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Grenoble, August 3, 2019.

Dear Pr Alex Huffman

Thank you for your consideration, please find enclosed our revised manuscript on “Arabitol, mannitol and glucose as tracers of primary biogenic organic aerosol: influence of environmental factors on ambient air concentrations and spatial distribution over France” by Abdoulaye Samaké et al. (MS No.: ACP-2019-434).

Thank you for your constructive technical comments that contribute to improve this work.

Concerning your comment about our recent work submitted for publication in Sci. Advances, mentioned in response to “the last big comment from referee #3”, you are right that this work was not referenced. Sorry about it. Please, find below a reference of this publication (still under review).

Samaké A., A. Bonin, J.-L. Jaffrezo, P. Taberlet, G. Uzu, S. Conil, and J.M.F. Martins. (2019): High levels of primary biogenic organic aerosols in the atmosphere in summer are driven by only a few microorganisms from the leaves of surrounding plants, Sci. Advances, In Review.

Additionally, as illustrate in the marked-up manuscript version (see below), we have considered all of your technical comments and we made corrections accordingly.

I therefore resubmit our paper after considering all remarks and I truly hope that our improvements will meet your requirements.

On behalf all co-authors,

Arabitol, mannitol and glucose as tracers of primary biogenic organic aerosol: influence of environmental factors on ambient air concentrations and spatial distribution over France

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1 **Abstract.** The primary sugar compounds (SC, defined as glucose, arabinol and mannitol) are widely recognized as
2 suitable molecular markers to characterize and apportion primary biogenic organic aerosol emission sources. This
3 work improves our understanding of the spatial behavior and distribution of these chemical species and evidences
4 their major effective environmental drivers. We conducted a large study focusing on the daily (24 h) PM₁₀ SC
5 concentrations for 16 increasing space scale sites (local to nation-wide), over at least one complete year. These
6 sites are distributed in several French geographic areas of different environmental conditions. Our analyses, mainly
7 based on the examination of the short-term evolutions of SC concentrations, clearly show distance-dependent
8 correlations. SC concentration evolutions are highly synchronous at an urban city-scale and remain well correlated
9 throughout the same geographic regions, even if the sites are situated in different cities. However, sampling sites
10 located in two distinct geographic areas are poorly correlated. Such pattern indicates that the processes responsible
11 for the evolution of the atmospheric SC concentrations present a spatial homogeneity over typical areas of at least
12 tens of kilometers. Local phenomena, such as resuspension of topsoil and associated microbiota, do not account for
13 the major emissions processes of SC in urban areas not directly influenced by agricultural activities. The
14 concentrations of SC and cellulose display remarkably synchronous temporal evolution cycles at an urban site in
15 Grenoble, indicating a common source ascribed to vegetation. Additionally, higher concentrations of SC at another
16 site located in a crop field region occur during each harvest periods, pointing out resuspension processes of plant
17 materials (crop detritus, leaf debris) and associated microbiota for agricultural and nearby urbanized areas. Finally,
18 ambient air temperature, relative humidity and vegetation density constitute the main effective drivers of SC
19 atmospheric concentrations.

20 **1. Introduction**

21 Primary biogenic organic aerosols (PBOA), which notably comprise bacterial and fungal cells or spores; viruses;
22 or microbial fragments such as endotoxins and mycotoxins; and pollens and plant debris, are ubiquitous particles
23 released from the biosphere to the atmosphere (Amato et al., 2017; Fang et al., 2018; Martin et al., 2010; Perrino
24 and Marcovecchio, 2016; Wéry et al., 2017). PBOA can contribute significantly to the total coarse aerosol mass
25 (Amato et al., 2017; Bozzetti et al., 2016; Coz et al., 2010; Fröhlich-Nowoisky et al., 2016; Jaenicke, 2005;
26 Manninen et al., 2014; Morris et al., 2011; Samaké et al., 2019; Vlachou et al., 2018; Yue et al., 2017). Besides
27 their expected negative human health effects (Fröhlich-Nowoisky et al., 2009, 2016; Humbal et al., 2018; Lecours
28 et al., 2017; Zamfir et al., 2019), they substantially influence the carbon and water cycles at the global scale,
29 notably acting as cloud and ice nuclei (Ariya et al., 2009; Elbert et al., 2007; Fröhlich-Nowoisky et al., 2016; Hill
30 et al., 2017; Humbal et al., 2018; Morris et al., 2014; Rajput et al., 2018). While recent studies have revealed highly
31 relevant information on the abundance and size partitioning of PBOA (Fröhlich- Nowoisky et al., 2017; Huffman
32 and Santarpia, 2017), their emission sources and contribution to total airborne particles are still poorly documented,
33 partly due to the analytical limitations to distinguish PBOA from other types of carbonaceous particulate matter
34 (Bozzetti et al., 2016; China et al., 2018; Di Filippo et al., 2013; Perrino and Marcovecchio, 2016; Yan et al.,
35 2019). Notably, the global emissions of fungal spore emitted into the atmosphere are still poorly constrained and
36 range from 8 Tg.y⁻¹ to 186 Tg.y⁻¹ (Després et al., 2012; Elbert et al., 2007; Jacobson and Streets, 2009; Sesartic
37 and Dallafior, 2011; Tanarhte et al., 2019).

38 Recently, source-specific tracer methodologies have been introduced to estimate their contribution to aerosol
39 loadings (Di Filippo et al., 2013; Gosselin et al., 2016; Li et al., 2018; Medeiros et al., 2006b; Verma et al., 2018;
40 Wang et al., 2018). Indeed, atmospheric organic aerosols (OA) contain specific chemical species that can be used
41 as reliable biomarkers in tracing the sources and abundance of PBOA (Bauer et al., 2008; Gosselin et al., 2016;
42 Holden et al., 2011; Jia et al., 2010; Li et al., 2018; Medeiros et al., 2006b; Wang et al., 2018). For instance, among
43 sugar alcohols, arabinol and mannitol (two common storage soluble carbohydrates in fungi) have been recognized
44 as tracers for airborne fungi, and their concentrations are widely used to estimate PBOA contributions to OA mass
45 (Amato et al., 2017; Bauer et al., 2008; Buiarelli et al., 2013; Golly et al., 2018; Medeiros et al., 2006b; Samaké

46 et al., 2019; Srivastava et al., 2018; Verma et al., 2018; Weber et al., 2018, 2019). Similarly, glucose has also been
47 used as a tracer for plant materials (such as pollen, leaves, and their fragments) or soil emissions within various
48 studies around the world (Chen et al., 2013; Medeiros et al., 2006b; Pietrogrande et al., 2014; Rathnayake et al.,
49 2017; Rogge et al., 2007; Wan et al., 2019; Xiao et al., 2018; Zhu et al., 2015).

50 In this context, atmospheric concentrations of specific sugar alcohols and/or primary monosaccharides (including
51 glucose) have been previously quantified at sites in several continental, agricultural, coastal or polar regions
52 (Barbaro et al., 2015; Chen et al., 2013; Glasius et al., 2018; Li et al., 2018; Pietrogrande et al., 2014; Verma et
53 al., 2018; Wan et al., 2019; Yan et al., 2019; Yttri et al., 2007). However, large datasets investigating their
54 (multi)annual cycles, seasonal and simultaneous short-term variations at multiple spatial scale resolutions (i.e.
55 from local to continental) are still lacking (Liang et al., 2013; Nirmalkar et al., 2018; Pietrogrande et al., 2014;
56 Yan et al., 2019). Such records are essential to better understand the spatial behavior of primary sugar compound
57 (SC) concentrations (i.e., glucose, arabinol and mannitol) and PBOA emission processes, and to isolate their
58 potential key drivers (e.g., vegetation type and density, topography, weather conditions, etc.), which are still
59 unclear (Bozzetti et al., 2016). This information would be essential for further implementation into chemical
60 transport models (Heald and Spracklen, 2009; Myriokefalitakis et al., 2017; Tanarhte et al., 2019).

61 It is commonly acknowledged that SC (particularly arabinol and mannitol) originate from primary biogenic derived
62 sources such as bacterial, fungal spores, and plant materials (Di Filippo et al., 2013; Golly et al., 2018; Gosselin et
63 al., 2016; Holden et al., 2011; Kang et al., 2018; Medeiros et al., 2006b; Wan et al., 2019; Yan et al., 2019; Yttri et
64 al., 2007; Zhu et al., 2018a). Some studies have characterized the composition of SC in topsoil samples (for
65 fractions larger than PM₁₀) from both, natural (i.e., uncultivated) and agricultural regions (Medeiros et al., 2006a;
66 Rogge et al., 2007; Simoneit et al., 2004; Wan and Yu, 2007). The authors suggested that the particulate arabinol,
67 mannitol and glucose are introduced into the atmosphere mainly through resuspended soils or dust particles and
68 associated biota derived from natural soil erosion, unpaved road dust or agricultural practices. Conversely, Jia and
69 Fraser (2011) reported higher concentrations of SC relative to PBOA in size-segregated aerosol samples collected
70 at a suburban site (Higley, USA) compared to the local size-fractionated soils (equivalent to atmospheric PM_{2.5}
71 and PM₁₀). This suggested that direct emissions from biota (microbiota, vascular plant materials) could also be a
72 significant atmospheric input process for SC at this suburban site.

73 A large database on SC concentrations was obtained over France in the last decade. It already allowed the
74 investigation of the size distribution and seasonal variabilities of SC concentrations in aerosols at 28 French sites,
75 notably showing that SC are ubiquitous primary aerosols, accounting for a significant proportion of PM₁₀ organic
76 matter (OM) mass (Samaké et al., 2019). Results confirmed that their ambient concentrations display a well-
77 marked seasonality, with maximum concentrations from late spring to early autumn, followed by an abrupt
78 decrease in late autumn, and a minimum concentration during wintertime in France. This study also showed that
79 the mean PBOA chemical profile is largely dominated by organic compounds, with only a minor contribution of
80 dust particle fraction. The latter result indicated that ambient polyols could most likely be associated with direct
81 biological particle emissions (e.g. active spore discharge, microbiota released from phylloplane or phyllosphere,
82 etc.) rather than with the microorganism-containing soil resuspension. These observations call for more
83 investigations of the predominant SC (and PBOA) emission sources.

84 Cellulose, a linear polymer composed of D-glucopyranose units linked by β -1,4 bonds, is the most frequent
85 polysaccharide occurring in terrestrial environments (Ramoni and Seiboth, 2016). Plant materials contain cellulose

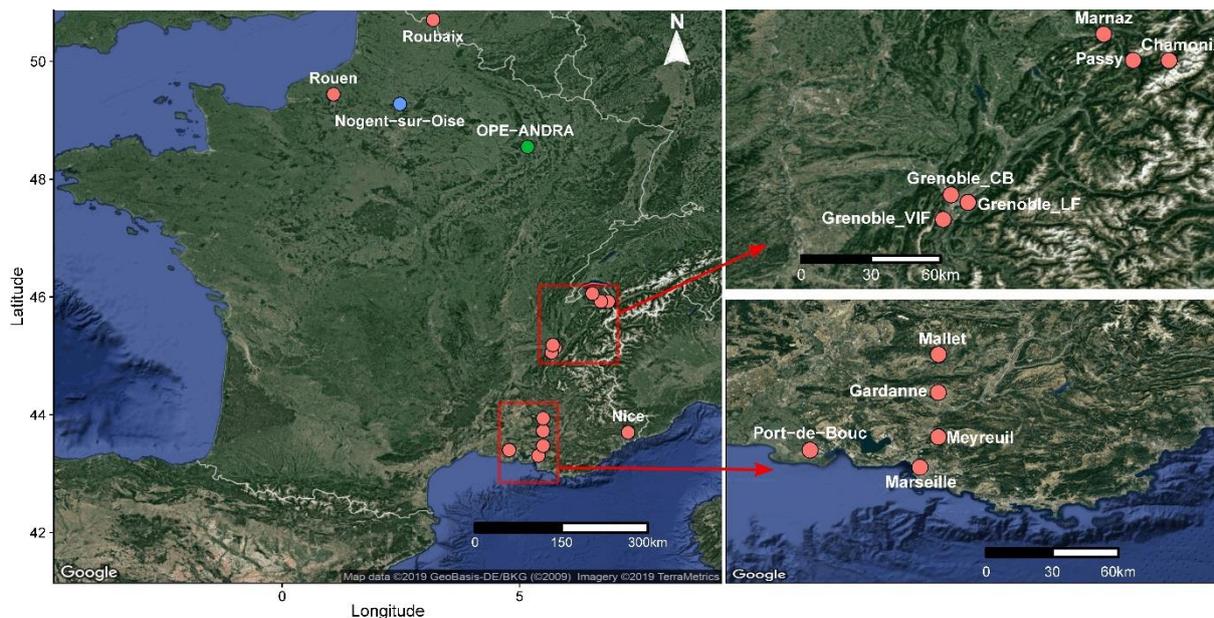
86 which has been reported as a suitable proxy to evaluate the vegetative debris contribution to OM mass (Bozzetti
87 et al., 2016; Daellenbach et al., 2017; Glasius et al., 2018; Hiranuma et al., 2019; Puxbaum and Tenze-Kunit, 2003;
88 Sánchez-Ochoa et al., 2007; Yttri et al., 2011b). The ambient PM₁₀ cellulose has been shown to be abundant in the
89 European semi-rural or background environments (accounting for 2 to 10 % of OM mass) (Glasius et al., 2018;
90 Sánchez-Ochoa et al., 2007) and Nordic rural environments in Norway (contributing to 12 to 18 % of total carbon
91 mass) (Yttri et al., 2011b). Thus, simultaneous concentration measurements of cellulose and SC can provide
92 essential information into their emission source dynamics.

93 As the continuation of our previous work (Samaké et al., 2019), the present paper aims to delineate the processes
94 that drive the atmospheric concentrations of SC and then PBOA. This is achieved through (i) the analysis of
95 simultaneous annual short-term time series of particulate SC concentrations over pairs of sites across multiple
96 space ranges, including local, regional and nationwide sites, and (ii) the investigation of links between
97 concentrations and series key parameters such as meteorological and phenological ones. Simultaneous annual
98 short-term concentration measurements of SC and cellulose was performed to better understand of their sources
99 correlations.

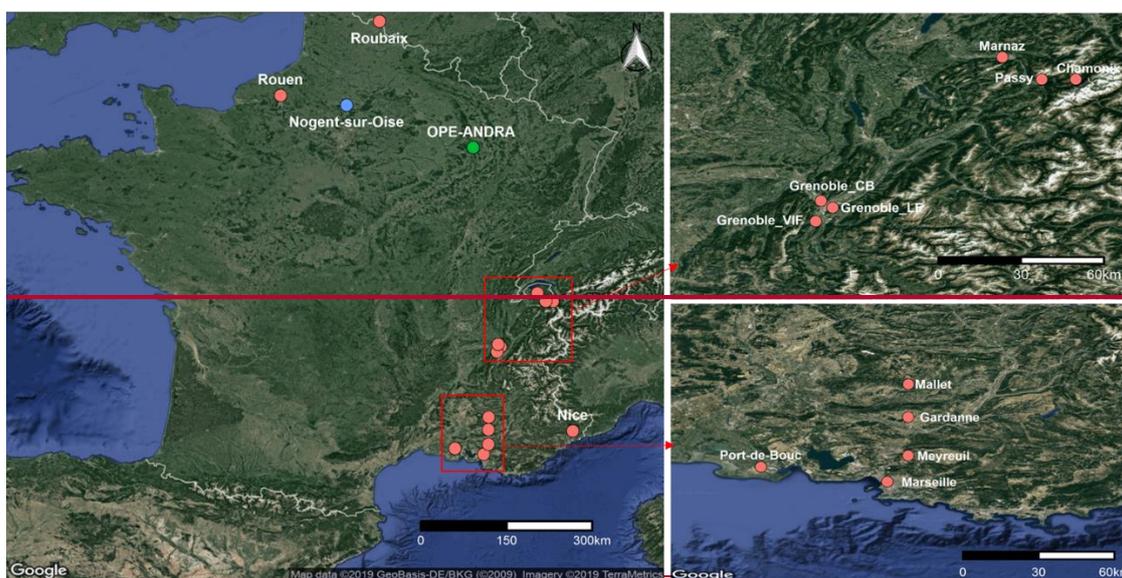
100 **2. Material and methods**

101 **2.1 Sampling sites**

102 Daily PM₁₀ concentrations reported in the present work were obtained from different research and monitoring
103 programs conducted over the last six years in France. Within the framework of the present study, we carefully
104 selected sites sharing at least one complete year of concurrent monitoring with another one, to be representative
105 of the annual variation cycles. The final dataset includes data from 16 sites, which are distributed in different
106 regions of France (Fig. 1) and cover several main types of environmental conditions in terms of site topography,
107 local vegetation, and climate. The characteristics and data available at each sampling site are listed in Table S1 of
108 the supplementary material (SM), together with the information on the annual average concentrations of aerosol
109 chemical composition (Table S2). Detailed information on the sampling conditions can be found in Samaké et al.
110 (2019), such as the campaign periods, number of collected PM samples, sampling flow rates, sample storage and
111 handling, etc. Note that, the previous database (Samaké et al., 2019) has been updated here with arabitol and
112 mannitol in PM₁₀ collected at the suburban site of Nogent-sur-Oise for a series covering the years 2013 to 2017.



113



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115

116 **Figure 1: Geographical location of the selected sampling sites. The red and blue dots indicate respectively urban and**
 117 **suburban sites while the green one corresponds to a rural site, surrounded by field crop areas.**

118 **2.2 Chemical analyses**

119 Daily (24 h) PM₁₀ samples were collected onto prebaked quartz fiber filter (Tissuquartz PALL QAT-UP 2500 150
 120 mm diameter) every third or sixth day, but not concurrently at all sites. They were then analyzed for various
 121 chemical species using subsampled fractions of the collection filters and a large array of analytical methods. Details
 122 of all the chemical analysis procedures are reported elsewhere (Golly et al., 2018; Samaké et al., 2019; Waked et
 123 al., 2014; Weber et al., 2018). Briefly, primary sugar compounds were extracted from filter aliquots (punches
 124 typically about 10 cm²) into ultrapure water. The extracts are then filtered using a 0.22 μm Acrodisc filter.
 125 Depending on the site, analyses were conducted either by the IGE (Institut des Géosciences de l'Environnement)
 126 or by the LSCE (Laboratoire des Sciences du Climat et de l'Environnement) (Samaké et al., 2019). At the IGE,
 127 extraction was performed during 20 min in a vortex shaker and analyses were achieved using high-performance

128 liquid chromatography with pulsed amperometric detection (HPLC-PAD). A first set of equipment was used until
129 March 2016, consisting of a Dionex DX500 equipped with three columns Metrosep (Carb 1-Guard + A Supp 15-
130 150 + Carb 1-150), the analytical program was isocratic with 70 mM sodium hydroxide (NaOH) as eluent for 11
131 min, followed by a gradient cleaning step with a 120 mM NaOH as eluent for 9 min. This procedure allows the
132 analysis of arabitol, mannitol and glucose (Waked et al., 2014). A second set of equipment was used after March
133 2016, with a Thermo-Fisher ICS 5000+ HPLC equipped with 4 mm diameter Metrosep Carb 2 × 150 mm column
134 and 50 mm pre-column. The analytical run was isocratic with 15 % of an eluent of sodium hydroxide (200 mM)
135 and sodium acetate (4 mM) and 85 % water, at 1 mL min⁻¹. At the LSCE, extraction was performed for 45 min by
136 sonication and analyses were achieved using ion chromatography instrument (IC, DX600, Dionex) with Pulsed
137 Amperometric Detection (ICS3000, Thermo- Fisher). In addition, a CarboPAC MA1 column has been used (4 ×
138 250 mm, Dionex) along with an isocratic analytical run with 480 mM sodium hydroxide eluent. This analytical
139 technique allows to quantify arabitol, mannitol and glucose (Srivastava et al., 2018). [Examples of standard solution
140 and sample raw HPLC-PAD chromatograms are presented in Fig. S1.](#)

141 For cellulose quantification, we used an optimized protocol based on that described by (Kunit and Puxbaum, 1996;
142 Puxbaum and Tenze-Kunit, 2003), in which the cellulose contained in the lignocellulosic material is enzymatically
143 hydrolyzed into glucose units before analysis. Since the alkaline peroxide pretreatment step used to remove lignin
144 in the original protocol results in a loss of sample material, it has been avoided in this study. Therefore, only the
145 “free cellulose” is reported in our samples. Note that Sánchez-Ochoa et al., (2007) consider that this free cellulose
146 could represent only about 70 % of the total cellulose in air samples and that the total cellulose could represent
147 only about 50 % of the “plant debris” content of atmospheric PM. Very few other results are available on this topic
148 (Bozzetti et al., 2016; Glasius et al., 2018; Vlachou et al., 2018; Yttri et al., 2011b). The protocol has been improved
149 to increase sensitivity and accuracy, by reducing the contribution of glucose in the blanks and by using an HPLC-
150 PAD as the analytical method for the determination of glucose concentrations. *Trichoderma reesei* cellulase (>700
151 u g⁻¹, Sigma Aldrich) and *Aspergillus Niger* glucosidase (>750 u g⁻¹, Sigma Aldrich) have been used as
152 saccharification enzymes. The protocol is detailed in Section 2 of the SM.

153 Field blank filters (about 10 % of samples) were handled as real samples for quality assurance. The present data
154 have been corrected from field blanks. The reproducibility of the analysis of primary sugar compounds (polyols,
155 glucose) and cellulose, estimated from the analysis of sample extracts from 10 punches of the same filters were in
156 the range of 10-15 %. The quantification limits primary sugar compounds and cellulose ranged from 0.63 to 0.89
157 ng m⁻³. About 2 800 samples are considered in this work for the polyols and glucose series, while 290 samples
158 (from the sites of Grenoble_LF and OPE-ANDRA) are considered for the cellulose series. Hereafter, the term
159 “Polyols” is used to refer uniquely to the sum of arabitol and mannitol concentrations.

160 **2.3 Meteorological data and LAI measurements**

161 Ambient weather data were not available at all monitoring sites (see Table S1). In this study, data including daily
162 relative humidity (%), night-time temperature (°C), average and maximum temperatures (°C), wind speed (m s⁻¹),
163 solar radiation (W m⁻²), and rainfall level (mm) for the sites of Marnaz and OPE-ANDRA (Fig. 1), representing
164 different climatic regions and environmental conditions, were obtained from the French meteorological data
165 sharing service system (Météo-France) and ANDRA (French national radioprotective agency, in charge of the
166 OPE-ANDRA site), respectively.

167 The leaf area index (LAI), which is defined as the projected area of leaves over a unit of land, is an important
168 measure of the local vegetation density variation (Heald and Spracklen, 2009; Yan et al., 2016a, 2016b). For this
169 study, we used the MODIS Collection 6 LAI product because it is considered to have the highest quality among
170 all the MODIS LAI products (Yan et al., 2016a, 2016b). The MCD15A3H product uses both Terra and Aqua
171 reflectance observations as inputs to estimate daily LAI at 500 m spatial resolution, and a 4-day composite is
172 calculated to reduce the noise from abiotic factors. Using a 2×2 km grid box around the monitoring site, the local
173 vegetation density variation was retrieved from LP DAAC (<https://lpdaac.usgs.gov/>, last accessed: 15 March 2019)
174 for the sites of Marnaz, OPE-ANDRA, and Grenoble_LF.

175 **2.4 Data analyses**

176 All the statistical analyses were carried out using the open-source R software (R studio interface, version 3.4.1).
177 Several statistical analyses were performed on the concentrations to identify the spatial patterns of emission
178 sources and the potential parameters of influence as explained below.

179 The normalized cross-correlation (NCC) test was chosen to examine the potential similarities among the
180 monitoring sites for particulate SC concentrations, in terms of short-term temporal trends (e.g. synchronized
181 periods of increase or decrease, simultaneous fluctuations during specific episodes). The main advantage of NCC
182 over the traditional correlation tests is that it is less sensitive to linear changes in the amplitudes of the two-time
183 series compared. Therefore, to reduce the possibility of spurious “anti-correlation” due to highly variable
184 concentration ranges, data were amplitude-normalized prior to correlation analysis. A thorough discussion on the
185 normalized cross-correlation method can be found elsewhere (Bardal and Sætran, 2016; Dai and Zhou, 2017;
186 Eisner et al., 2009; Kaso, 2018; Lainer et al., 2016; Le Pichon et al., 2019). To achieve pair-wise correlation
187 analysis between the sampling sites collected during the same periods, the original raw daily measurements were
188 processed as follows: starting on identical days for each pairs of sites, arrangement on the original daily data into
189 consecutive 3-day intervals (or 6-day intervals in the case of OPE-ANDRA) and calculation of the average
190 concentration values for the middle-day were performed. The resultant data were used for correlation analysis
191 between site pairs (Table S3).

192 Multiple linear regression (MLR) was used to assess the strength of the relationships between atmospheric
193 concentrations of particulate SC and local environmental factors including the daily mean relative humidity, night-
194 time temperature, average and maximum temperature, wind speed, solar radiation, rain levels and LAI. Because
195 the LAI is a 4-day composite, daily values of the other variables were re-scaled into consecutive 4-day averaged
196 values. The linear regression (linear model or lm) package in R was employed for multiple regression analyses.
197 The concentration data were log-transformed to obtain regression residual distributions as close as possible to the
198 normal Gaussian one (Fig. S24). Stepwise forward selection was used to select the predictors that explain well the
199 temporal variation of SC concentrations at the site of Marnaz.

200 It should be noted that due to the limited availability of external parameters, the environmental factors driving SC
201 atmospheric levels have been extensively investigated for only two monitoring sites with contrasted
202 characteristics: the urban background site of Marnaz located in an Alpine valley, and the rural OPE-ANDRA site
203 surrounded by field crop areas spreading over several tens of km.

204

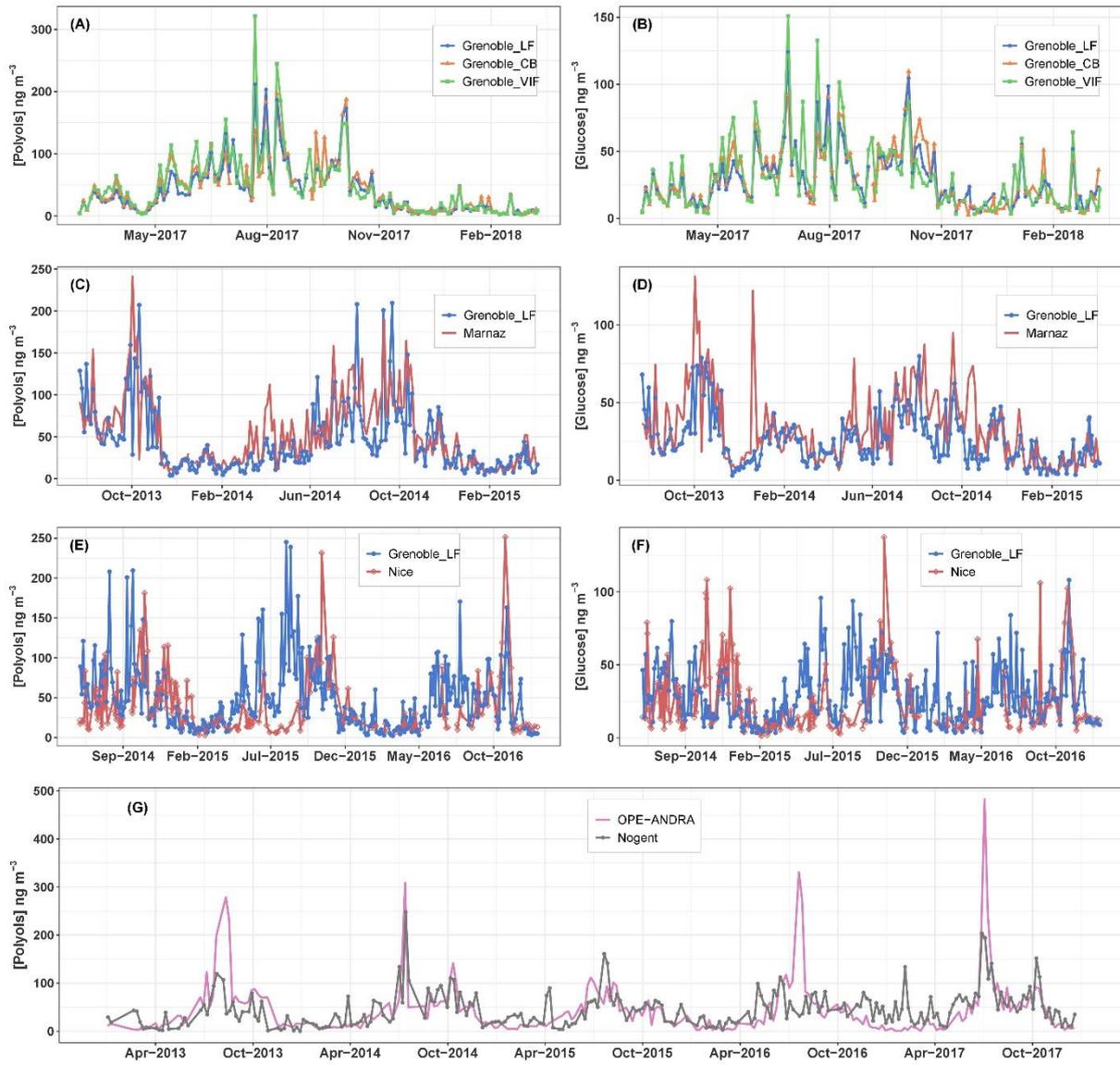
205 **3. Results and discussion**

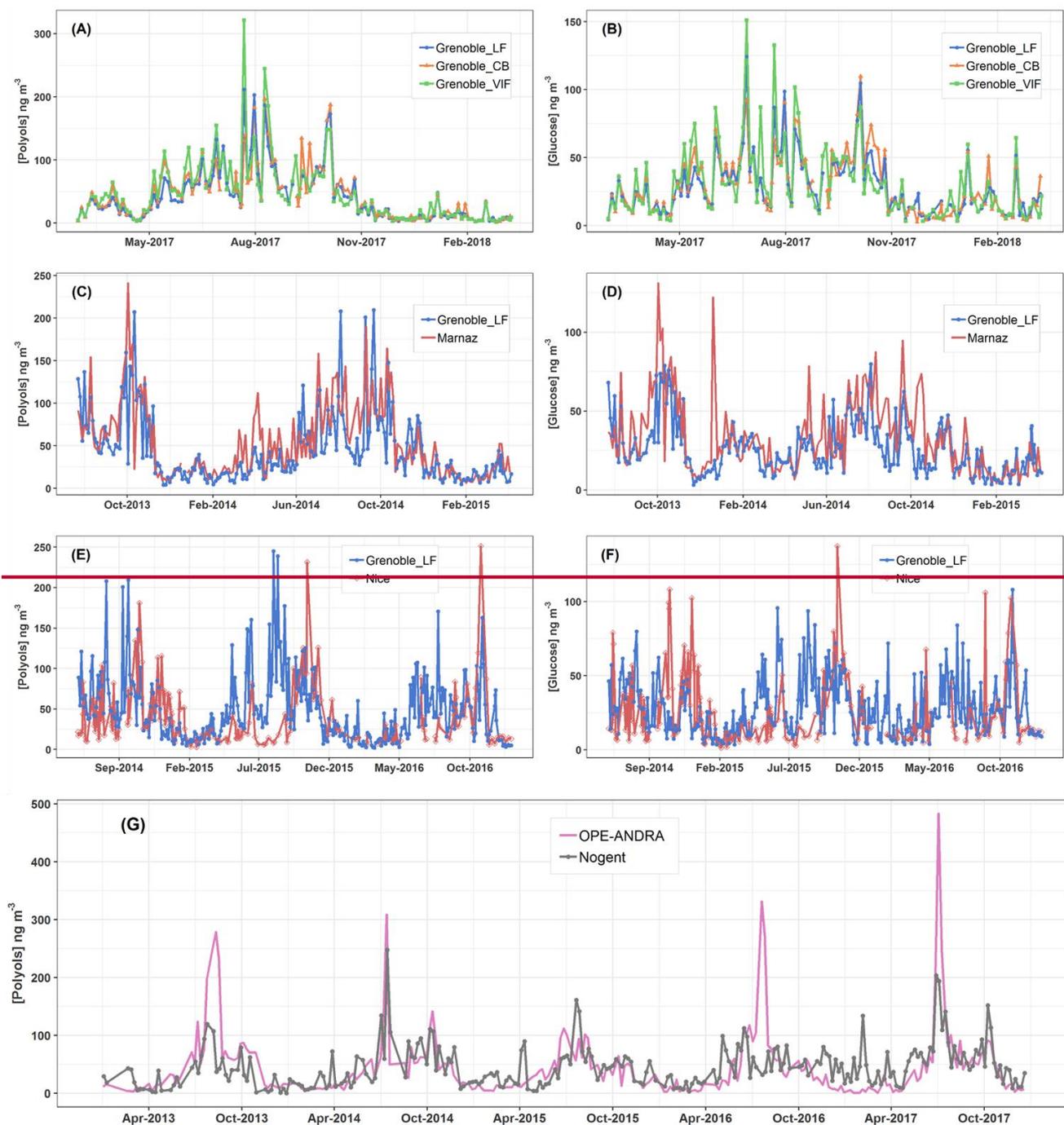
206 **3.1 Example of spatial coherence of the concentrations at different scales**

207 Our previous work (Samaké et al., 2019) showed that particulate polyols and glucose are ubiquitous primary
208 compounds with non-random spatial and seasonal variation patterns over France. Here, an inter-site comparison
209 of their short-term concentration evolutions has been carried out at different space scales (from local to national)
210 for the pairs that can be investigated in our data base. Figure 2 presents some of these comparisons for 3 spatial
211 scales (15, 120, and 205 km).

212 The daily average concentrations of polyols (defined as sum of arabitol and mannitol) and glucose display highly
213 synchronous evolutionary trends (i.e., homogeneity in the concentrations, the timing of concentration peaks,
214 simultaneity of the daily specific episodes of increase/decrease of concentrations) over 3 neighboring monitoring
215 sites located 15 km apart in the Grenoble area (Figs. 2A and B). Interestingly, remarkable synchronous patterns
216 both for short term (near-daily) and longer term (seasonal) still occur for sites located 120 km apart, as exemplified
217 for 2 sites in Alpine environments (Grenoble and Marnaz) (Figs. 2C and D). However, as shown in Figs. 2E and
218 F, the evolutions of concentrations become quite dissimilar and asynchronous in terms of seasonal and daily
219 fluctuations for more distant sites (Grenoble and Nice, 205 km apart), that are located in different climatic regions
220 (Alpine for Grenoble, Mediterranean for Nice). This is contrasting with results from the rural background site of
221 OPE-ANDRA and the suburban site of Nogent-sur-Oise, both located in a large field crop region of extensive
222 agriculture, and about 230 km apart from each other (Fig. 2G). Indeed, they present very similar variations of daily
223 concentrations for multi-year series, despite their distance apart, with concentration peaks generally more
224 pronounced at the rural site of OPE-ANDRA.

225 The following sections are dedicated to the investigation of the processes that can lead to these similarities and
226 differences according to these spatial scales.





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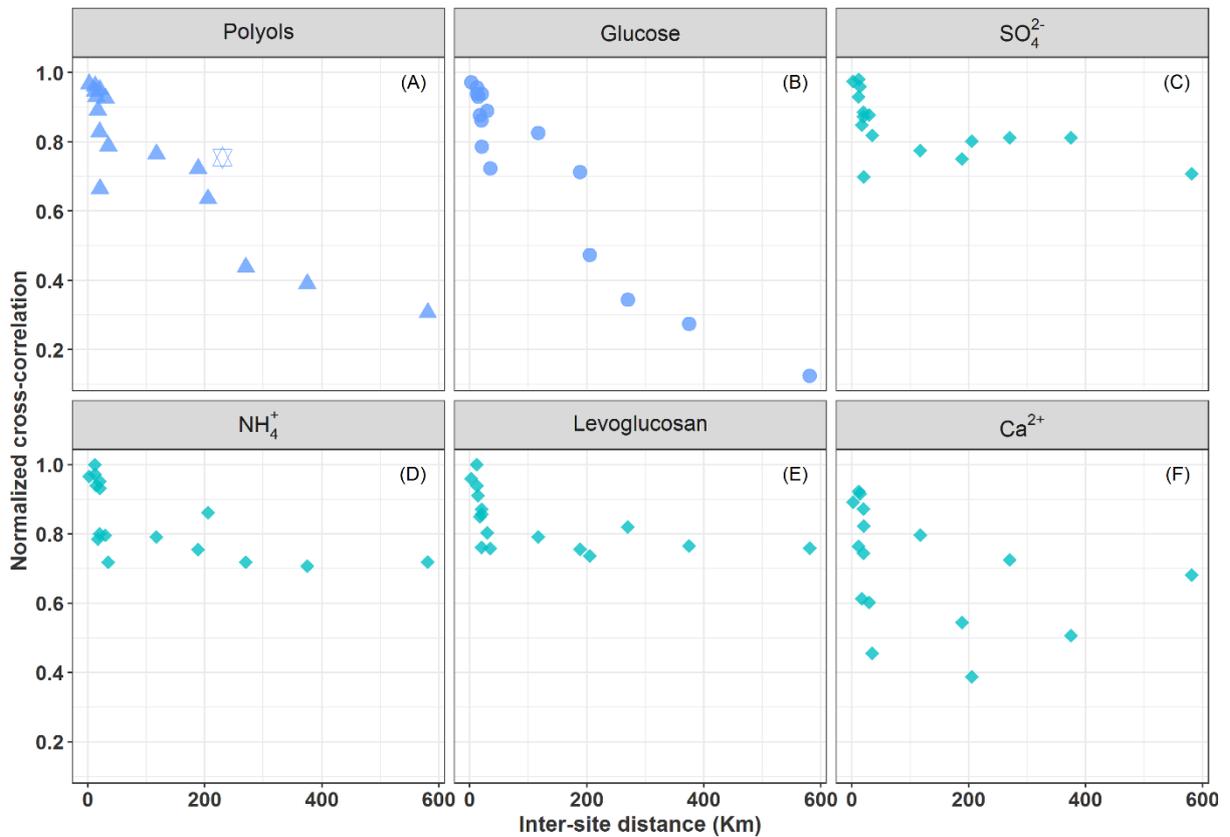
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230 **Figure 2: Concentrations (in ng m^{-3}) of (left) ambient particulate polyols (defined as the sum of arabitol and mannitol)**
 231 **and glucose (right) over different monitoring sites in France. Since PM_{10} were collected every 3-days at Nogent-sur-Oise**
 232 **and 6-days at OPE-ANDRA, the original data sets are averaged over consecutive 6-day intervals (bottom graph).**

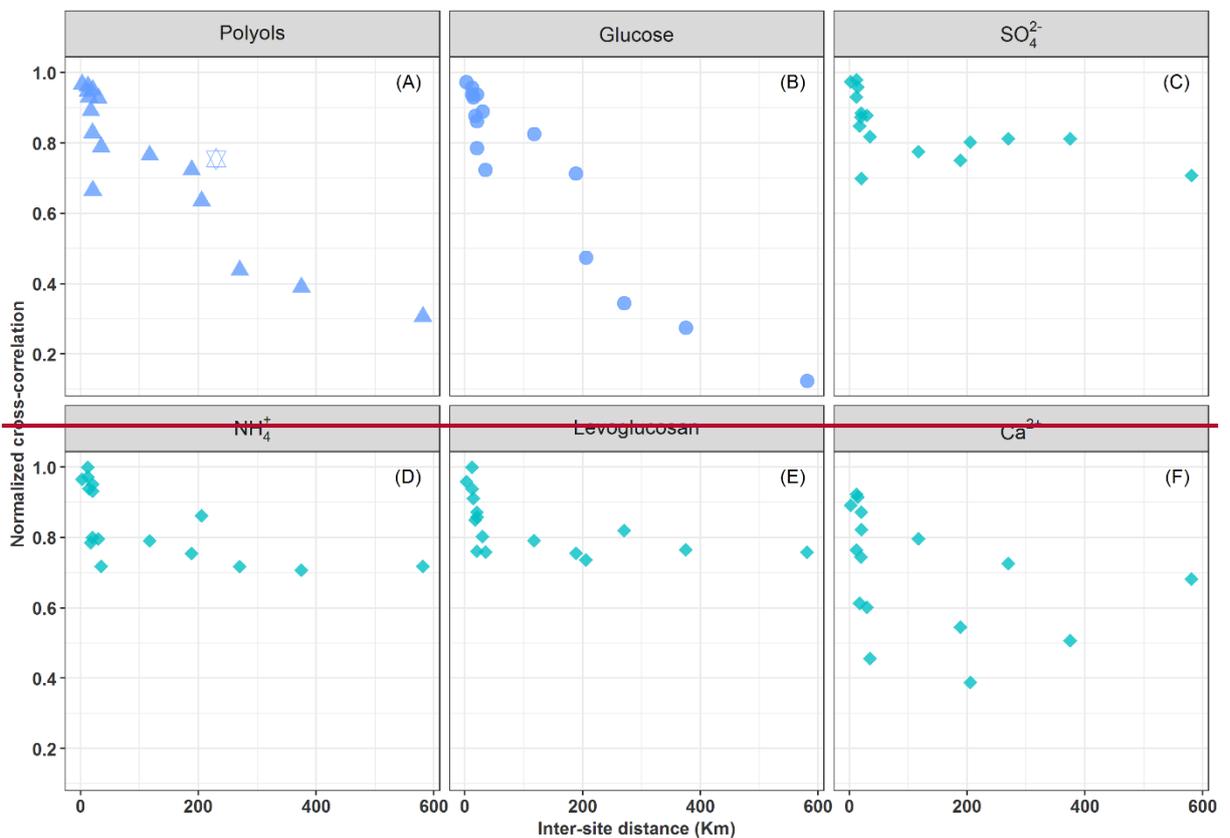
233 **3.2 Inter-site correlations and spatial scale variability**

234 Figures 3A and 3B provide an overview of the cross-correlation coefficients for the daily evolution of
 235 concentrations (for polyols and glucose (SC)) between pairs of sites located at multiple increasing space scales
 236 across France (Table S3). Time series of concentrations for both SC show a clear distance-dependent correlation.
 237 The strength of the correlations is highly significant for distances up to 150-190 km ($R > 0.72$, $p < 0.01$) and
 238 gradually decreases with increasing inter-site distances. One exception is the pair OPE-ANDRA and Nogent-sur-

239 Oise (high correlation for a distance above 230 km), both sites being located in highly-impacted agricultural areas.
240 This overall pattern suggests that the processes responsible for the atmospheric concentrations of SC present a
241 spatial homogeneity over typical areas of at least several tens of km.



242



243

244 **Figure 3: Normalized cross-correlation values for the daily evolution of particulate polyols (A), glucose (B), sulfate (C),**
245 **ammonium (D), levoglucosan (E) and calcium (F) concentrations over pairs of sites located at multiple increasing space**
246 **scales across France. The hexagram corresponds to the correlation between the sites of OPE-ANDRA and Nogent-sur-**
247 **Oise, both sites being surrounded by crop field areas.**

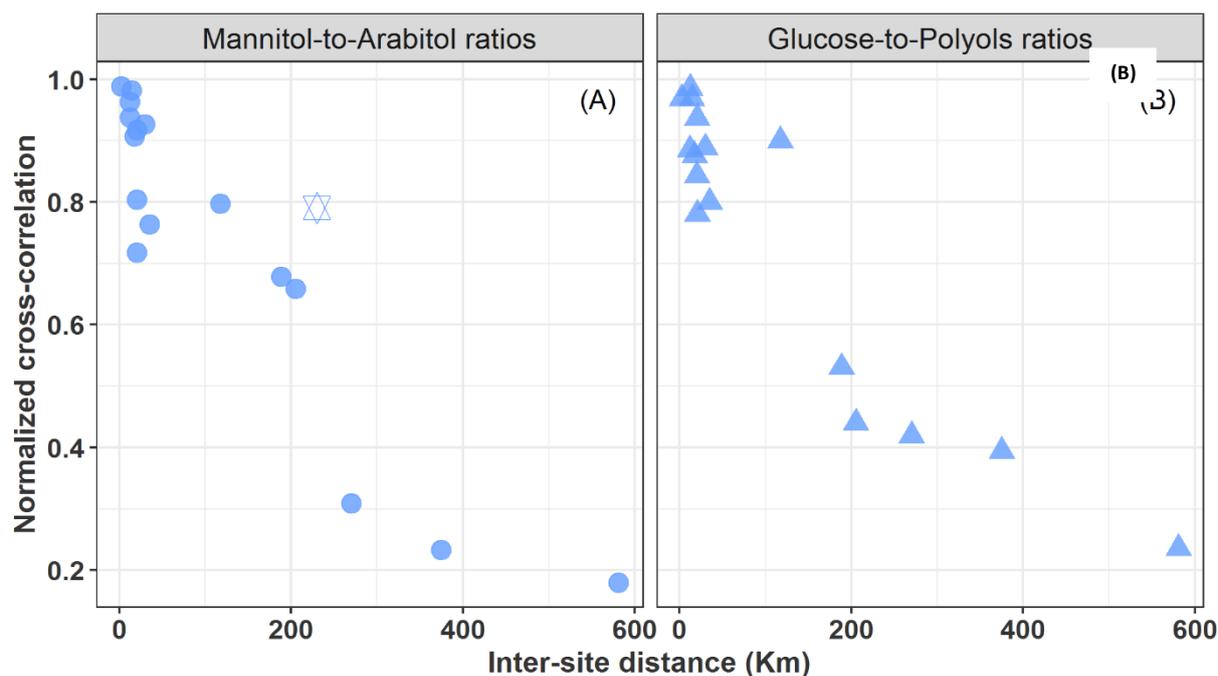
248 Unlike SC, ambient air concentrations of sulfate (Fig. 3C) and ammonium (Fig. 3D), associated with long-range
249 aerosol transport (Abdalmogith and Harrison, 2005; Amato et al., 2016; Coulibaly et al., 2015; Pindado and Perez,
250 2011; Waked et al., 2014) and levoglucosan ((Fig. 3E), associated with biomass burning ~~in cold season~~ (Weber et
251 al., 2019; Xiao et al., 2018), display stronger positive correlations ($R > 0.72-0.98$, $p < 0.01$) at all pairs of sites
252 considered in the present work. The concentrations of levoglucosan and those of SC clearly display very different
253 annual atmospheric evolution cycles: i.e., higher concentrations of levoglucosan in France are observed in the
254 coldest season (winter) due to the increased biomass burning while those of SC are observed in warm seasons and
255 coinciding with negligible ambient concentrations of levoglucosan (Fig. S2). Moreover, ambient concentrations
256 of calcium (Fig. 3F), associated with local fugitive dust sources or/and long-range aerosol transport (Ram et al.,
257 2010; Wan et al., 2019) display random correlation patterns. These results are in agreement with Zhu et al. (2018)
258 who also reported non-significant correlations between SC and sulfate in $PM_{2.5}$ aerosols measured at Shanghai,
259 China. The distinct spatial behaviors between sulfate (or Ca^{2+}) and SC in the present work further suggest a
260 dominant regional influence for atmospheric SC, as opposed to processes associated with either local sources for
261 calcium or long-range transport for sulfate.

262 Mannitol and arabitol are well-known materials of fungal spores, serving as osmo-regulatory solutes (Medeiros et
263 al., 2006b; Simoneit et al., 2004; Verma et al., 2018; Xiao et al., 2018; Zhang et al., 2015). Based on parallel
264 measurements of spore counts and PM_{10} polyol concentrations at three sites within the area of Vienna (Austria),
265 Bauer et al. (2008a) found an average arabitol and mannitol content per fungal spores of respectively $1.2 \text{ pg spore}^{-1}$
266 1 (range $0.8-1.8 \text{ pg spore}^{-1}$) and $1.7 \text{ pg spore}^{-1}$ (range $1.2-2.4 \text{ pg spore}^{-1}$). Mannitol and arabitol have also been
267 often identified in the green algae and lower plants (Buiarelli et al., 2013; Di Filippo et al., 2013; Gosselin et al.,
268 2016; Véléz et al., 2007; Xu et al., 2018; Zhang et al., 2010). Gosselin et al., 2016 observed a relatively low ($R^2 =$
269 0.31) to high ($R^2 = 0.84$) coefficient of determination between mannitol and arabitol for total suspended particles
270 (TSP) collected at a pine-forested area during dry and rainy periods, respectively. High correlation in rainy periods
271 possibly suggested that both chemical species in the TSP fraction in this pine-forested area could have been derived
272 mainly from the same sources, i.e., actively wet-discharged ascospores and basidiospores, while the relatively poor
273 correlation in dry periods could have been likely due to more complex -sources, i.e., dry discharged spores, plants,
274 algae, etc. Being important chemical species for the metabolism of the microorganisms (Shcherbakova, 2007), it
275 may well be that the concentration ratio of mannitol-to-arabitol could deliver some information on the spatial or
276 temporal evolution of their emission processes (Gosselin et al., 2016). The annual average mannitol-to-arabitol
277 ratio at all sites is about 1.15 ± 0.59 , with ratios for the warm period (Jun-Sept) being 1 to 2 times higher than
278 those in the cold period (Dec-May) (Table S1). These ratios are within the range of those previously reported for
279 PM_{10} aerosols collected at various urban and rural background sites in Europe (Bauer et al., 2008; Yttri et al.,
280 2011b). Similarly, Burshtein et al. (2011) also reported comparable ratios for PM_{10} aerosols collected during
281 autumn and winter from a Mediterranean region in Israel.

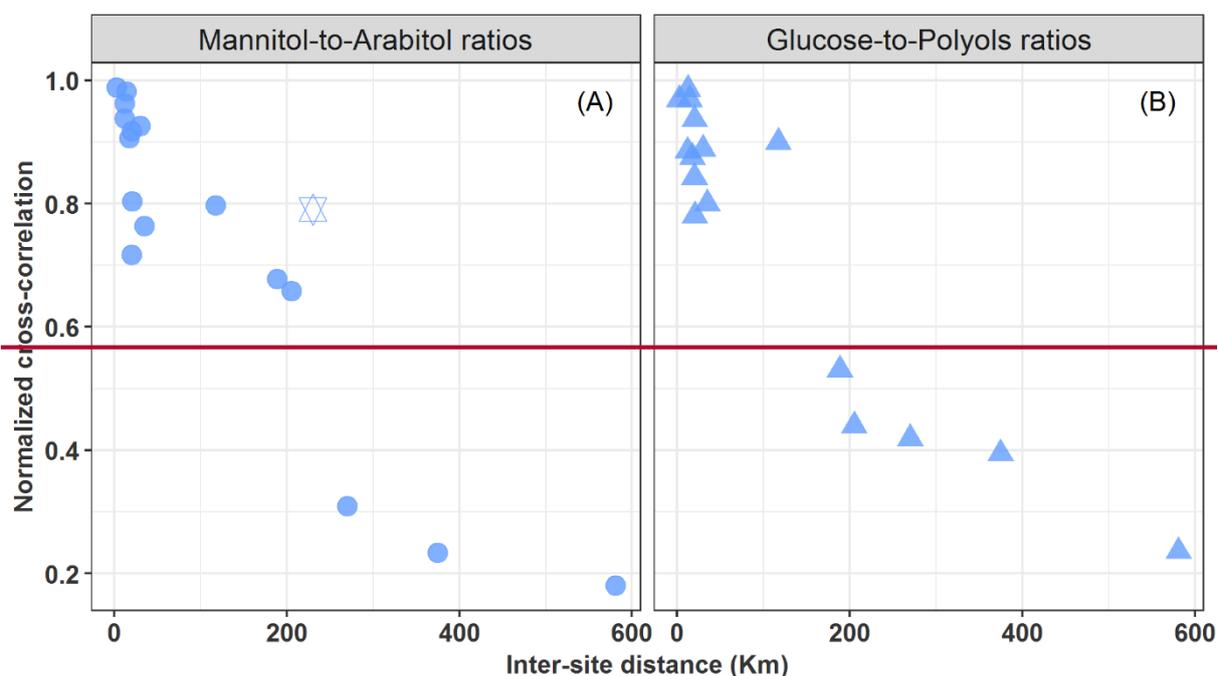
282 Similarly, the annual average glucose-to-polyols ratio at all sites is about 0.79 ± 0.77 . No literature data are
283 currently available for comparison. Further work is needed to relate these variations with microorganism
284 communities and plant growing stages.

285 However, as evidenced in Fig. 4, both mannitol-to-arabitol and glucose-to-polyols ratios show a clear distance-
286 dependent correlation, with higher correlations ($R = 0.64$ to 0.98 , $p < 0.01$) observed for pairs of sites within 150-
287 190 km distance. This spatial consistency highlights once again that the dominant emission processes should be
288 effective regionally, rather than being specific local input processes, and that atmospheric dynamics of the
289 concentration levels (i.e., driven by the interplay of emission and removal processes) are determined by quite
290 similar environmental factors (e.g. meteorological conditions, vegetation, land use, etc.) at such a regional scale.
291 This implies that local events and phenomena, such as the mechanical resuspension of topsoil and associated biota
292 (like bacteria, fungi, plant materials, etc.) might not be their major atmospheric input processes, particularly in
293 urban background areas typically characterized by less bare soil, and with a variable nature of the unpaved topsoil
294 at the regional scale (Karimi et al., 2018). Furthermore, Karimi et al. (2018) also recently reported heterogeneous
295 topsoil microbial structure within patches of 43 to 260 km across different regions of France. It follows that the
296 hypotheses of emissions related to mechanical resuspension of topsoil particles and associated biota, or microbiota
297 emitted actively from surface soil into the air generally assumed in most pioneering reports (Medeiros et al., 2006b;
298 Rogge et al., 2007; Simoneit et al., 2004; Wan and Yu, 2007) are most probably not valid.

299 Alternatively, the vegetation leaves have also been suggested as sources of atmospheric SC (Bozzetti et al., 2016;
300 Golly et al., 2018; Jia et al., 2010; Myriokefalitakis et al., 2017; Pashynska et al., 2002; Sullivan et al., 2011;
301 Verma et al., 2018; Wan et al., 2019). In fact, vascular plant leaf surfaces is an important habitat for endophytic
302 and epiphytic microbial communities (Kembel and Mueller, 2014; Lindow and Brandl, 2003; Lympelopoulou et
303 al., 2016; Mhuireach et al., 2016; Whipps et al., 2008). Our results are more in agreement with a dominant
304 atmosphere entrance process closely linked to vegetation, which is more homogeneous than topsoil at the climatic
305 regional scale. Consistent with this, Sullivan et al. (2011) also observed evident distinct regional patterns for daily
306 $PM_{2.5}$ polyols and glucose concentrations at ten urban and rural sites located in the upper Midwest (USA). The
307 authors attributed such a spatial pattern to the differences in vegetation types and microbial diversity over distinct
308 geographical regions. Accordingly, the vegetation structure and composition have been previously shown to play
309 essential roles on airborne microbial variabilities in nearby areas (Bowers et al., 2011; Laforest-Lapointe et al.,
310 2017; Lympelopoulou et al., 2016; Mhuireach et al., 2016).



311



312

313 **Figure 4: Normalized cross-correlation values for daily evolution of particulate mannitol-to-arabitol (A) glucose-to-**
 314 **polyols (B) and ratios over pairs of sites located at multiple increasing space scales across France. The hexagram**
 315 **corresponds to the correlation between the sites of OPE-ANDRA and Nogent-sur-Oise, both sites being surrounded by**
 316 **crop field areas.**

317 **3.3 Influence of the vegetation on polyols and glucose concentrations**

318 The relationships between SC PM₁₀ concentrations and vegetation (plant materials) can be examined at the site of
 319 Grenoble Les Frênes (Grenoble_LF) by comparing the annual evolutions of SC and the free atmospheric cellulose
 320 concentrations, together with LAI ones.

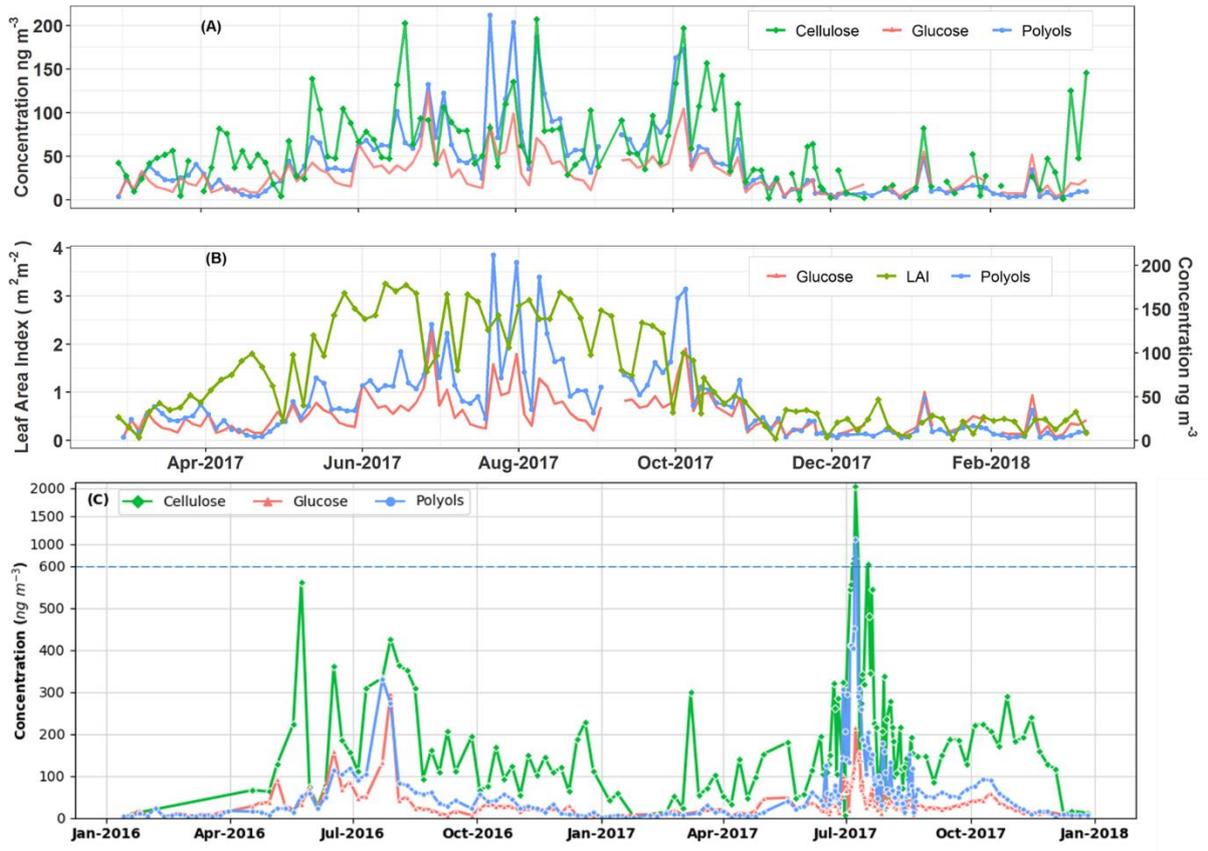
321 The daily ambient concentration levels of SC and cellulose range respectively from 5.0 to 301.9 ng m⁻³ (with an
 322 average of 41.2 ± 39.9 ng m⁻³) and 0.7 to 207.2 ng m⁻³ (with an average of 52.9 ± 44.2 ng m⁻³), which correspond

323 to respectively to 0.1 to 6.6 % and 0.01 to 5.3 % of total organic matter (OM) mass in PM₁₀. These values are
324 comparable to those previously reported for various sites in Europe (Daellenbach et al., 2017; Sánchez-Ochoa et
325 al., 2007; Vlachou et al., 2018; Yttri et al., 2011b). Thus, a major part of PBOA could possibly be ascribed cellulose
326 and SC derived sources.

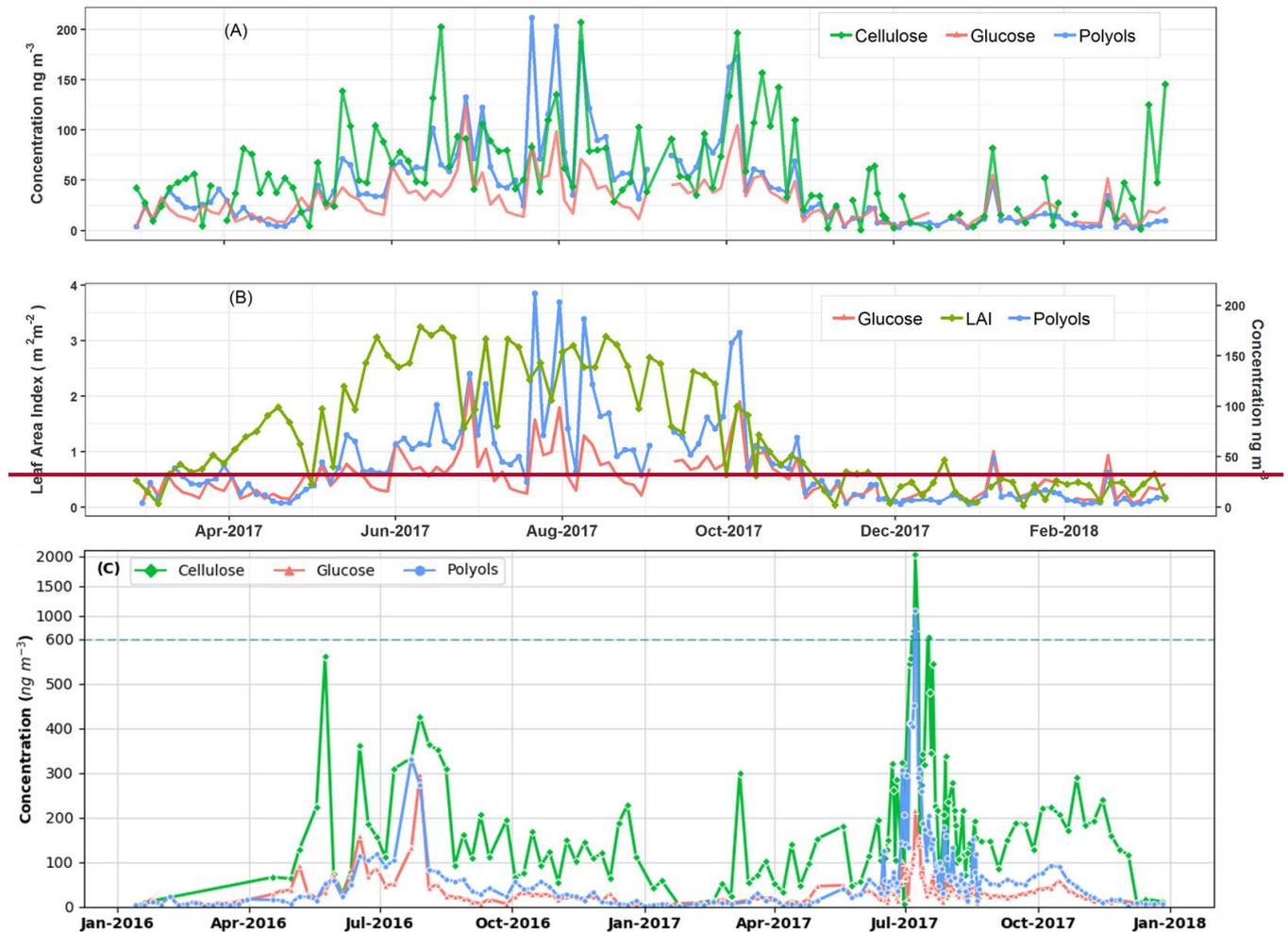
327 As evidenced in Fig. 5A, ambient free cellulose concentrations vary seasonally, with maximum seasonal average
328 values observed in summer ($81.4 \pm 47.6 \text{ ng m}^{-3}$) and autumn ($64.2 \pm 49.2 \text{ ng m}^{-3}$), followed by spring
329 ($52.6 \pm 37.8 \text{ ng m}^{-3}$), and lower levels in winter ($23.0 \pm 19.9 \text{ ng m}^{-3}$). This is the same global pattern for polyols,
330 that are also more abundant in summer ($82.4 \pm 47.4 \text{ ng m}^{-3}$) and autumn ($48.7 \pm 41.6 \text{ ng m}^{-3}$), followed by spring
331 ($24.9 \pm 16.3 \text{ ng m}^{-3}$), and winter ($10.2 \pm 9.6 \text{ ng m}^{-3}$) in the Grenoble area. On a daily scale, the episodic increases
332 or decreases of polyols in PM₁₀ are very often well synchronized with that of cellulose (Fig. 5A). Moreover, the
333 maximum atmospheric concentrations of polyols also mainly occur when the vegetation density (LAI) is at its
334 highest in late summer (Fig. 5B). Similar global behaviors are also observed for atmospheric particulate glucose
335 and LAI (Figs. 5A and B). To further assess the relationships between SC PM₁₀ concentrations and vegetation at
336 a rural area, a two-year measurement of cellulose concentrations at the highly-impacted agricultural rural site of
337 OPE-ANDRA has been conducted. The average concentration of cellulose at OPE-ANDRA ($197.9 \pm 217.8 \text{ ng m}^{-3}$)
338 is 3.5 times higher than that measured in the urban area of Grenoble. In terms of temporal dynamics, the
339 evolution cycles (i.e., peaks and decreases) of both polyols and glucose are also very often well synchronized with
340 that of cellulose at OPE-ANDRA (Fig. 5C).

341 Altogether, these findings highlight that SC in PM₁₀ and cellulose in both urban background and rural agricultural
342 areas most probably share a common source related to the vegetation. This is an additional evidence in support of
343 the hypothesis suggested in previous studies (Bozzetti et al., 2016; Burshtein et al., 2011; Daellenbach et al., 2017;
344 Pashynska et al., 2002; Verma et al., 2018; Vlachou et al., 2018; Wan and Yu, 2007; Yttri et al., 2007). It is also
345 in line with studies indicating that the PBOA source profile identified using offline aerosol mass spectrometry
346 (offline-AMS) correlates very well with coarse cellulose concentrations (Bozzetti et al., 2016; Vlachou et al.,
347 2018). Noticeable contribution of cellulose to PBOA mass (26 %) at the rural background site of Payerne
348 (Switzerland), during summer 2012 and winter 2013, was reported by Bozzetti et al. (2016).

349 As also evidenced in Fig. 5, the cellulose concentration peaks are not systematically correlated to those of polyols.
350 The development stage of the plants (developing or mature leaves, flowering plants) in addition to the metabolic
351 activities of endophytic and epiphytic biota (growth, sporulation), all closely related to meteorological conditions
352 (Bodenhausen et al., 2014; Bringel and Couée, 2015; Lindow and Brandl, 2003; Pirttilä and Frank, 2011; Reddy
353 et al., 2017), could explain such observations. The influence of local meteorological conditions for an urban Alp
354 valley site is discussed in Section 3.4. Consistent with our observations, previous studies conducted at various
355 urban background sites in Europe have suggested that particulate polyols are associated to mature plant leaves and
356 microorganisms (bacterial and fungal spores) while glucose, which is a monomer of cellulose, would most likely
357 be linked to the developing leaves (Bozzetti et al., 2016; Burshtein et al., 2011; Pashynska et al., 2002; Yttri et al.,
358 2007; Zhu et al., 2015).



359



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361

362 **Figure 5: Temporal covariation cycles of the daily particulate polyols and glucose concentrations along with vegetation**
 363 **indicators at the urban background site of Grenoble (A and B) and the rural agricultural background site of OPE-**
 364 **ANDRA (C), respectively. Note that PM₁₀ aerosols are intensively collected at OPE-ANDRA every day (24-h) from 12**
 365 **June 2017 to 22 August 2017, and that the concentration scale is changing above 600 ng m⁻³ in Figure C, due to extreme**
 366 **concentration peak in July 2017.**

367 3.4 Influence of meteorological parameters on ambient concentrations of polyols and glucose

368 We used here a multiple linear regression analysis (MLR) approach to gain further insight about the environmental
 369 factors influencing the annual and short time variation cycles of atmospheric SC concentrations. This tentative
 370 MLR analysis is focused on the urban background site of Marnaz only since meteorological and other data are
 371 readily available for this site and are not influenced too much by some large city effects. Several variables were
 372 tested, that are already mentioned in the literature as drivers of SC concentrations. It includes the ambient relative
 373 humidity, rainfall level, wind speed, solar radiation, night-time temperature, average (or maximum) temperature,
 374 and LAI. Night-time temperature was selected since the time series in Marnaz and Grenoble indicate that the major
 375 drop of concentrations in late fall (Fig. 2C) is related to the first night of the season with night-time temperature
 376 below 5°C. The use of the night-temperature is also consistent with the bi-modal distribution of polyols during
 377 night and day time found in previous studies (Claeys et al., 2004; Graham et al., 2003; Yan et al., 2019; Yttri et
 378 al., 2011a).

379 Overall, the environmental factors including the mean night-time temperature, relative humidity, wind speed and
 380 the leaf area index explain up to 82 % (adjusted $R^2 = 0.82$, see Table 1) of the annual temporal variation cycles of
 381 SC concentrations. The mean night-time temperature and LAI contribute respectively to 54 % and 37 % of the
 382 observed annual variabilities of SC concentrations. The atmospheric humidity is also a driver for these chemical
 383 species (3 % of the explained variation). These results are consistent with previous studies showing that
 384 concentrations of mannitol (in both PM_{10} and $PM_{2.5}$ size fractions) linearly correlate best with the LAI, atmospheric
 385 water vapor and temperature (Heald and Spracklen, 2009; Hummel et al., 2015; Myriokefalitakis et al., 2017). All
 386 of these drivers have been previously shown to induce the initial release and influence the long-term airborne
 387 microbial (i.e. bacteria, fungi) concentrations (China et al., 2016; Elbert et al., 2007; Grinn-Gofroń et al., 2019;
 388 Jones and Harrison, 2004; Rathnayake et al., 2017; Zhang et al., 2015).
 389 Besides, the wind speed (range of 0.2 to 5.6 $m s^{-1}$) seems an additional effective driver affecting the contribution
 390 of the local vegetation to SC concentrations in the atmosphere. Albeit enough air movement is required to passively
 391 release microorganisms along with plant debris into the atmosphere, strong air motions induce higher dispersion.
 392 These observations are in good agreement with those previously reported (Jones and Harrison, 2004; Liang et al.,
 393 2013; Zhang et al., 2010, 2015; Zhu et al., 2018b). For instance Liang et al. (2013) have found a negative
 394 correlation between wind speed and polyols concentrations, and the highest atmospheric fungal spores
 395 concentrations were observed for a wind speed range of 0.6 to 1.0 $m s^{-1}$.

396 **Table 1: Multiple linear regression for ambient polyols and glucose concentrations and their effective environmental**
 397 **factors at the Marnaz site. Contributions of predictor are normalized to sum 1. “Relaimpo package under R” was**
 398 **used to compute bootstrap confidence intervals for importance of effective predictors (n=1000) (Grömping, 2006).**

	<i>Dependent variable</i>	<i>Variability explained by effective predictors</i>
	log(Polyols + Glucose)	
Night-time temperature (°C)	0.112*** (0.090, 0.133)	0.538 (0.453, 0.604)
Relative Humidity (%)	0.017*** (0.005, 0.030)	0.030 (0.018, 0.067)
Leaf Area Index	0.386** (0.034, 0.737)	0.372 (0.286, 0.444)
Wind speed ($m s^{-1}$)	0.226 (-0.203, 0.655)	0.021 (0.015, 0.058)
Leaf Area Index × Wind Speed ^a	-0.596*** (-1.001, -0.191)	0.039 (0.014, 0.085)
Constant	2.023*** (0.787, 3.260)	
Observations	87	
R ²	0.837	
Adjusted R ²	0.824	
Residual Std. Error	0.297 (df = 81)	
F Statistic	66.677*** (df = 5; 81)	
Note	**p < 0.01; ***p < 0.001	^a stands for interaction between predictors

399
 400 One of the limitations of this study is that 4-day averaged observations do not allow to evaluate the driver
 401 contributions that might explain some short term events for which the influence of meteorological parameters such
 402 as rainfall or solar radiation could also be significant (Grinn-Gofroń et al., 2019; Heald and Spracklen, 2009; Jones
 403 and Harrison, 2004). However, such simple parameterizations could be a first step in considering SC
 404 concentrations in CTM models, and further work is required in this direction in order to generate a robust
 405 parametrization of the emissions.

406 3.5 Specific case of a highly-impacted agricultural area

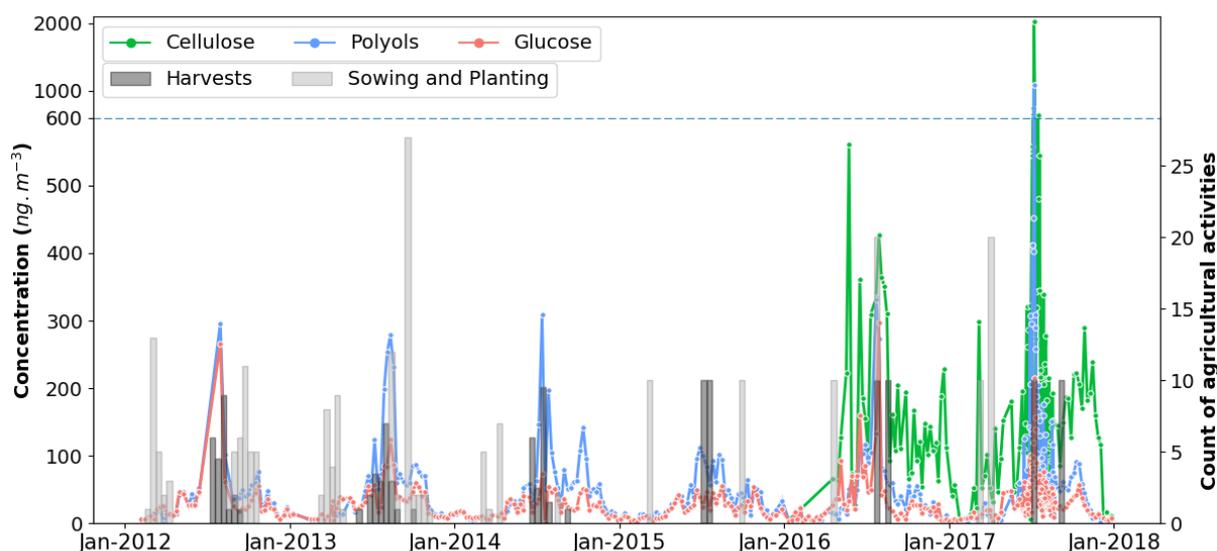
407 This section focuses on evidencing the environmental drivers of PM_{10} SC concentrations specific to agricultural
 408 areas. To achieve this objective, the site of OPE-ANDRA has been selected because it is extensively impacted by

409 agricultural activities, without being too prone to influences by other sources. OPE-ANDRA is a specific rural
 410 background observatory located at about 230 km east of Paris at an altitude of 392 m. It is characterized by a low
 411 population density (< 22 inhabitants km^{-2} within an area of 900 km^2), with no surrounding major transport road or
 412 industrial activities. The air monitoring site itself lies in a “reference sector” of 240 km^2 , in the middle of a field
 413 crop area (tens of kilometers in all directions). The daily agricultural practices within this reference sector are
 414 recorded and made available by ANDRA. The parcels within the agricultural area are submitted to a 3-year crop-
 415 rotation system. The major crops are wheat, barley, rape, pea and sunflower. Additionally, OPE-ANDRA is also
 416 characterized by a homogeneous type of soil, with a predominance of superficial clay-limestone.

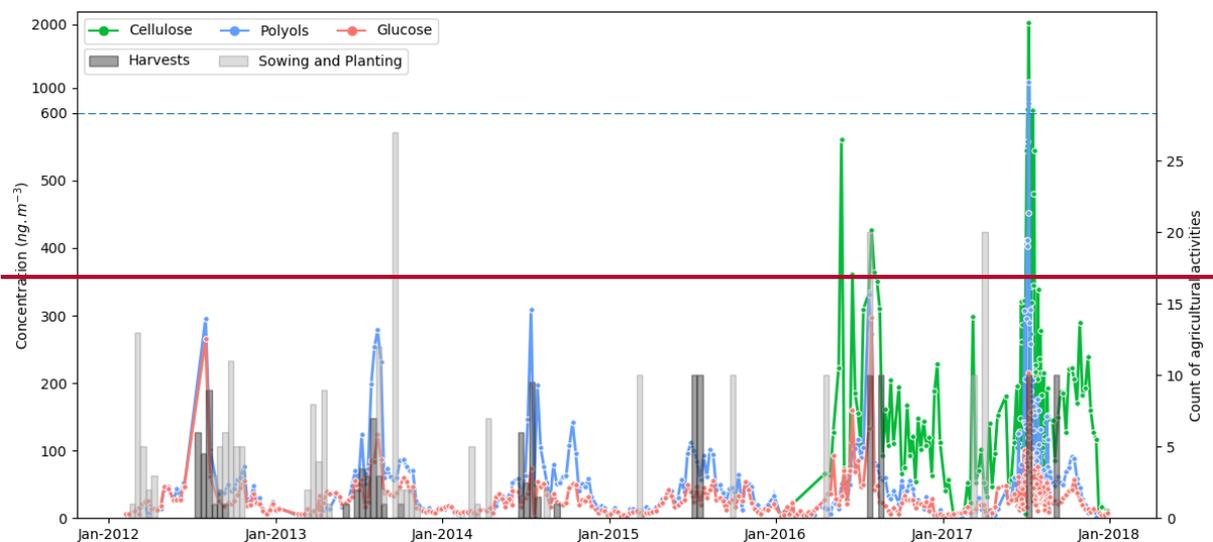
417 Figure 6 shows the daily evolution of polyols concentrations in the PM_{10} fraction at OPE-ANDRA from 2012 to
 418 2018, together with the agricultural activities recorded daily and averaged over 12 days.

419 Although the concentration of polyols fluctuates from a year to another, they display clear annual variation cycles,
 420 with higher values in the warm periods (Jun. to Nov.) and lower concentration values in the cold periods (Oct. to
 421 May). Interestingly, the annual concentrations of polyols in 2015 ($4.2\text{-}111.7 \text{ ng m}^{-3}$; annual average:
 422 $37.0 \pm 29.1 \text{ ng m}^{-3}$) are significantly lower than those observed for the other years ($0.6\text{-}1084.6 \text{ ng m}^{-3}$; annual
 423 average: $62.9 \pm 96.8 \text{ ng m}^{-3}$). Similar inter-annual evolution trends, but with variable intensities, are also observed
 424 for glucose concentrations (Fig. 6). Year 2015 has been found to be particularly hot and dry at OPE-ANDRA (Fig.
 425 7) whereas the local averaged wind conditions are quite stable over the years within the period of study, suggesting
 426 that the wind conditions are not the main driver of the observed inter-annual variability. These results highlight
 427 that ambient air temperature and humidity are key meteorological drivers of the annual variation cycles of polyols
 428 and glucose concentrations. Hot and dry ambient air conditions may decrease the metabolic activity of the
 429 microorganisms (e.g. microbial growth and sporulation) (Fang et al., 2018; Liang et al., 2013; Meisner et al., 2018).

430 Finally, maximum ambient concentration levels for both SC and cellulose are observed in excellent temporal
 431 agreement with the harvest periods (late summer) at the OPE-ANDRA site (Fig. 6). Harvesting activities have
 432 been previously reported as the major sources for particulate polyols and glucose to the atmosphere in agricultural
 433 and nearby urbanized areas (Golly et al., 2018; Rogge et al., 2007; Simoneit et al., 2004). Hence, the resuspension
 434 of plant materials (crop detritus, leaves debris) and associated microbiota (e.g., bacteria, fungi) originating from
 435 cultivated lands are most-likely major input processes of PM_{10} polyols and glucose at field crop sites.



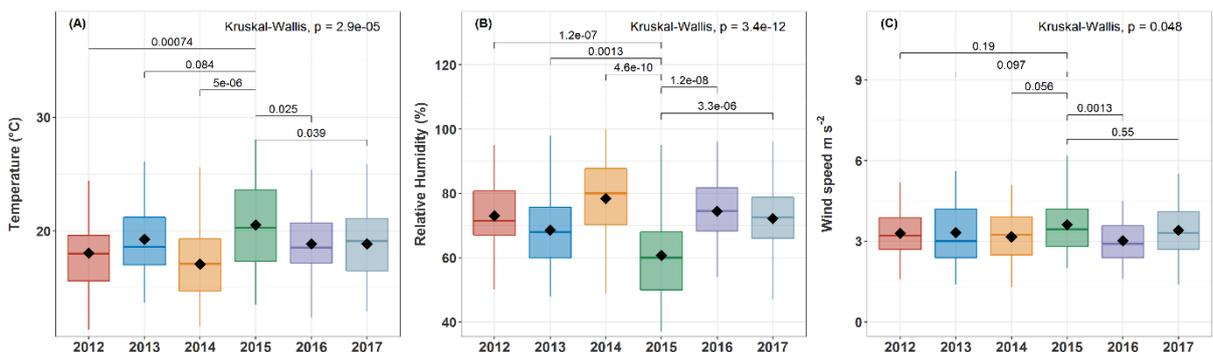
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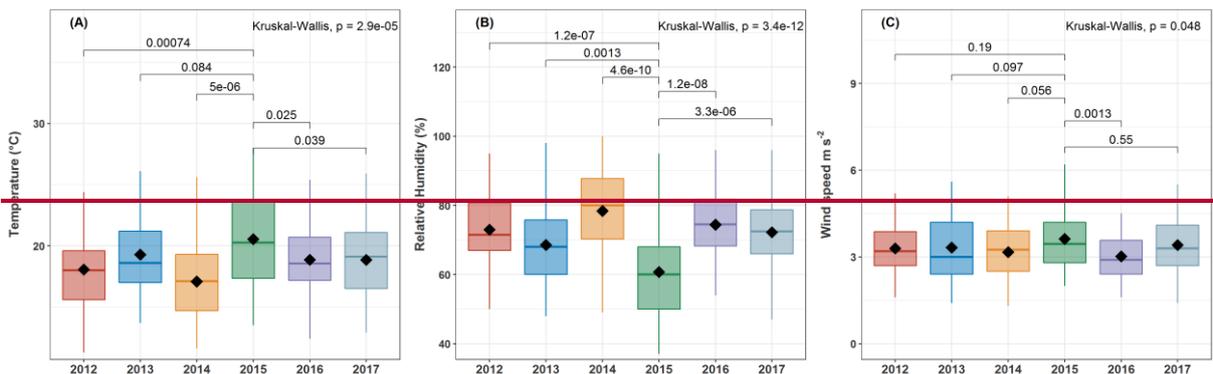
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438 **Figure 6: Daily evolution cycles of polyols and glucose concentrations in aerosols collected from the OPE-ANDRA**
 439 **monitoring site, from 2012 to 2018. Cellulose concentrations have been measured from January 2016 to January 2018.**
 440 **Colored bars correspond to the sum of the various agricultural practices performed (data for 69 parcels are averaged**
 441 **over 12 days for better clarity). Records of agricultural activities after October 2014 were available for only two parcels**
 442 **within the immediate vicinity of the PM₁₀ sampler. Records are multiplied by 10 for this period.**

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446 **Figure 7: Boxplots of (A) maximum ambient temperature, (B) relative humidity and (C) wind speed at OPE-ANDRA**
 447 **from 2012 to 2017. Analyses are performed for warmer periods (June to November). Only statistically different**
 448 **meteorological factors are presented. The black marker inside each boxplot indicates the average value, while the top,**
 449 **middle and bottom of the box represent the 75th, median and 25th percentiles, respectively. The whiskers at the top and**
 450 **bottom of the box extend from the 95th to the 5th percentiles. Statistical differences between average values were assessed**
 451 **with the Kruskal-Wallis method ($p < 0.05$).**

452 4. Conclusions

453 The short-term temporal (daily) and spatial (local to nation-wide) evolutions of particulate polyols (defined here
454 as the sum of arabitol and mannitol) and glucose concentrations are rarely discussed in the current literature. The
455 present work aimed at investigating the spatial behavior of these chemicals and evidencing their major effective
456 environmental drivers. The major results mainly showed that:

- 457 • The short-term evolution of ambient polyols and glucose concentrations is highly synchronous across an
458 urban city-scale and remains very well correlated throughout the same geographic areas of France, even
459 if the monitoring sites are situated in different cities at about 150-190 km. However, sampling sites
460 located in two distinct geographic areas are poorly correlated. This indicates that emission sources of
461 these chemicals are uniformly distributed, and their accumulation and removal processes are driven by
462 quite similar environmental parameters at the regional scale. Therefore, local phenomena such as
463 atmospheric resuspension of topsoil particles and associated microbiota, microbial direct emissions (e.g.
464 sporulation), cannot be the main emission processes of particulate polyols and glucose in urban areas not
465 directly influenced by agricultural activities.
- 466 • The atmospheric concentrations of polyols (or glucose) and cellulose display remarkably synchronous
467 temporal evolution cycles at the background urban site of Grenoble, indicating a common source related
468 to plant debris.
- 469 • Higher ambient concentrations of polyols and glucose at the rural site of OPE-ANDRA occur during each
470 harvest period, pointing out resuspension processes of plant materials (crop detritus, leaves debris) and
471 associated microbiota for agricultural and nearby urbanized areas. This is associated with higher PM₁₀
472 cellulose concentration levels, as high as 0.4 to 2.0 µg m⁻³ on a daily basis (accounting up to 7.5 to 32.4 %
473 of the OM mass).
- 474 • Multiple linear regression analysis of the yearly series from the site of Marnaz gave insightful information
475 on which parameter controls the ambient concentrations of polyols and glucose. Ambient air night-time
476 temperature, relative humidity and vegetation density are the most important drivers, whilst wind speed
477 conditions tend to affect the contribution of local vegetation.

478 Altogether, these results improve our understanding of the spatial behavior tracers of PM₁₀ PBOA emission sources
479 in France, and in general, which is imperative for further implementation of this important mass fraction of OM
480 into chemical transport models. Further investigations of airborne microbial fingerprint (bacteria and fungi) are
481 ongoing, which may deepen our understanding of the PBOA source profile.

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499 the PhD of AS or SW. EP, OF, and VR supervised the PhD of DMO who investigated the sites in northern France.
500 OF, JL-J, JL-B, AA and NM were coordinating and partners of the different initial programs for the collection and
501 chemical analysis of the samples. VJ developed the analytical techniques for polyols and cellulose measurements.
502 TC performed the cellulose measurements. Samples analyses at LSCE were performed by NB. AC gave advices
503 for the statistical aspects of the data processing. AS and JLJ processed the data and wrote up the manuscript. SW
504 participated to the visualization of the results. SC is supervising the OPE station and collected the agricultural
505 activities records. All authors from AASQA (author affiliation nos. 9 to 16) are representatives for each network
506 that conducted the sample collection and the general supervision of the sampling sites. All authors reviewed and
507 commented on the manuscript.

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

509 **Data availability:** [All relevant data for this paper are archived at the IGE \(Institut des Géosciences de](#)
510 [l'Environnement\), and are available upon request from the corresponding author \(Jean-Luc Jaffrezo\).](#)

511

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