia, Environ. Sci. Technol., 50(22),
562   12179–12186, 2016.

563   Cho, A. K., Sioutas, C., Miguel, A. H., Kumagai, Y., Schmitz, D. A., Singh, M., Eiguren-Fernandez, A., and
564   Froines, J. R.: Redox activity of airborne particulate matter at different sites in the Los Angeles Basin, Environ.
565   Res., 99(1), 40–47, 2005.

566   Després, V. R., Alex Huffman, J., Burrows, S. M., Hoose, C., Safatov, A. S., Buryak, G., Fröhlich-Nowoisky, J.,
567   Elbert, W., Andreae, M. O., Pöschl, U., and Jaenicke, R.: Primary biological aerosol particles in the atmosphere:
568   a review, Tellus B: Chemical and Physical Meteorology, 64:1, 15598, 2012.

569   Di Filippo, P., Pomata, D., Riccardi, C., Buiarelli, F., and Perrino, C.: Fungal contribution to size-segregated
570   aerosol measured through biomarkers, Atmos. Environ., 64, 132–140, 2013.

571   Elbert, W., Taylor, P. E., Andreae, M. O., and Pöschl, U.: Contribution of fungi to primary biogenic aerosols in
572   the atmosphere: wet and dry discharged spores, carbohydrates, and inorganic ions, Atmospheric Chem. Phys.,
573   7(17), 4569–4588, 2007.

574   Favez, O., Salameh, D., and Jaffrezo, J.-L.: Traitement harmonisé de jeux de données multi-sites pour l'étude de
575   sources de PM par Positive Matrix Factorization (PMF) | LCSQA. [online] Available from:
576   http://www.lcsqa.org/rapport/2016/ineris/traitement-harmonise-jeux-donnees-multi-sites-etude-sources-pm-
577   positive-matrix-f, 2016.

578   Forbes, M. S., Raison, R. J., and Skjemstad, J. O.: Formation, transformation and transport of black carbon
579   (charcoal) in terrestrial and aquatic ecosystems, Sci. Total Environ., 370(1), 190–206,
580   doi:10.1016/j.scitotenv.2006.06.007, 2006.

581   Fortenberry, C. F., Walker, M. J., Zhang, Y., Mitroo, D., Brune, W. H., and Williams, B. J.: Bulk and molecular-
582   level characterization of laboratory-aged biomass burning organic aerosol from oak leaf and heartwood fuels,
583   Atmospheric Chem. Phys., 18(3), 2199–2224, 2018.

584   Fröhlich-Nowoisky, J., Kampf, C. J., Weber, B., Huffman, J. A., Pöhlker, C., Andreae, M. O., Lang-Yona, N.,
585   Burrows, S. M., Gunthe, S. S., Elbert, W., Su, H., Hoor, P., Thines, E., Hoffmann, T., Després, V. R., and Pöschl,
586   U.: Bioaerosols in the Earth system: Climate, health, and ecosystem interactions, Atmospheric Res., 182, 346–
587   376, 2016.

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

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

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

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

604   Golly, B., Waked, A., Weber, S., Samake, A., Jacob, V., Conil, S., Rangonio, J., Chrétien, E., Vagnot, M., Robic,
605   P., Besombes, J.-L., and Jaffrezo, J. L.: Organic markers and OC source apportionment for seasonal variations of
606   PM2.5 at 5 rural sites in France, Submit Atmos. Environ. 24 04, 2018.

607   Gosselin, M. I., Rathnayake, C. M., Crawford, I., Pöhlker, C., Fröhlich-Nowoisky, J., Schmer, B., Després, V. R.,
608   Engling, G., Gallagher, M., Stone, E., Pöschl, U., and Huffman, J. A.: Fluorescent bioaerosol particle, molecular
609   tracer, and fungal spore concentrations during dry and rainy periods in a semi-arid forest, Atmos. Chem. Phys.,
610   16(23), 15165–15184, 2016.

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

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

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

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

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

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

634   Jia, Y., Bhat, S., and Fraser, M. P.: Characterization of saccharides and other organic compounds in fine particles
635   and the use of saccharides to track primary biologically derived carbon sources, Atmos. Environ., 44(5), 724–732,
636   2010a.

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

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

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

644 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
645 chemical composition of PM2.5 on visibility in a semi-rural city of Sichuan basin, Aerosol Air Qual. Res., 18(4),
646 957–968, 2018.

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

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

651 Manninen, H. E., Bäck, J., Sihto-Nissilä, S.-L., Huffman, J. A., Pessi, A.-M., Hiltunen, V., Aalto, P. P., Hidalgo
652 Fernández, P. J., Hari, P., Saarto, A., and others: Patterns in airborne pollen and other primary biological aerosol
653 particles (PBAP), and their contribution to aerosol mass and number in a boreal forest, Boreal Environ. Res., 383–
654 405, 2014.

655 Medeiros, P. M., Conte, M. H., Weber, J. C., and Simoneit, B. R. T.: Sugars as source indicators of biogenic
656 organic carbon in aerosols collected above the Howland Experimental Forest, Maine, Atmos. Environ., 40(9),
657 1694–1705, 2006.

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

661 Nozière, B., Kalberer, M., Claeys, M., Allan, J., D'Anna, B., Decesari, S., Finessi, E., Glasius, M., Grgić, I.,
662 Hamilton, J. F., Hoffmann, T., Iinuma, Y., Jaoui, M., Kahnt, A., Kampf, C. J., Kourtchev, I., Maenhaut, W.,
663 Marsden, N., Saarikoski, S., Schnelle-Kreis, J., Surratt, J. D., Szidat, S., Szmigielski, R., and Wisthaler, A.: The
664 molecular identification of organic compounds in the atmosphere: state of the art and challenges, Chem. Rev.,
665 115(10), 3919–3983, doi:10.1021/cr5003485, 2015.

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

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

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

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

677 Putaud, J.-P., Raes, F., Van Dingenen, R., Brüggemann, E., Facchini, M.-C., Decesari, S., Fuzzi, S., Gehrig, R.,
678 Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Querol, X., Rodriguez, S., Schneider,
679 J., Spindler, G., Brink, H. ten, Tørseth, K., and Wiedensohler, A.: A European aerosol phenomenology 2: chemical
680 characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, Atmos. Environ.,
681 38(16), 2579–2595, 2004a.

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

685 Putaud, J.-P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R.,
686 Hansson, H. C., Harrison, R. M., Herrmann, H., Hitzenberger, R., Hüglin, C., Jones, A. M., Kasper-Giebl, A.,
687 Kiss, G., Kousa, A., Kuhlbusch, T. A. J., Löschau, G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J.,
688 Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J.,
689 Spindler, G., ten Brink, H., Tursic, J., Viana, M., Wiedensohler, A., and Raes, F.: A European aerosol

Atmospheric
Chemistry
and Physics
Discussions

690   phenomenology – 3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside
691   sites across Europe, Atmos. Environ., 44(10), 1308–1320, 2010.

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

694   Rathnayake, C. M., Metwali, N., Jayarathne, T., Kettler, J., Huang, Y., Thorne, P. S., O'Shaughnessy, P. T., and
695   Stone, E. A.: Influence of rain on the abundance of bioaerosols in fine and coarse particles, Atmos. Chem. Phys.,
696   17(3), 2459–2475, 2017.

697   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
698   Visser, J.: Mannitol Is Required for Stress Tolerance in Aspergillus niger Conidiospores, Eukaryot. Cell, 2(4),
699   690–698, doi:10.1128/EC.2.4.690-698.2003, 2003.

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

703   Salameh, D., Weber, S., Favez, O., Riffault, V., Perdrix, E., Albinet, A., Jacob, V., Alleman, L., Waked, A.,
704   Olievera, D. M., Chevrier, F., Guillaud, G., Meshba, B., Rocq, B., Hulin, A., Le Meur, S., Chrétien, E. and Jaffrezo,
705   J. L.: A harmonized PM source apportionment at 15 different sites in France using a constrained PMF approach
706   (2018), Atmosphere, in prep.

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

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

713   Simoneit, B. R. T.: Composition and major sources of organic compounds of aerosol particulate matter sampled
714   during the ACE-Asia campaign, J. Geophys. Res., 109 (D19): D19S10, 2004.

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

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

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

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

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

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

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

Atmospheric
Chemistry
and Physics
Discussions

734   Vlachou, A., Tobler, A., Lamkaddam, H., Canonaco, F., Daellenbach, K. R., Jaffrezo, J.-L., Minguillón, M. C.,
735   Maasikmets, M., Teinemaa, E., Baltensperger, U., El Haddad, I., and Prévôt, A. S. H.: Seasonal variation of organic
736   aerosol sources in Estonia: advanced source apportionment and uncertainty estimation, Atmos. Chem. Phys.
737   Discuss., (2018b), in prep.

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

742   Yang, Y., Chan, C., Tao, J., Lin, M., Engling, G., Zhang, Z., Zhang, T., and Su, L.: Observation of elevated fungal
743   tracers due to biomass burning in the Sichuan Basin at Chengdu City, China, Sci. Total Environ., 431, 68–77,
744   2012.

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

747   Zhan, C., Zhang, J., Cao, J., Han, Y., Wang, P., Zheng, J., Yao, R., Liu, H., Li, H., and Xiao, W.: Characteristics
748   and sources of black carbon in atmospheric dustfall particles from Huangshi, China, Aerosol Air Qual. Res., 16(9),
749   2096–2106, doi:10.4209/aaqr.2015.09.0562, 2016.

750   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.:
751   Contribution of fungal spores to particulate matter in a tropical rainforest, Environ. Res. Lett., 5(2), 24010, 2010.

752   Zhang, Z., Engling, G., Zhang, L., Kawamura, K., Yang, Y., Tao, J., Zhang, R., Chan, C., and Li, Y.: Significant
753   influence of fungi on coarse carbonaceous and potassium aerosols in a tropical rainforest, Environ. Res. Lett.,
754   10(3), 34015, 2015.

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

758