Response to the Editor's comments

Comments to the Author:

The language and grammar of the Main text should be improved and the Conclusions section is too much a repetition of the Abstract; it should also be improved. Both these comments can be dealt with after the ACPD discussion phase.

Response: Thanks for the handling of our paper. Following the Editor's recommendation, we have corrected the grammatical mistakes and significantly improved the English of the revised MS. We also revised the conclusion section carefully.

Responses to the Anonymous Referee's comments

Referee #1 Evaluations

The work by Haque et al presents a range of organic compounds in atmospheric aerosols from a year-long campaign in South Korea. The authors used well established analytical techniques for their analysis. The experimental procedure is well designed and in general the data is well presented. My detailed comments are listed below.

Response: Thanks for the careful reading and valuable suggestions to improve the scientific content of the manuscript. Following the reviewer's comment, we have carefully made corrections in the revised MS. Our responses to all comments made by the reviewer are given below. Please refer to the revised MS, in which changes are highlighted in yellow.

Comment: First of all, although the work is of relatively good quality (as can be judged from the draft); I felt it is largely of a routine nature (at least the way it is presented). I believe that such type of publications can be useful but if considered for publication at ACP they need to go under the Measurement report's category.

Response: We respectfully do not comply with the reviewer's argument but would like to highlight the two key features that make this study suitable for publication in ACP under the Research article category.

1. Here, we present a new finding on the contribution of coal combustion sources in East Asia in controlling the atmospheric levels of levoglucosan (*Lev*) apart from the traditional biomass/biofuel burning emissions. This is based on the prevailing linear relationship between the radiocarbon based nonfossil-EC and *Lev* in the year-round TSP samples collected from the Korean Climate Observatory at Gosan (KCOG) site in Jeju Island. The Gosan supersite is the best location to understand how the chemical composition of source-emissions from East Asia affects the outflow regions in winter and spring. Recent studies have highlighted the potential contribution of *Lev* from residential coal combustion in China (Yan et al., 2018), with estimated annual emission of ~2.2 Gg of *Lev* from domestic coal combustion (Wu et al., 2021). Given this background information, the prevailing significant linear relationship between *Lev* and nonfossil-EC (P-value < 0.05) over the KCOG clearly emphasizes the need

for reconsideration of the previous assessments on the impact of biomass burning in East Asian outflow to the western North Pacific.

2. Another important highlight is the detailed study on the atmospheric abundances of biogenic SOA tracers along with those of other primary biological particles from the KCOG for the year 2013. This dataset is further compared with the molecular distributions and relative abundances of these organic tracers in the TSP samples collected over Gosan during 2001, a decade ago (Fu et al., 2012). This comparison allows us to better understand the regional changes in the emission sources (*e.g.,* fugitive dust, biomass burning, and fossil-fuel combustion) on a decadal basis.

These points have been added in the revised MS. Please see lines 682-697.

Major comment:

Comment: I would like to know if the authors considered atmospheric stability of the measured organic compounds especially in the light of a long-range transport or/and correlation and statistical analysis of the reported species. For example, it has been demonstrated that levoglucosan can decay in particles exposed to OH. ''*The extent of decay ranged from 20 to 90% and was strongly correlated to the integrated OH exposure. Increased relative humidity did not enhance or impede reaction. Relative kinetics indicate that levoglucosan has an atmospheric lifetime of 0.7–2.2 days when biomass burning particles are exposed to 1×106 molecules cm^{-3} of OH (typical average summertime conditions). This implies that levoglucosan reacts with OH on a timescale similar to that of transport and deposition, which has important implications for the use of levoglucosan as a tracer for biomass burning emissions in source apportionment studies''* Hennigan et al. 2010.

I trust the above also applies to other measured organic compounds for some of which the information on reactivity is not available. My question to the authors - how does this affect the presented results? The authors present correlation of different organic compounds and discuss their potential similar source based on these correlations and statistical analysis. Does the stability of considered organic compounds can play a role in the observed absence of correlation? The same applies to the discussion on long range transport of the observed organics. I doubt that stability of considered sugars in Figure 4 is the same for all compounds.

Response: As the reviewer rightly pointed out that levoglucosan (*Lev*) undergoes a photooxidation with OH radicals during atmospheric transport (half-life: <2.2 days) and, this would cause lower abundances of this anhydrosugar (Hennigan et al., 2010). *Lev* concentration measured over the KCOG includes contributions from both fossil and nonfossil sources in the East Asian outflow. In such a case, we found the moderately significant correlations of *Lev* with nonfossil EC (i.e., biomass burning) and fossil-EC (e.g., Miocene lignite coals) over the KCOG. It is very likely that this weakened relationship is because of the photo-degradation of *Lev* during atmospheric transport. This result would be an otherwise high atmospheric abundance of *Lev* and its pronounced linear relationships with the nonfossil- and fossil-EC, which implies a much stronger impact of both these source emissions in the East Asian continental outflow in winter and spring. This is also applicable for low concentrations and poor correlations of other organics such as primary saccharides and BSOA tracers. Considering the feasibility of photooxidation, it is likely that secondary OA undergoes much faster cycling than the primary sugar compounds. This would mean a slight underestimation of BSOA over the KCOG in the East Asian outflow and their atmospheric abundances over Gosan reflect a lower limit.

These explanations have been added in the revised MS. Please see lines 370-374, 452-453, 458-460, and 676-681.

Comment: Moreover, besides anhydrosugars, the authors state that ''*Cis-pinonic acid showed poor correlation with pinic acid (r = 0.35, p = 0.12) (Figure 6f), suggesting that they formed from different monoterpenes such as α-pinene, β-pinene, or δ-limonene*.'' Such assumptions can be made only if the measurements are taken very close to their emission sources **and/or** assuming that both compounds have similar atmospheric stability or reactivity. Is it the case for all considered compounds in this study? I believe this needs to be considered when discussing correlations or long range transport.

Response: We comply with the reviewer's view. Likely, the extent of loss of BSOA by the photooxidation during transport would also cause such poor correlations, influencing their abundances over KCOG. We have added a few sentences in the revised MS. Please see lines 476-478 and 499-501.

Minor comment:

Comment: It is hard to read Figure 2 (especially Figure 2a). Please either split the concentration axis so that all minor compounds can be clearly seen in the plot or move it into the SI and increase the size of the figure.

Response: Following the reviewer's suggestion, we have added an additional figure in the supplement for the visualization of minor compounds in the temporal plot. Please see Figure S2.

Reference:

Hennigan, C.J., Sullivan, A. P., Collett, J. L., Robinson, A. L.: Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals, Geophys. Res. Lett., 37, https://doi.org/10.1029/2010GL043088, 2010.

Response: Added in the reference list of the main text.

Reviewer #2 Evaluations

The authors present the results of the chemical composition of organic aerosol in South Korea with a focus on primary organic compounds and biogenic secondary organic aerosol tracers. Seasonal variations and sources of studied compounds were analysed. The paper is suitable for publication in the journal Atmospheric Chemistry and Physics, however, several comments reported below should be addressed before acceptance for publication. Minor revisions of the paper are requested.

Response: We thank the reviewer for the positive assessment of this work. We have carefully revised the manuscript following the reviewer's comments and suggestions. Our responses to all comments made by the reviewer are given below. Please refer to the revised MS, in which changes are highlighted in yellow.

Comments:

Comment: Lines 277-281: Glucose and other saccharides may be partly formed also during biomass burning, which explains their contribution during the winter period.

Response: Following the reviewer's comment, we have added the following sentence in the revised MS as: "Since glucose, fructose, and sucrose showed moderately significant correlations (R^2 = 0.44-0.48, p<0.01) with levoglucosan in winter, it is somewhat possible that BB source emission could also influence the concentrations of these saccharides in this season (Haque et al., 2019; Fu et al., 2008)." Please see lines 279-283.

It can be noted that levoglucosan showed a poor/negative correlation with other saccharides except xylose (lines 404-405) and inositol in winter (discussed in the main text). Please see lines 302-305 in the revised MS.

Comment: Line 283-294: Sources of inositol and other polyols are only perfunctorily characterized focusing on prevailing sources. Sources of inositol are entirely missing.

Response: Following the reviewer's suggestion, more discussion on sources of polyols along with inositol has been added in the revised MS as: "The major sources of arabitol and mannitol are airborne fungal spores (Bauer et al., 2008), accompanying detritus from mature leaves (Pashynska et al., 2002). Heald and Spracklen (2009) reported that mannitol and arabitol are considerably associated with terrestrial biosphere activity. Inositol is largely derived from the developing leaves in summer (Pashynska et al., 2002) and BB in winter (Fu

et al., 2010b). Zhu et al. (2015b) found similar seasonal behavior of inositol with those of other sugar alcohols with the predominance in summer, associated with microbial activities in local forests from Okinawa. Inositol showed a moderately significant correlation with levoglucosan (R^2 = 0.33, p< 0.01) in winter; however, there were no positive linear relationships between levoglucosan and other sugar alcohols, implying a partial emission of inositol from the BB during winter in Gosan aerosols." Please see lines 296-305. More information regarding the sources of polyols are already interpreted in section 3.4 (lines 409-419).

Comment: Line 306-307: Unlike other studies, the concentration of mannosan in this study is surprisingly lower than those of galactosan, do you have an explanation of this fact?

Response: Following the reviewer's comment, we have added the following sentences in the revised MS as: "Galactosan is more abundant in crop-residue burning emissions than mannosan (Engling et al., 2009; Sheesley et al., 2003). It is very much likely that the impact of crop-residue burning emissions in East Asia over Gosan is more prominent in winter/spring. Such high abundances of galactosan over mannosan were found in the North China Plain (Fu et al., 2008) and in the Indo-Gangetic Plain outflow sampled over the Bay of Bengal (Bikkina et al., 2019)." Please see lines 320-325.

Comment: Line 400-404: Ratios levoglucosan/mannosan and levoglucosan/(mannosan + galactosan) also allow to distinguish biomass burning and lignite combustion as the source of these anhydrosugars. In addition, the empirical equation using levoglucosan and mannosan data allows you to calculate the contribution of softwood and hardwood to the total amount of combusted wood.

Response: Based on the reviewer's comment, we have added the results of these diagnostic ratios in the revised MS as "Ratios of *Lev/Man* and *Lev/(Man + Gal)* can be useful to distinguish BB and coal combustion contributions. The average ratios of *Lev/Man* (15.1 ± 6.76) and *Lev/(Man + Gal)* (4.27 ± 1.23) in Gosan aerosols are much closer to those from wood burning and coal combustion sources emissions, respectively (Yan et al., 2018). It reveals that *Lev* could originate from both biomass and coal burning source emissions, which is consistent with the linear relationship between *Lev*-C and fossil-/nonfossil carbon fraction

(section 3.7). Please see lines 422-427 in the main text. Unfortunately, we are not familiar with the empirical equation to calculate the contribution of softwood and hardwood.

Comment: Line 426: Add references to levoglucosan degradation.

Response: Added. Please see line 453 in the revised MS.

Comment: Line 536: Add missing information into Table 3, such as analysed PM fraction and studied season.

Response: Added. Please see Table 3 in the revised MS.

Comment: Line 562: Another key factor is a higher concentration of ozone and other oxidation agents in summer.

Response: Added. Please see lines 591-592 in the revised MS.

1 **Regional heterogeneities in the emission of airborne primary sugar**

2 **compounds and biogenic secondary organic aerosols in the East Asian**

3 **outflow: Evidence for coal combustion as a source of levoglucosan**

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ABSTRACT

Biomass burning (BB) significantly influences the chemical composition of organic aerosols (OA) in the East Asian outflow. Source apportionment of BB-derived OA is an influential factor for understanding their regional emissions, which is crucial for reducing uncertainties in their projected climate and health-effects. We analyzed here three different classes of atmospheric sugar compounds (anhydrosugars, primary sugars, and sugar alcohols) and two types of biogenic secondary organic aerosol (BSOA) tracers (isoprene- and monoterpene derived SOA products) in a year-long collected total suspended particulate matter (TSP) from an island-based receptor site in South Korea, the Gosan. We investigate seasonal variations in the source-emissions of BB-derived OA using mass concentrations of anhydrosugars and radiocarbon (^{14}C-) isotopic composition of organic carbon (OC) and elemental carbon (EC) in ambient aerosols. Levoglucosan (*Lev*) is the most abundant anhydrosugar, followed by galactosan (*Gal*) and mannosan (*Man*). Strong correlations of *Lev* with *Gal* and *Man*, along with their ratios (*Lev/Gal:* 6.65 ± 2.26; *Lev/Man*: 15.1 ± 6.76) indicate the contribution from hardwood burning emissions. The seasonal trends revealed that the BB impact is more pronounced in winter and fall, as evidenced by the high concentrations of anhydrosugars. Likewise, significant correlations among three primary sugars (i.e., glucose, fructose, and sucrose) emphasized the contribution of airborne pollen. The primary sugars showed higher concentrations in spring/summer than winter/fall. The fungal spore tracer compounds (i.e., arabitol, mannitol, and erythritol) correlated well with trehalose (i.e., a proxy for soil organic carbon), suggesting the origin from airborne fungal spores and soil microbes in the East Asian outflow. These sugar alcohols peaked in summer, followed by spring/fall and winter. Monoterpene-derived SOA tracers were most abundant compared to isoprene-SOA tracers. Both BSOA tracers were dominant in summer, followed by fall, spring, and winter. The source apportionment based on multiple linear regressions, diagnostic mass ratios, and positive matrix factorization analysis altogether revealed that biomass burning (41.9%) and biogenic SOA (21.1%) mostly dictate the OA loading in the ambient aerosols from East Asian outflow. We also found significant positive linear relationships of ^{14}C-based nonfossil- and fossil-derived organic carbon fractions with *Lev-C* along with the comparable regression slopes, suggesting the importance of BB and coal combustion sources in the East Asian outflow.

Keywords: Biomass burning tracers, primary biological aerosol particles, biogenic SOA tracers, radiocarbon-based source apportionment, organic aerosols, East Asian outflow

1. Introduction

Organic aerosols (OA), which account for a major fraction of up to 50% of airborne total suspended particulate matter, have considerable effects on regional and global climate by absorbing or scattering sunlight (Kanakidou et al., 2005). However, the climate effects of OA are involved with large uncertainties due to our limited understanding of the contributing sources. OA can be derived from both primary emissions and secondarily formed species. Sugars are an important group of water-soluble, primarily organic compounds whose concentrations are significant in atmospheric aerosols over the continent (Jia and Fraser, 2011; Fu et al., 2008; Yttri et al., 2007; Graham et al., 2003). Anhydrosugars such as levoglucosan, galactosan, and mannosan are the key tracers of biomass burning (BB) emissions (Simoneit, 2002). Sugar alcohols, along with glucose, trehalose and sucrose are mostly originated from primary biological particles such as fungal spores, pollen, bacteria, and viruses, and vegetative debris (Graham et al., 2003; Simoneit et al., 2004a; Bauer et al., 2008; Deguillaume et al., 2008). Primary sugars and sugar alcohols are predominantly present in the coarse mode aerosols, accounting for 0.5-10% of atmospheric aerosol carbon matter (Yttri et al., 2007; Pio et al., 2008).

Secondary organic aerosol (SOA) is a large fraction of OA, while there were only limited studies about the key factors controlling SOA formation. The SOA formation significantly increased with the enhancement of the ambient aerosol mass (Liu et al., 2018). SOA is formed by both homogenous and heterogeneous reactions of volatile organic compounds (VOCs) in the atmosphere (Surratt et al., 2010; Robinson et al., 2007; Claeys et al., 2004). On a global estimation, biogenic VOCs (BVOCs) such as isoprene, monoterpenes (e.g., α/β-pinene), and sesquiterpenes (e.g., β-caryophyllene) are one order of magnitude higher than those of anthropogenic VOCs (e.g., toluene) (Guenther et al., 2006). The global emissions of annual BVOCs were estimated to be 1150 TgC yr^{-1}, accounting for 44% isoprene and 11% monoterpenes (Guenther et al., 1995). Isoprene is highly reactive and promptly reacts with oxidants such as O_3, OH, and NO_x in the atmosphere to form SOA (Kroll et al., 2005, 2006; Ng et al., 2008; Surratt et al., 2010; Bikkina et al., 2021), estimated to be 19.2 TgC yr^{-1}, consisting of ~70% of the total SOA budget (Heald et al., 2008). Monoterpenes are important sources of biogenic secondary organic aerosol (BSOA), accounting for ~35% of the global BVOCs emissions (Griffin et al., 1999).

Anthropogenic activities such as coal and biofuel combustion over East Asia, including China, are responsible for the vast emission of OA (Huebert et al., 2003; Zhang et al., 2016). Understanding the ambient levels OA in the East Asian outflow is crucial for

99   assessing their regional climatic effects. As part of this effort, Korean Climate Observatory at

100 Gosan (KCOG), a super site located in South Korea, is an ideal location for investigating the

101 atmospheric outflow characteristics from East Asia (Fu et al., 2010a; Kundu et al., 2010;

102 Ramanathan et al., 2007; Kawamura et al., 2004; Arimoto et al., 1996). For instance, primary

103 OA associated with soil/desert dust in East Asia, along with forest fires in

104 Siberia/northeastern China, are transported over Gosan in spring (Wang et al., 2009a). BSOA

105 during long-range transport from the continent and Open Ocean, as well as local vegetation,

106 can significantly contribute to Gosan aerosols. Although these investigations were carried out

107 almost a decade ago, no such observations are available in contemporary times from Gosan.

108 Here, we attempt to understand the current states of East Asian OA using both the molecular

109 marker approach and radiocarbon data of carbonaceous components.

110 The KCOG, located on the western side of Jeju Island adjacent to the Yellow Sea and

111 the East China Sea, is facing the Asian continent but is isolated from public areas of the

112 island (Kawamura et al., 2004). Simoneit et al. (2004b) have documented during the ACE-

113 Asia campaign that OA from the BB and fossil fuel combustion sources are transported along

114 with desert dust to the KCOG during continental outflow. An intensive campaign was

115 organized at the KCOG during spring 2005 to observe the physical properties of East Asian

116 aerosols while two dust events were detected (Nakajima et al., 2007). Here, we focus on the

117 characterization of airborne anhydrosugars, primary sugars, sugar alcohols, and BSOA

118 tracers from the KCOG. Gosan is influenced by the continental outflow from East Asia

119 during winter, spring and fall, whereas the site is influenced by the maritime air masses from

120 the Pacific Ocean and other marginal seas. This makes the KCOG ideal for characterizing the

121 regional heterogeneities in the emissions of organic compounds in the East Asian outflow

122 based on the TSP samples collected during April 2013-April 2014.

123 **2. Methods**

124 **2.1. Aerosol sampling and prevailing meteorology**

125 Total suspended particles (TSP) were collected on pre-combusted (450°C for 6 h) quartz fiber

126 filters (20 cm × 25 cm, Pallflex) at the KCOG (33.17 °N, 126.10 °E, see Figure 1), South

127 Korea. To get enough signal for the radiocarbon measurements, each TSP sample was

128 collected for 10–14 days from April 2013 to April 2014. Twenty-one samples were collected

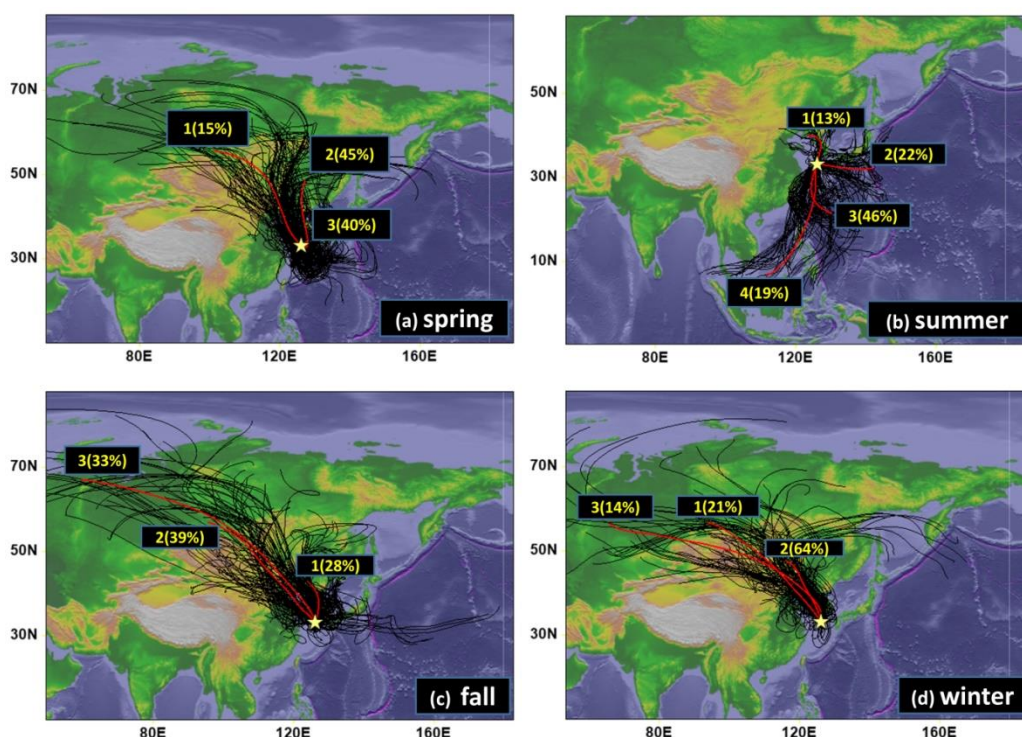
129 using a high-volume air sampler (Kimoto AS-810, ~65 m^3 h^{-1}) installed on the rooftop of a

130 trailer house (~3 m above the ground). After the collection, aerosol filters were transferred to

131 a pre-combusted (450°C for 6 h) glass jar (150 mL) equipped with a Teflon-lined screw cap

132 and transported to the laboratory in Sapporo. These TSP samples were stored in a dark

133 freezer room at -20°C until the analysis. Three field blank filters were also collected during
134 the campaign.

135   The ambient temperatures at the Gosan site were on average 6.9°C in winter, 14.1°C
136 in spring, 27.0°C in summer, and 17.1°C in fall. Likewise, the average relative humidity was
137 found to be highest in summer (71.3%), followed by spring (64.9%), fall (63.5%), and winter
138 (54.7%). Gosan is influenced by the pollution sources in East Asia during winter as well as
139 other transition periods (spring and fall) due to the prevailing westerlies. In contrast, winds in
140 summer blew mostly from the western North Pacific (WNP) by the easterly winds. The
141 spring season is, in particular, important for the transport of mineral dust mixed with polluted
142 OA to Gosan (Kundu et al., 2010).

155 **Figure 1.** Cluster analysis of backward air mass trajectories over Gosan (indicated by a star
156 symbol) for the TSP collected during (a) spring, (b) summer, (c) fall, and (d) winter seasons.

158 **2.2. Extraction and analysis of organic compounds**
159 Approximately 3.14 cm^2 filter cuts were extracted with dichloromethane/methanol (2:1; v/v).
160 The extracts were concentrated using a rotary evaporator under vacuum and then blown down
161 to near dryness with pure nitrogen gas. The dried residues were subsequently reacted with N,
162 O-bis(trimethylsilyl)trifluoroacetamide containing 1% trimethylchlorosilane (BSTFA+1%

163   TMCS, SUPELCO[©], Sigmaaldrich[®]) and pyridine at 70 °C for 3 h to derive OH and COOH

164   groups of polar organic compounds to trimethylsilyl ethers and esters, respectively. After the

165   derivatization followed by the addition of a known amount of internal standard solution

166   (Tridecane; 1.43 ng L^{-1} in n-hexane), the derivatized extracts were injected onto a gas

167   chromatograph (Hewlett-Packard model 6890 GC) coupled to a mass spectrometer (Hewlett-

168   Packard model 5973, MSD) (GC-MS). More details on the quantification of polar organic

169   compounds using GC-MS are described in Haque et al. (2019).

170   The target compounds (anhydrosugars, primary sugars, sugar alcohols, and BSOA

171   tracers) were separated on a DB-5MS fused silica capillary column (30 m x 0.25 mm i.d., 0.5

172   μm film thickness) using helium as a carrier gas at a flow rate of 1.0 ml min^{-1}. The GC oven

173   temperature was programmed from 50°C for 2 min and then increased from 50 to 120°C at

174   30°C min^{-1} and to 300°C at 6°C min^{-1} with a final isotherm hold at 300°C for 16 min. The

175   sample was injected in a splitless mode with the injector temperature at 280°C. The MS was

176   operated at 70 eV and scanned from 50 to 650 Da on an electron impact (EI) mode. Mass

177   spectral data were acquired and processed using the Chemstation software. The organic

178   compounds were identified individually by comparison with retention times and mass spectra

179   of authentic standards and NIST library and literature data of mass fragmentation patterns

180   (Medeiros and Simoneit, 2007). For assessing the recoveries, ~100-200 ng of the standard

181   solution was spiked on the blank filter and analyzed as a real sample. Overall, the average

182   recoveries were found to be 80-104% for target compounds. The field and laboratory blank

183   filters (n = 3) were also analyzed by the same procedures as a real sample. Target compounds

184   were not found in the field blanks. The analytical errors based on concentrations by replicate

185   sample analyses (n = 3) were less than 15%.

186   **2.3. Radiocarbon isotopic composition of TC and EC**

187   The concentrations of total carbon (TC) in TSP samples were analyzed using an elemental

188   analyzer. For the radiocarbon isotopic composition ($\Delta^{14}C$), the aerosol filter punches were

189   exposed for ~12 h to HCl fumes in a vacuum desiccator. Subsequently, these filters were

190   analyzed for $\Delta^{14}C$ on a modified elemental analyzer coupled via a gas interface to Accelerator

191   Mass Spectrometer Mini Carbon Dating System (MICADAS) at the University of Bern,

192   Switzerland (Salazar et al., 2015). The evolved CO_2 of TC from the elemental analyzer was

193   passed through a moisture trap (Sicapent, Merck) and isolated it from other residual gasses

194   using a temperature-controlled zeolite trap. The purified CO_2 was introduced through a gas

195   interface system to MICADAS, where $^{14}C/^{12}C$ ratios are measured according to the analytical

196 procedures detailed in Zhang et al. (2016). Likewise, the evolved CO_2 of elemental carbon

197 from the Sunset Lab OC/EC analyzer using Swiss 4S protocol (Zhang et al., 2012), was

198 directed to the MICDAS and measured for the $^{14}C/^{12}C$ ratio relative to standard calibration

199 gas. These results were expressed as fractions of modern carbon (f_M) by normalizing with a

200 $\delta^{13}C$ value of the reference standard in the year 1950 (−25‰) according to Stuiver and Polach

201 (1997) for the fractionation effects. The $f_M(OC)$ can be estimated by using the $f_M(TC)$ and

202 $f_M(EC)$ in an isotope mass balance equation (Zhang et al., 2015). Additionally, we estimated

203 the relative contributions of OC and EC from the nonfossil and fossil sources ($f_{nonfossil}$ and

204 f_{fossil}, respectively) using the following equations.

205 $\qquad f_{nonfossil-OC} = f_M(OC\text{-}sample)/f_M(OC\text{-}ref); f_M(OC\text{-}ref) \approx 1.07 \pm 0.04$ (1)

206 $\qquad f_{nonfossil-EC} = f_M(EC\text{-}sample)/f_M(EC\text{-}ref); f_M(EC\text{-}ref) \approx 1.10 \pm 0.05$ (2)

207 $\qquad f_{fossil-OC} = 1 - f_{nonfossil-OC}$ (3)

208 $\qquad f_{fossil-EC} = 1 - f_{nonfossil-EC}$ (4)

209 $\qquad$ The reference values of OC and EC were obtained from Mohn et al. (2008). Using

210 the fractions of $f_{fossil-OC}$ and $f_{nonfossil-OC}$, we can, therefore, estimate the mass concentration of

211 ambient organic carbon (OC-ambient) from fossil and nonfossil sources (OC_{fossil} and

212 $OC_{nonfossil}$, respectively).

213 $\qquad OC_{nonfossil} = f_{nonfossil-OC} \times [OC]_{ambient}$ (5)

214 $\qquad OC_{fossil} = f_{fossil-OC} \times [OC]_{ambient}$ (6)

215 $\qquad$ More details on the radiocarbon isotopic composition data over Gosan were reported

216 elsewhere (Zhang et al., 2016).

217 **3. Results and discussion**

218 **3.1. Trajectory and cluster analysis**

219 Backward air mass trajectories are useful for assessing the impact of local versus regional

220 source emissions over Gosan. Seven-day isentropic backward air mass trajectories were

221 computed using the hybrid single-particle Lagrangian integrated trajectory model (HYSPLIT,

222 version 4: Stein et al., 2015) over the KCOG for the sampling period using the

223 meteorological datasets of the Global Data Assimilation System (GDAS) network. The

224 trajectory endpoint files from the HYSPLIT model were further used for the cluster analysis

225 using the Trajstat package (Wang et al., 2009b) for all four seasons (Figure 1). Although

226 cluster analysis revealed the predominance of continental transport in spring, fall, and winter

227 seasons, the air masses over the KCOG in summer mostly originated from the WNP. Since

228 spring is a transition of winds switching from westerlies to easterlies, Gosan is likely
229 influenced by the long-range transport of dust, pollution, and sea-salt aerosols.

230 The vertical mixing of pollutants within the boundary layer height also plays an
231 important role in controlling the strength of continental outflow alongside regional
232 meteorology. For instance, the mixing height of air parcels from the HYSPLIT model is
233 mostly confined to 1000 m in winter but somewhat increased towards spring and fall seasons
234 (Figure S1). This vertical enhancement in the boundary layer height facilitates the transport
235 of mineral dust particles from the arid and semiarid regions in East Asia along with urban
236 pollutants to Gosan in spring and fall compared to winter. However, the strength of
237 continental outflow somewhat depends on several factors, including source emissions,
238 meteorology, and mixing height of air parcels.

239 Gosan is influenced by three types of air masses in spring (Figure 1a), from the
240 Mongolian Desert (cluster 1: 15%), North China (cluster 2: 45%), and from the Yellow Sea
241 (cluster 3: 40%). In contrast, the easterlies from the WNP in summer mostly influenced the
242 composition of TSP over the KCOG. This inference is based on the cluster analysis for
243 summer samples (Figure 1b), which showed four regimes, including transport from the Sea of
244 Japan (cluster 1: 13%), WNP (cluster 2: 22%), South China Sea (cluster 3: 46%), and East
245 China Sea (cluster 4: 19%). In contrast, cluster analysis revealed three major transport
246 regimes from East Asia in fall and winter (Figure 1c-d). However, there are subtle differences
247 that exist between winter and fall in terms of influence from nearby versus distant pollution
248 sources. For instance, long-range transport of air masses from west Mongolia (cluster 1:
249 21%) and the Russian Far East (cluster 3: 14%) exerted a weak influence on the TSP sampled
250 over Gosan in winter. Besides, we observed a somewhat larger impact of air masses from the
251 North China Plain over Gosan (cluster 2: 64%) in winter. In contrast, Gosan is less influenced
252 by air masses originating from the North China Plain, contributing ~28% (cluster 1) than
253 those from Mongolia (cluster 2: 39%) and Russian Far East (cluster 3: 33%) in fall.
254 Therefore, the impact of East Asian outflow is stronger in winter than in spring and fall.

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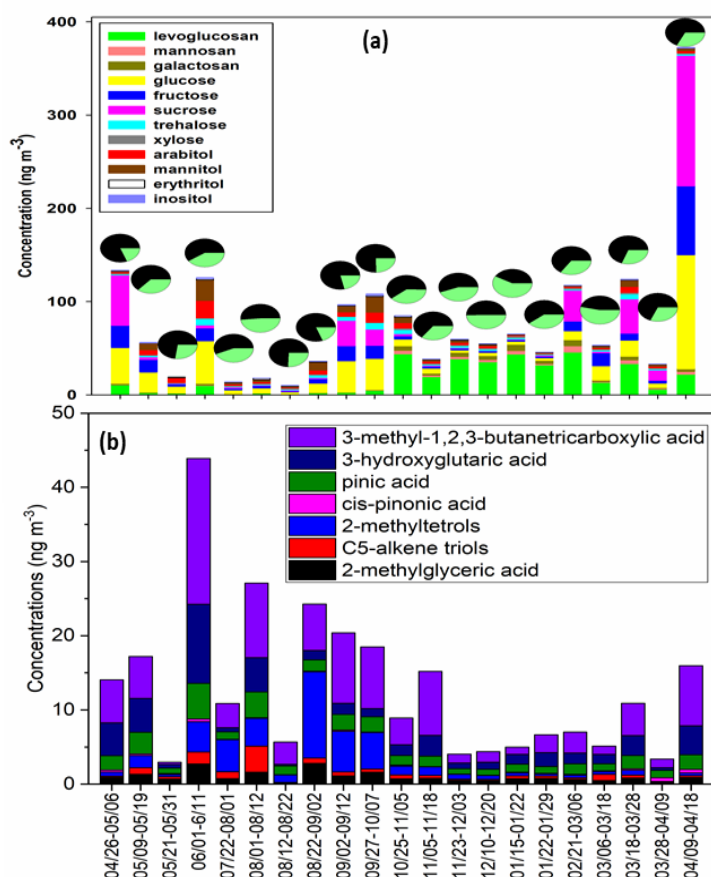
Figure 2. (a) Cumulative concentration levels of anhydrosugars, primary sugars, and sugar alcohols (i.e., represented by bars), and depicting the contributions of nonfossil (green color) and fossil (black color) organic carbon (i.e., pie charts), (b) Cumulative concentration levels of isoprene- and monoterpene SOA tracers in each TSP sample collected over Gosan.

3.2. Temporal and seasonal variability of sugars

The temporal/seasonal trends of sugar compounds over the KCOG provide useful information on the emission strengths of various sources in the East Asian outflow. All three anhydrosugars showed similar temporal and seasonal trends with higher concentrations in winter and fall than spring and summer (Figures 2a and S2). As levoglucosan and other two anhydrosugars (mannosan and galactosan) are the pyrolysis products of cellulose/hemicellulose, their higher concentrations along with an increase in nonfossil fraction of OC (Figure 2a; pie charts) in TSP from winter and fall revealed the impact of BB emissions. The MODIS satellite-based fire counts (Figure S1) together with cluster analysis in winter and fall (Figure 1) have revealed an influence of active BB emissions in the North China Plain, Mongolia, and Russian Far East. The temporal trends of glucose, fructose, and sucrose exhibited less variability throughout the sampling period; however, we observed a

275 slight increase in their concentration towards spring/summer (Figure 2a). Glucose and
276 fructose have origins from leaf fragments and pollen species (Fu et al., 2012a). Sucrose is a
277 potential tracer for airborne pollen (Fu et al., 2012a) and late spring/early summer is often
278 regarded as a season of "pollen-allergies". Therefore, similar temporal trends of glucose and
279 fructose with sucrose indicate their common source, pollens (Figure 2a). Since glucose,
280 fructose, and sucrose showed moderately significant correlations (R^2 = 0.44-0.48, p<0.01)
281 with levoglucosan in winter, it is somewhat possible that BB source emission could also
282 influence the concentrations of these saccharides in this season (Haque et al., 2019; Fu et al.,
283 2008).

284   BB also contributes to xylose and, hence, the temporal variability of xylose is
285 mimicking that of anhydrosugars. Trehalose is a primary sugar and a useful tracer for organic
286 carbon associated with soil dust particles (Fu et al., 2012a). The temporal variability of
287 trehalose closely resembled that of fungal spore tracers (arabitol, mannitol, and erythritol),
288 showing high concentrations in spring, summer, and fall seasons (Figures 2a and S2) (Zhu et
289 al., 2015a; Fu et al., 2012a). The KCOG is under the influence of a large-scale advection of
290 mineral dust from East Asia to the WNP during these three seasons (Tyagi et al., 2017;
291 Huebert et al., 2003). The mineral dust transport from East Asia to the WNP can be traced by
292 the high concentrations of non-sea-salt Ca^{2+} in the TSP samples from Gosan (Arimoto et al.,
293 1996). Similar temporal trends of trehalose and nss-Ca^{2+}, particularly in spring samples
294 (Figure S3), suggest that the abundance of OA specific to fungal spores over Gosan is likely
295 associated with the Kosa (Asian dust) events.

296   The major sources of arabitol and mannitol are airborne fungal spores (Bauer et al.,
297 2008), accompanying detritus from mature leaves (Pashynska et al., 2002). Heald and
298 Spracklen (2009) reported that mannitol and arabitol are considerably associated with
299 terrestrial biosphere activity. Inositol is largely derived from the developing leaves in summer
300 (Pashynska et al., 2002) and BB in winter (Fu et al., 2010b). Zhu et al. (2015b) found similar
301 seasonal behavior of inositol with those of other sugar alcohols with the predominance in
302 summer, associated with microbial activities in local forests from Okinawa. Inositol showed a
303 moderately significant correlation with levoglucosan (R^2 = 0.33, p< 0.01) in winter; however,
304 there were no positive linear relationships between levoglucosan and other sugar alcohols,
305 implying a partial emission of inositol from the BB during winter in Gosan aerosols.
306 Therefore, the temporal variability of inositol differs from other sugar alcohols (Figure S2).
307 The sources of sugar compounds are further discussed in section 3.4.

308   The seasonally averaged concentrations of all the anhydrosugars and xylose are
309   higher in winter/fall than spring/summer (Figure 3a-d), possibly due to a greater influence of
310   long-range transport from East Asia. In contrast, glucose, fructose, and sucrose peaked in
311   spring but decreased in other seasons (Figure 3e-g), mainly because of the contribution of
312   airborne pollen. Trehalose showed higher concentrations in fall and summer, followed by
313   spring and winter (Figure 3h). Arabitol, mannitol, and erythritol showed higher
314   concentrations in summer/fall than in winter and spring (Figure 3i-k). This seasonal trend is
315   consistent with those of soil-derived fungal spores. This feature is consistent with earlier
316   observations from a remote oceanic island in the WNP (Okinawa) during the impact of East
317   Asian outflow (Zhu et al., 2015a). The seasonally averaged mass concentrations of inositol
318   are highest in spring, followed by summer, fall, and winter (Figure 3l). Overall, the molecular
319   compositions of anhydrosugars showed the predominance of levoglucosan followed by
320   galactosan and mannosan (Figure S4). Galactosan is more abundant in crop-residue burning
321   emissions than mannosan (Engling et al., 2009; Sheesley et al., 2003). It is very much likely
322   that the impact of crop-residue burning emissions in East Asia over Gosan is more prominent
323   in winter/spring. Such high abundances of galactosan over mannosan were found in the North
324   China Plain (Fu et al., 2008) and in the Indo-Gangetic Plain outflow sampled over the Bay of
325   Bengal (Bikkina et al., 2019). Although the temporal variability of primary sugars in the TSP
326   samples from Gosan showed a characteristic peak of glucose and sucrose (Figure 2a), the
327   seasonally averaged distributions are different (Figure S4). The molecular distributions of
328   sugar alcohols are characterized by high loadings of arabitol and mannitol, followed by
329   erythritol and inositol (Figure S4).

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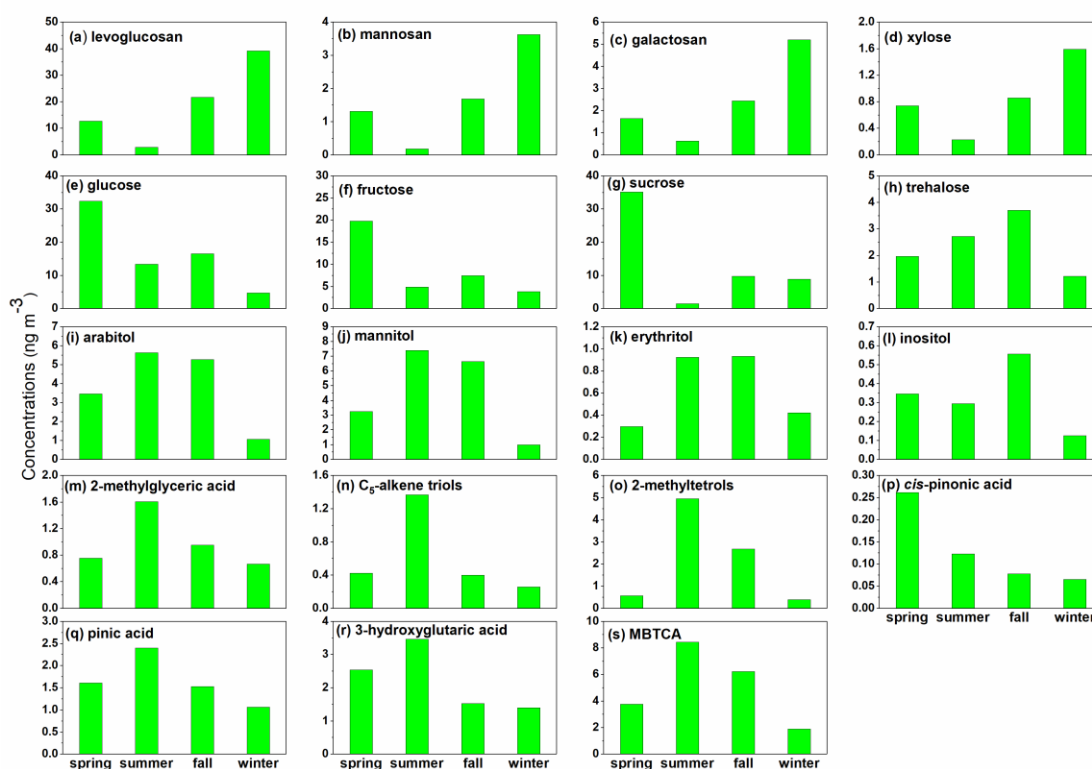
Figure 3. Seasonal variability of atmospheric levels of sugar compounds and BSOA tracers in TSP samples from Gosan during April 2013-April 2014.

334

3.3. Temporal and seasonal variability of BSOA tracers

We identified six isoprene-SOA tracers such as 2-methylglyceric acid (2-MGA), three C_5-alkene triols, and two 2-methyltetrols (2-methylthreitol and 2-methylerythritol) (2-MTs) in Gosan aerosol samples (Table 1). The sum of isoprene-SOA tracers ranged from 0.35 to 15.1 ng m^{-3} (avg. 3.69 ng m^{-3}) with the predominance of 2-MTs (avg. 2.09 ng m^{-3}). 2-MGA is the second most abundant isoprene-SOA tracer (avg. 0.99 ng m^{-3}), a high-generation product probably formed by further photooxidation of methacrolein and methacrylic acid. A similar molecular composition was observed over the North Pacific and California Coast (Fu et al., 2011). All the isoprene SOA tracers exhibited similar temporal variations with higher concentrations in the summer/spring months compared to autumn and winter (Figure 2b). Conversely, four monoterpene-SOA tracers, i.e., *cis*-pinonic acid, pinic acid, 3-hydroxyglutaric acid (3-HGA), and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), were detected in Gosan samples (Table 1). Total concentrations of monoterpene-SOA tracers were found to be 1.65 to 35.5 ng m^{-3} (avg. 9.24 ng m^{-3}) with a high concentration of MBTCA (avg. 5.11 ng m^{-3}). All the monoterpene-SOA tracers showed similar temporal trends with high values in summer/spring periods than autumn/winter (Figure 2b). Nevertheless, *cis*-

pinonic acid was ascribed somewhat different temporal variability with other monoterpene-SOA tracers. It is likely that *cis*-pinonic acid might be further photo-oxidized to form MBTCA (Szmigielski et al., 2007).

The seasonal average of isoprene-SOA tracers showed high concentrations in summer, followed by spring/fall and winter (Figure 3m-o). One key feature of the data presented here is that two fall samples (KOS984; 2-12 September and KOS986; 27 September to 07 October) exhibited high concentrations for 2-MTs over Gosan (Figure 2b). We presumed that local vegetation might contribute significantly to the formation of 2-MTs as it is a first-generation product. Moreover, 2-MTs can be derived from the open ocean under low NO_x conditions (Hu et al., 2013). 3-HGA and pinic acid showed somewhat higher concentrations in summer/spring than fall/winter (Figure 3q-r). *Cis*-pinonic acid was more abundant in spring compared to summer (Figure 3p) because of its photo-degradation, as discussed above. In contrast, MBTCA was dominant in summer/fall than spring/winter (Figure 3s). Here, the formation of MBTCA could be enhanced in fall during atmospheric transport from East Asia. The molecular distributions of isoprene-SOA tracers were characterized by a high loading of 2-MTs, followed by 2-MGA and C_5-alkene triols in all seasons (Figure S4). The Molecular composition of monoterpene-SOA tracers was dominated by MBTCA, followed by 3-HGA, pinic acid, and *cis*-pinonic acid in all seasons (Figure S4). Overall, BSOA tracers were found to be most abundant in summer, followed by fall, spring, and winter (Table 1). Interestingly, it is likely that secondary OA undergoes much faster cycling than the primary sugar compounds, considering the feasibility of photooxidation. This would mean a slight underestimation of BSOA over the KCOG in the East Asian outflow and, hence, their atmospheric abundances over Gosan reflect a lower limit.

Kang et al. (2018b) reported that monoterpene-SOA tracers were more abundant than isoprene-SOA tracers in spring-summer over the East China Sea, which is consistent with this study. Although the mass budget calculations showed that isoprene and monoterpenes are largely emitted by terrestrial plants; however, the open ocean can also contribute to isoprene and monoterpenes significantly (Conte et al., 2020; Shaw et al., 2010; Broadgate et al., 1997). Air mass back trajectory and cluster analysis (Figure 1) implied that air masses mostly originated from the ocean during summer. This means the open ocean significantly contributed to isoprene-SOA production. However, terrestrial sources from the continent also substantially enhanced the formation of BSOA. For example, one sample (KOS: 979; 1-11

384   June 2013) during summer showed the highest loading of BSOA tracers (Figure 2b) when air

385   masses are transported from the continent (Zhang et al., 2016).

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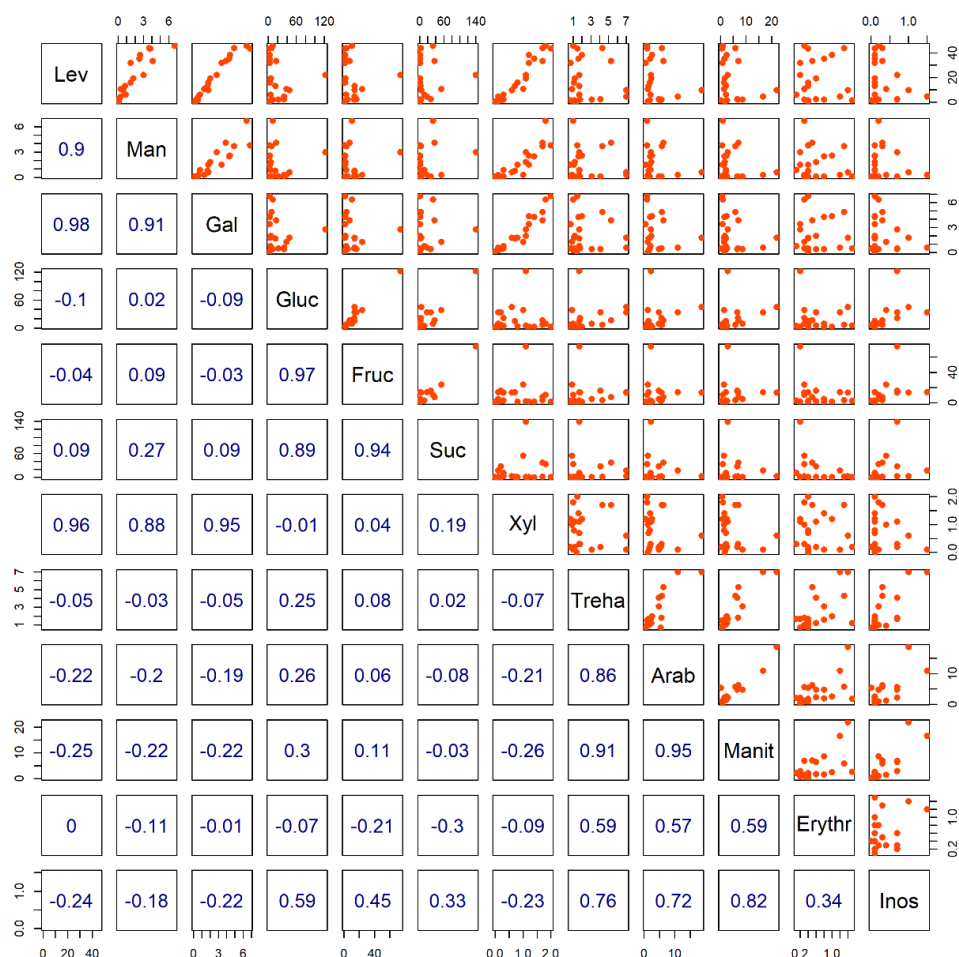
Figure 4. Multiple linear regression (MLR) analysis of airborne sugar compounds in TSP
collected over Gosan.

3.4. Source apportionment- regression analysis and diagnostic ratios

Anhydrosugars strongly correlated with xylose (Figure 4), suggesting their common source as
BB emission in East Asia. Fu et al. (2012a) analyzed pollen from different tree species (*e.g.*,
White birch, Chinese willow, Peking willow, Sugi, Hinoki), which are enriched in sucrose
(182-37,300 µg g^{-1}), glucose (378-3601 µg g^{-1}) and fructose (162-1813 µg g^{-1}). In our
samples, sucrose strongly correlated with glucose and fructose (Figure 4), suggesting their
origin from plant-derived airborne pollen. Likewise, a strong correlation was found between
arabitol and mannitol, indicating a mutual origin from a similar type of fungal spores (Zhu et
al., 2015a; Fu et al., 2012a; Bauer et al., 2008; Yttri et al., 2007). Bauer et al. (2008) ascribed

412 weak correlations between arabitol and mannitol to the diverse nature of ambient fungal

413 spores. Furthermore, both sugar alcohols correlated well with trehalose, a tracer for soil

414 organic carbon (Fu et al., 2012a). This observation suggests their common origin from soil

415 organic matter associated with fungal spores. Erythritol also originates from fungal spores;

416 however, its abundance is affected by the atmospheric aging process. Kessler et al. (2010)

417 reported that erythritol is degraded during long-range transport in 12.7 days. Consequently,

418 arabitol and mannitol were moderately correlated with erythritol in the Gosan samples due to

419 the degradation of latter sugar alcohol in the East Asian outflow.

420   The linear relationship of levoglucosan (*Lev*) with mannosan (*Man*), galactosan (*Gal*),

421 and nss-K^+ provide useful information on the type of BB emissions (hardwood, softwood, or

422 crop-residue). Ratios of *Lev/Man* and *Lev*/(*Man + Gal*) can be useful to distinguish BB and

423 coal combustion contributions. The average ratios of *Lev/Man* (15.1 ± 6.76) and *Lev*/(*Man +*

424 *Gal*) (4.27 ± 1.23) in Gosan aerosols are much closer to those from wood burning and coal

425 combustion sources emissions, respectively (Yan et al., 2018). It reveals that *Lev* could

426 originate from both biomass and coal burning source emissions, which is consistent with the

427 linear relationship between *Lev*-C and fossil-/nonfossil carbon fraction (section 3.7).

428 Furthermore, different types of biomass are characterized by distinct *Lev/Man* ratios. For

429 instance, *Lev/Man* ratios from the softwood burning emissions (3-10) differ from those of

430 hardwood (15-25) and crop-residues (>40) (Singh et al., 2017; Schmidl et al., 2008a, b; Fu et

431 al., 2008; Engling et al., 2006, 2009; Fine et al., 2001, 2004). We found the *Lev/Man* ratios

432 (Table 2) over the KCOG overlap between seasons and somewhat close to that of hardwood

433 burning emissions in northern China, Mongolia, and the Russian Far East, as corroborated by

434 the backward air mass trajectories and MODIS fire counts (Figures 1 and S1). Besides,

435 *Lev/*K^+ and *Man/Gal* ratios in summer differ from those of other seasons (Table 2). Cheng et

436 al. (2013) have apportioned qualitatively the source contributions of anhydrosugars over a

437 receptor site based on the comparison of *Lev/*K^+ and *Lev/Man* ratios in aerosols to those from

438 various sources profiles compiled from the literature. This approach of using the mass ratios

439 of *Lev/Man* and *Lev/*K^+ has been proven useful for deciphering the difference in BB-derived

440 OA (Bikkina et al., 2019).

441   Here, we adopted this methodology to ascertain the likely contributing sources of

442 anhydrosugars, which are BB tracers from different seasons (Figure 5). This source

443 apportionment relies on the fact that *Lev/*K^+ from the softwood burning (10-1000) is higher

444 than hardwood (1-100) (Fine et al., 2004). In contrast, *Lev/Man* ratios for softwood are lower

445 than those of hardwood burning (10-100) (Fine et al., 2004). Likewise, the *Lev/Man* and

446   *Lev*/K$^+$ ratios from grasses and crop-residues are 10-100 and 0.01-1.0, respectively (Bikkina

447   et al., 2019). On a similar note, the *Lev*/K$^+$ ratios from the burning of pine needles (0.1-1.0)

448   somewhat overlap with hardwood burning emissions but are characterized by distinct

449   *Lev/Man* ratios (Bikkina et al., 2019). The burning of dead leaves (duff) showed higher

450   *Lev*/K$^+$ than pine needles and grasses, but their *Lev/Man* is on the lower side than the former

451   biomass type and the softwood burning emissions. However, *Lev* is more susceptible to

452   degradation by ==photooxidation with OH radicals during atmospheric transport (half-life: <2.2

453   days) (Hennigan et al., 2010) and, this would cause lower abundances of this anhydrosugar.==

454   Hence, the hardwood *Lev*/K$^+$ ratios could slightly shift downwards. Therefore, caution is

455   required while interpreting the ambient data from a receptor site (Bikkina et al., 2019).

456   Overlapping the seasonal data on this scatter plot of *Lev*/K$^+$ versus *Lev/Man* (Figure 5)

457   clearly revealed a mixed contribution of burning of hardwood and crop-residue in the East

458   Asian outflow. ==It should be noted that the photooxidation process during atmospheric

459   transport is also applicable for low concentrations and poor correlations of other primary

460   saccharides.==
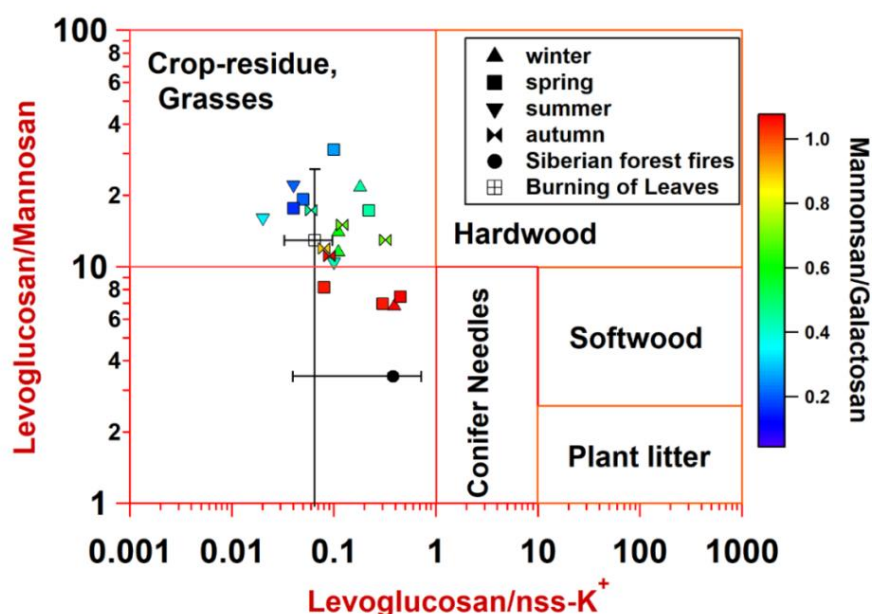
Figure 5. Scatter plot of levoglucosan/K$^+$ versus levoglucosan/mannosan ratios in TSP collected over Gosan during April 2013-April 2014. The data for Siberian forest fires and burning leaves were adopted from Sullivan et al. (2008).

475   The correlation coefficients and diagnostic ratios of BSOA tracers specify their source

476   origin or formation pathway. ==Nevertheless, atmospheric stability or reactivity of BSOA==

477   ==tracers through the photooxidation during long-range transport may bias the correlation==

478   ==coefficients in Gosan aerosols.== 2-MGA showed significant correlation with 2-MTs ($r = 0.79$,

479    $p<0.01$) and C_5-alkene triols ($r = 0.50$, $p<0.05$) (Figure 6a-b), suggesting their similar

480   formation pathway or common sources of isoprene SOA tracers. However, a poor correlation

481   coefficient between 2-MTs and C_5-alkene triols ($r = 0.33$, $p = 0.13$) (Figure 6c) indicates their

482   different formation process over the Gosan atmosphere. Wang et al. (2005) documented that

483   polyols are formed from isoprene through diepoxy derivatives, which further convert into 2-

484   MTs by acid-catalyzed hydrolysis. On the other hand, C_5-alkene triols are produced from the

485   precursor of hydroxyperoxy radicals that are initially derived from isoprene through

486   rearrangement reactions (Surratt et al., 2006). It can be noted that the formation mechanisms

487   of 2-MGA and 2-MTs are different while depending on the NO_x concentrations (Surratt et al.,

488   2010). Thus, the ratio of 2-MGA/2-MTs attributes to the influence of NO_x on isoprene SOA

489   formation. We found a low ratio of 2-MGA/2-MTs (0.67) (Figure S5a, Table 2) in summer,

490   implying enhancement of 2-MTs formation over the open ocean due to the low-NO_x

491   environment in the ocean atmosphere. On the contrary, 2-MGA/2-MTs ratios for other

492   seasons were >1.0 (Figure S5a, Table 2), indicating an elevated formation of 2-MGA through

493   continental high NO_x condition, which is consistent with air masses back trajectory.

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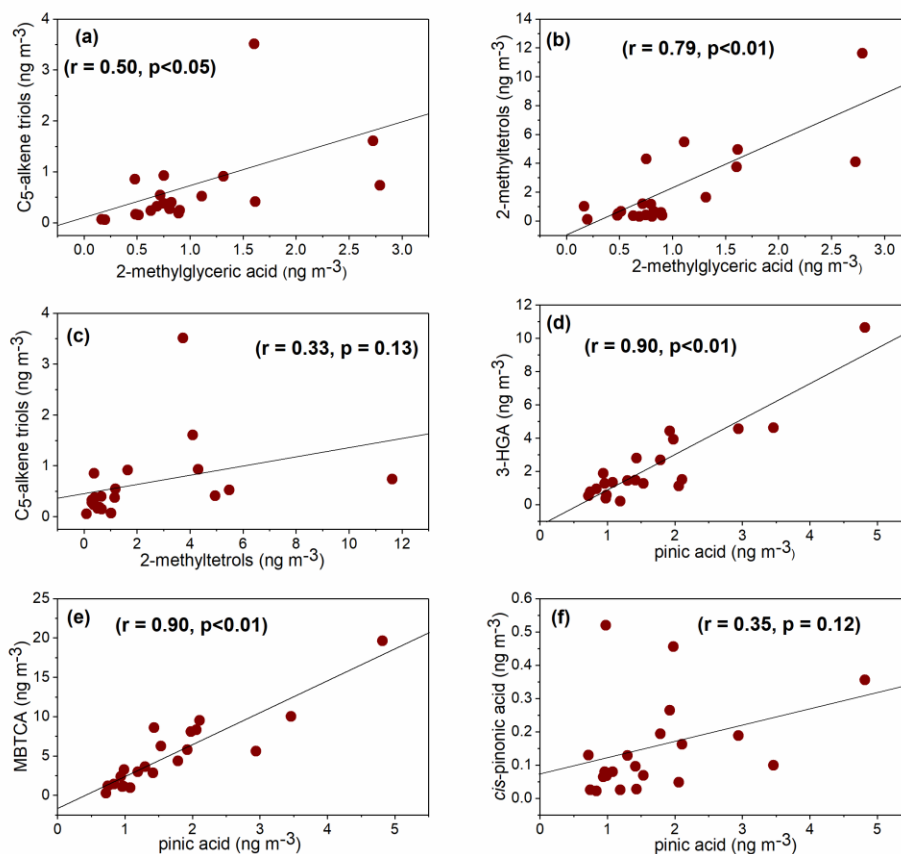
Figure 6. Pearson linear correlation coefficient analysis of BSOA tracers in Gosan TSP aerosols during April 2013-April 2014.

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Cis-pinonic acid showed a weak correlation with pinic acid (r = 0.35, p = 0.12) (Figure 6f), suggesting that different atmospheric reactivity of cis-pinonic/pinic acids during transport would cause such poor correlation. In contrast, pinic acid exhibited a strong positive linear correlation with 3-HGA (r = 0.90, p<0.01) and MBTCA (r 0.90, p<0.01) (Figure 6d-e), implying their similar sources. It should be noted that the formation processes of pinic acid, 3-HGA, and MBTCA are different because pinic acid is a first-generation product, and 3-HGA and MBTCA are high-generation products (Claeys et al., 2007; Müller et al., 2012; Szmigielski et al., 2007). The ratio of *cis*-pinonic acid + pinic acid to MBTCA (P/M) is used to evaluate the aging of monoterpene SOA.

A low P/M ratio suggests the transformation of *cis*-pinonic and pinic acids to MBTCA and thus relatively aged monoterpene-SOA, whereas a high ratio reflects relatively fresh monoterpene-SOA (Gómez-González et al., 2012; Ding et al., 2014). Gómez-González et al. (2012) reported aged monoterpene-SOA (P/M = 0.84) from a Belgian forest site while fresh chamber-produced α-pinene-SOA tracers showed P/M ratios of 1.51 to 3.21 (Offenberg

513 et al., 2007). The average ratio of P/M in this study showed 0.62 with the low value in
514 summer (Figure S5b, Table 2), which is lower than those of Guangzhou (fresh monoterpene-
515 SOA; 28.9) while the air masses originated from southern China (Ding et al., 2014). This
516 observation indicates that monoterpenes SOA have undergone substantial aging during
517 transport to Gosan, particularly in summer when extensive photochemical oxidation occurred
518 due to the high temperature and intense solar radiation.

3.5. Source apportionment - Positive Matrix Factorization (PMF) analysis

520 We used the positive matrix factorization (PMF) analysis of airborne sugar compounds and
521 BSOA tracers to assess their sources over Gosan. Five-factor profiles were chosen that could
522 best explain the data (Figure 7). In factor 1, we found higher loadings of sucrose (88%),
523 fructose (57%), and glucose (40%). Sucrose is a well-known tracer for airborne pollen as
524 these types of biogenic sources also contain significant levels of glucose and fructose; we
525 attribute this factor to contribution from "pollen". Likewise, factor 2 has higher loadings of
526 C_5-alkene triols (54%), 2-MGA (38%), *cis*-pinonic acid (34%), pinic acid (33%), and 3-HGA
527 (33%). These SOA tracers are formed by the photochemical oxidation of BVOCs (e.g.,
528 isoprene and monoterpene), which are emitted from terrestrial vegetation and oceanic
529 phytoplankton. Therefore, we attribute factor 2 to biogenic secondary oxidation products.
530 Factor 3 was abundantly loaded by non-sea-salt fraction of calcium (nss-Ca^{2+}), implying that
531 the component is associated with soil dust as nss-Ca^{2+} is a specific tracer of Earth surface soil
532 (Athanasopoulou et al., 2010; Brahney et al., 2013). It should be noted that significant
533 loadings were also observed for trehalose (39%), glucose (35%), and fructose (35%) in factor
534 3, indicating their association with soil microbes.

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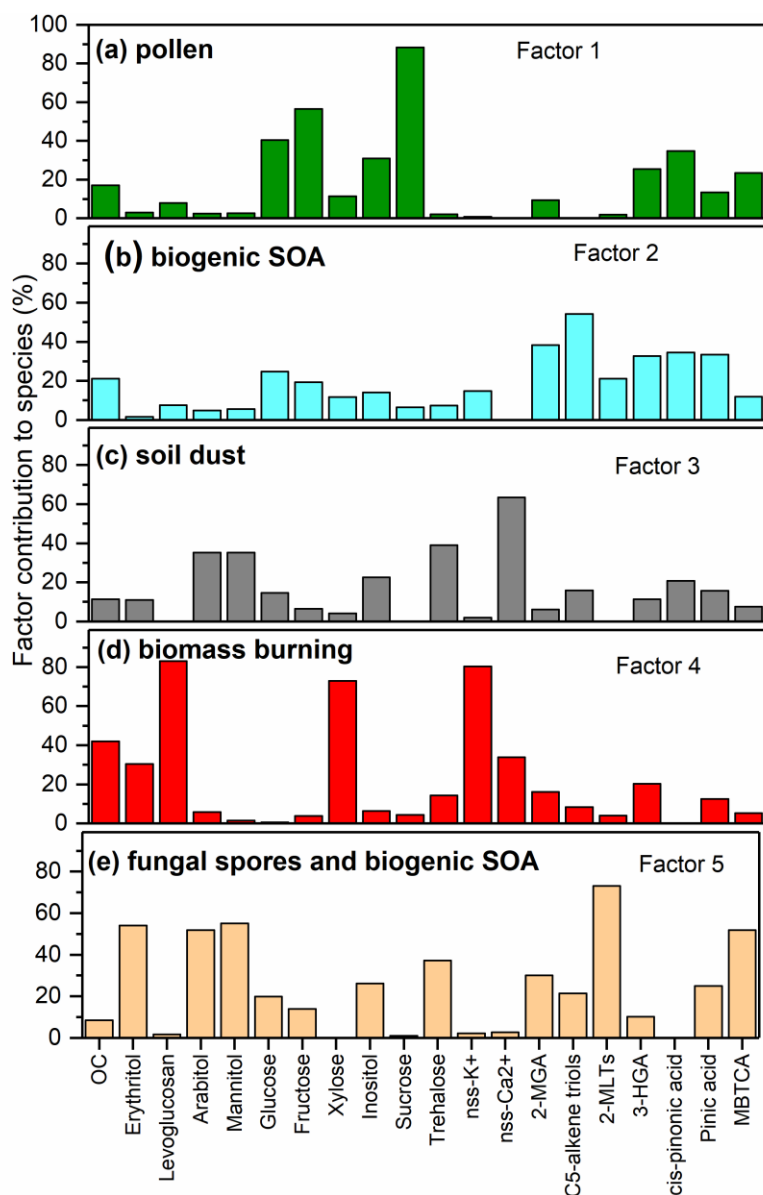
Figure 7. Positive Matrix Factorization (PMF)- based Source profiles resolved for the measured primary saccharides in TSP collected over Gosan during April 2013-April 2014.

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We found high loadings of levoglucosan (83%), nss-K$^+$ (80%), and xylose (73%) in factor 4. Such high contributions of levoglucosan and K$^+$ (hemicellulose/cellulose pyrolysis tracers) and xylose (wood sugar) are typical of wood burning emissions. We, therefore, ascribe this factor to the influence of BB emissions in East Asia over Gosan. Factor 5 is dominated by 2-MTs (73%), MBTCA (53%), mannitol (55%), erythritol (54%), and arabitol (52%). 2-MTs and MBTCA are BSOA tracers, which are produced by the photooxidation of isoprene and monoterpene, respectively. In contrast, arabitol, mannitol, and erythritol are typical tracers of airborne fungal spores (Lewis and Smith, 1967; Bauer et al., 2008). Thus,

547   factor 5 is associated with mixed sources of 'fungal spores' and 'biogenic secondary

548   oxidation products'. PMF results were further utilized to calculate the relative contributions

549   from various sources to OC over Gosan (Figure S6). BB was the dominant source of OC over

550   Gosan (41.9%), followed by BSOA (21.1%), pollen (17.1%), and soil dust (11.4%).

551   **3.6. Relative abundances in WSOC and OC**

552   Levoglucosan is the most abundant anhydrosugar, contributing 0.05-1.54% of WSOC and

553   0.03-1.02% of OC. Likewise, sucrose, glucose, and fructose were more abundant primary

554   sugars, contributing 0.01-2.83%, 0.03-1.22%, and 0.02-0.74% of WSOC, respectively.

555   Contributions of the three primary sugars varied from 0.05% to 3.41% of OC. Arabitol and

556   mannitol are the most abundant sugar alcohols, whose contribution to WSOC and OC ranged

557   from 0.02% to 0.93% and 0.01% to 0.85%, respectively. Figure 8 depicts the contribution of

558   sugar compounds to WSOC and OC in TSP collected over Gosan during the study period.

559   We also compared the atmospheric abundances of sugar compounds from Gosan with the

560   literature data (Table 3). This comparison revealed the less influence of BB tracer compounds

561   (i.e., anhydrosugar levels) over Gosan, a factor of 5-10 times lower than those reported for

562   the BB-influenced source regions in China and East Asia (Fu et al., 2012b; Kang et al.,

563   2018a; Wang and Kawamura, 2005; Wang et al., 2012). However, the levels of anhydrosugar

564   over Gosan are higher than those observed over the remote Canadian High Arctic site (Fu et

565   al., 2009a). In contrast, Gosan is characterized by high concentrations of primary sugars

566   compared to other remote sampling sites in Table 3. This is because of the overwhelming

567   contribution of primary sugars associated with soil dust particles over Gosan during the East

568   Asian outflow. Such high loadings of primary sugars were observed from other remote island

569   receptor sites in the WNP (Okinawa) during the spring season (Zhu et al., 2015a). Likewise,

570   the concentrations of sugar alcohols from Gosan are similar to those from other receptor sites

571   influenced by the East Asian outflow (Verma et al., 2018; Zhu et al., 2015a).

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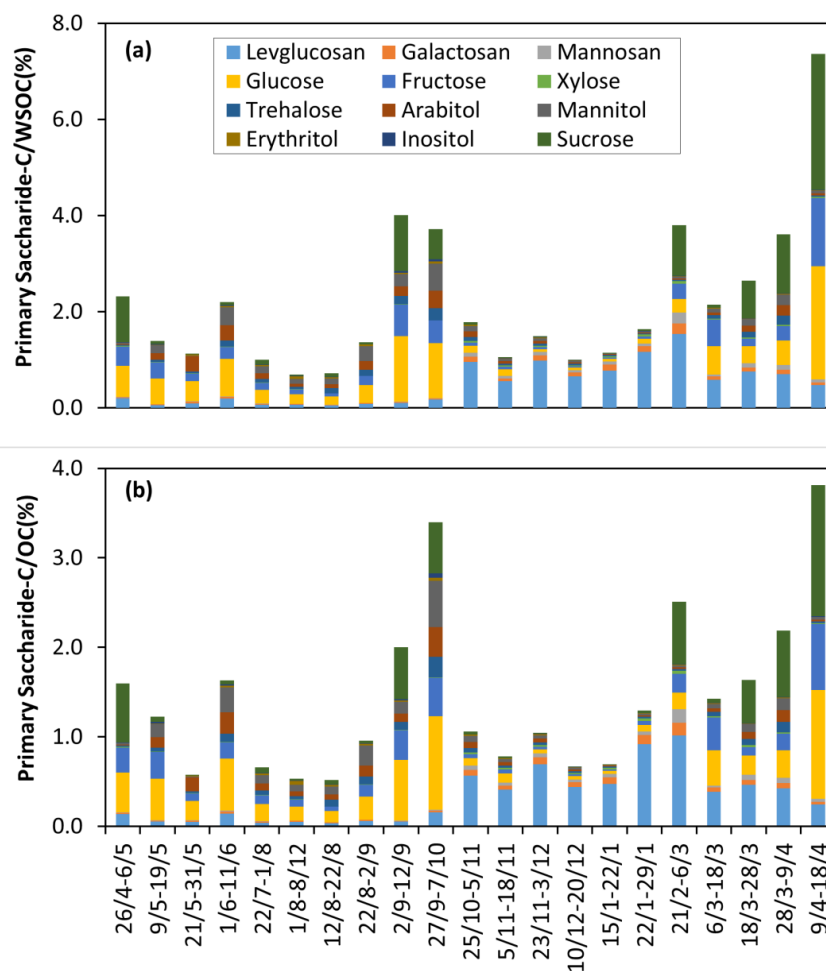
Figure 8. Contribution of primary saccharide-C in (a) WSOC(%) and (b) OC(%) in TSP collected over Gosan during April 2013-April 2014.

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Contributions of isoprene-SOA tracers to ambient OC (0.01-0.40%, avg. 0.09%) and WSOC (0.02-0.57%, 0.13%) were lower than monoterpene-derived SOA (0.04-0.63%, 0.23% for OC and 0.06-0.82%, 0.33% for WSOC). The contributions of isoprene oxidation products to OC and WSOC were found to be highest in summer (0.23% and 0.32%, respectively), followed by fall (0.09% and 0.13%), spring (0.04% and 0.06%), and winter (0.02% and 0.03%). Likewise, the contributions of monoterpene-SOA products to aerosol OC and WSOC exhibited highest value in summer (0.40% and 0.55%, respectively), followed by fall (0.24% and 0.35%), spring (0.18% and 0.27%), and winter (0.10% and 0.14%). We found that the contribution of BSOA products to carbonaceous components was twice in summer (Figure 9, Table 2). This means SOA formation was occurred in summer to a greater extent due to the intensive BVOCs emission with key factors of meteorological parameters

 (higher temperature and radiation), i.e., higher concentrations of ozone, and other oxidizing

 agents (NO$_x$, OH, etc.).

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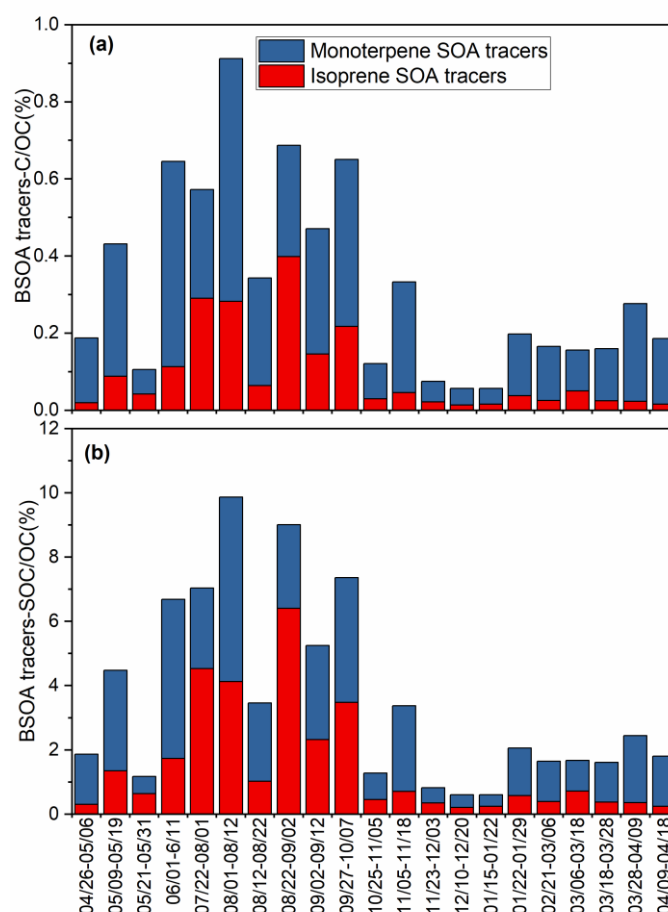
Figure 9. Contribution of (a) isoprene- and monoterpene SOA tracers-C in ambient OC(%) and (b) isoprene- and monoterpene SOA tracers-SOC in ambient OC(%) in Gosan aerosol samples during April 2013-April 2014.

598

We estimated secondary organic carbon (SOC) derived from isoprene and monoterpenes, using the measured values of BSOA tracers and following the SOA tracer-based method first proposed by Kleindienst et al. (2007). A summary of the estimated SOC is provided in Table 2. The contribution of isoprene to SOC was calculated 2.26 to 97.4 ngC m^{-3} (avg. 23.7 ngC m^{-3}), accounting for 1.45% of OC and 35.5% of total BSOC with the predominance in summer (3.56% and 46.6% for OC and SOC, respectively). The estimation of monoterpene SOA to SOC (avg. 40.1 ngC m^{-3}) was observed around two times higher than isoprene (Table 2). Interestingly, the contribution of monoterpene-derived SOC to ambient

607 OC (3.65%) was dominant in summer, but monoterpene SOC to total SOC (72.1%) was most

608 abundant in spring (Figure 9b). The seasonal distributions of biogenic SOC (Table 2) implied

609 that a substantial amount of SOC was formed from monoterpenes in spring. The estimated

610 biogenic SOC at the KCOG is almost one order of magnitude lower than those from other

611 continental sites in China urban areas (e.g., Pearl River Delta: 446 ngC m^{-3}) (Ding et al.,

612 2012). However, the estimated biogenic SOC load from the KCOG is much higher than that

613 reported from a remote site in the Canadian High Arctic (Alert: 9.4 ngC m^{-3}) (Fu et al.,

614 2009b) and comparable with over the East China Sea (Kang et al., 2018b).

615 It should be noted that concentrations of SOA tracers cannot always provide the

616 actual contribution of the biogenic source to ambient organic aerosol mass. For example,

617 loadings of monoterpene-SOA tracers were lower in sample KOS999 (28 March - 9 April

618 2014) (3.02 ng m^{-3}) compared to sample KOS1000 (9 - 18 April 2014) (14.4 ng m^{-3}), whereas

619 the estimated contribution of SOC to ambient OC showed an opposite trend (KOS999:

620 2.08%; KOS1000: 1.56%). This result demonstrates that the estimation of SOC is an

621 important factor in evaluating the contribution of BSOA to organic aerosol mass. We

622 calculated biogenic OC using radiocarbon (^{14}C) data following the method proposed by

623 Szidat et al. (2006). Biogenic OC showed poor correlation with biogenic SOC (r = 0.36, p =

624 0.09) but significant linear relationship with primary sugars (i.e., glucose, fructose and

625 sucrose) (r = 0.54, p<0.5), suggesting that primary bioaerosols from plant-derived airborne

626 pollen dictate on biogenic OC over Gosan.

627 **3.7. Significance of fossil fuel as a source for levoglucosan**

628 The ambient levoglucosan (*Lev*) levels showed a significant linear relationship with the

629 OC$_{fossil}$, suggesting the fossil source contribution of this molecular marker (Figure 10a).

630 However, such a significant correlation was not evident between OC$_{fossil}$ and other major

631 sugar compounds. Until recently, *Lev* has been thought to originate primarily from the

632 hemicellulose/cellulose pyrolysis of vegetation and, hence, can be employed as a powerful

633 tracer for biomass smoke particles (Fraser and Lakshmanan, 2000; Simoneit et al., 1999).

634 Nevertheless, residential coals (*e.g.,* lignite and bituminous coal) have been shown to contain

635 high concentrations of '*Lev*' but also emit traces of *Man and Gal* (Kourtchev et al., 2011;

636 Fabbri et al., 2008). Recently, Yan et al. (2018) found a significant linear relationship

637 between the ^{14}C-based fossil fraction of WSOC and *Lev*-C in the aerosols generated from

638 coal combustion and the ambient aerosol samples. Therefore, the prevailing linear

639 relationship between OC$_{fossil}$ and *Lev*-C in Gosan samples (Figure 10a) is likely due to a

640 common source contribution from coal combustion in East Asia.

641
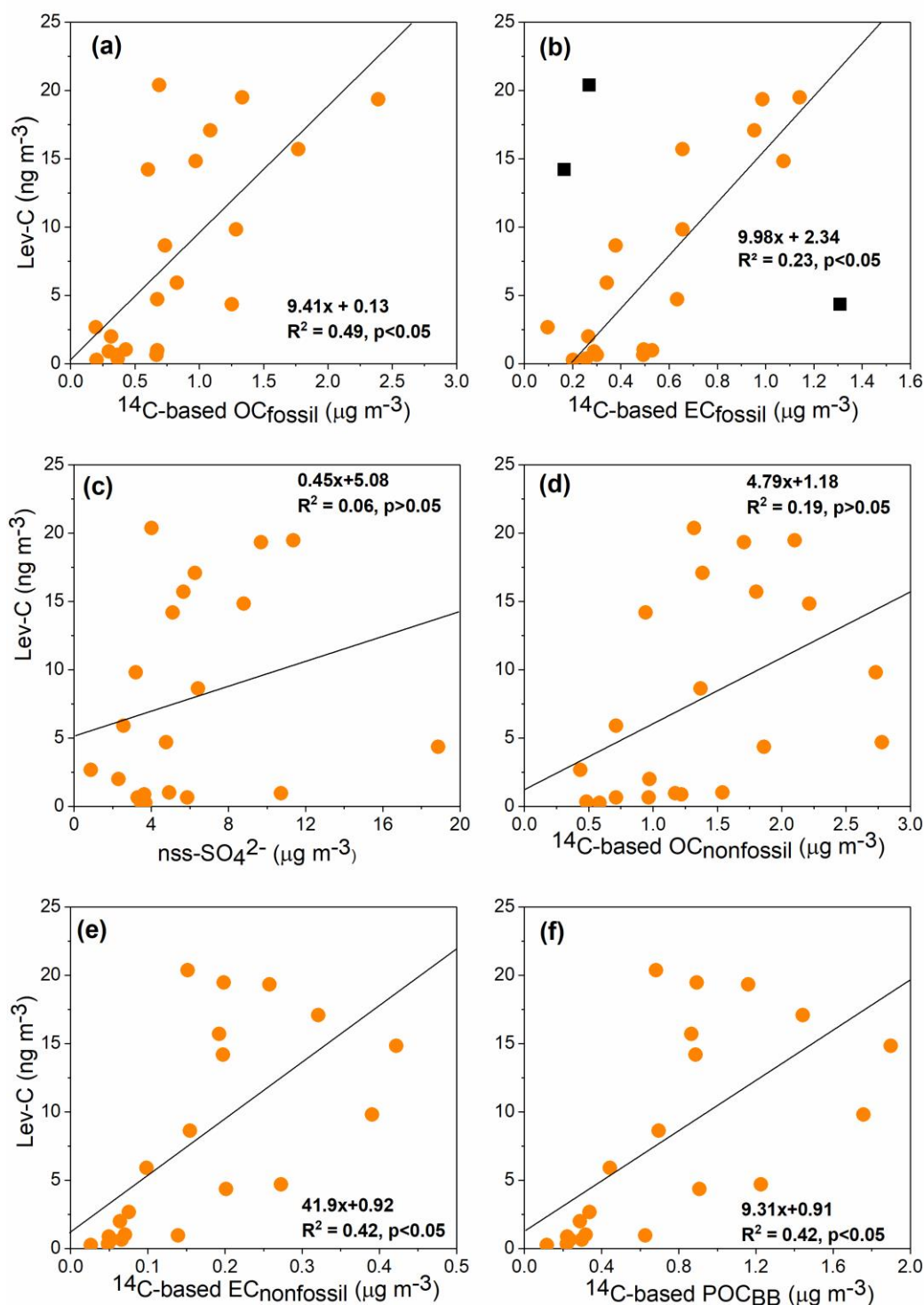
Figure 10. Linear regression analysis between levoglucosan in terms of their carbon content (*Lev*-C) and ^{14}C-based mass concentrations of (a) organic carbon and (b) elemental carbon of fossil origin (OC_{fossil} and EC_{fossil}, respectively), (c) nss-SO_4^{2-}, (d) nonfossil derived organic carbon ($OC_{nonfossil}$), (e) nonfossil derived elemental carbon ($EC_{nonfossil}$), and (f) biomass burning derived primary OC (POC_{BB}) in TSP collected over Gosan during April 2013-April 2014. In panel (b), the squares represent three outliers (i.e., samples with rather high and low *Lev*/EC ratios; please see text for more details).

649 The slope of the linear regression between *Lev-C* and OC_{fossil} (0.0094; Figure 10a) is

650 higher than those documented for the coal combustion source in China (~0.004±0.007) (Yan

651 et al., 2018). Moreover, *Lev-C* moderately correlated with the EC_{fossil} with the regression

652 slope (~0.01) in Gosan samples (Figure 10b), being comparable to that observed for the coal

653 combustion in China (0.044±0.076) (Yan et al., 2018). It should be noted that excluding the

654 three outliers as shown in Figure 10b (black square), *Lev-C* showed a stronger correlation

655 with EC_{fossil} (R^2 = 0.74, p < 0.05). Of these, two outliers in winter (KOS995: 22-29 January

656 2014; KOS996: 21 February - 3 March 2014) have higher *Lev*-C levels over that of EC_{fossil},

657 when air mass trajectories showed the impact of BB emissions in the North China Plain. In

658 contrast, the third outlier in summer (KOS979: 1-11 Jun'2013) has a lower *Lev*-C/EC_{fossil},

659 while air parcels transported from nearby cities in China, Korea, and Japan, thus, have more

660 contribution from vehicular emissions. Overall, both the regression slopes are, thus, the

661 representative nature of *Lev*-C/OC_{fossil} and *Lev*-C/EC_{fossil} in the East Asian outflow. *Lev*-C and

662 nss-SO_4^{2-} exhibited a poor correlation (Figure 10c), although both were transported from East

663 Asia.

664 *Lev*-C exhibited a rather weak correlation with $OC_{nonfossil}$ (R^2 = 0.19) than that with

665 $EC_{nonfossil}$ (R^2 = 0.42) over Gosan during the study period (Figure 10d-e). This could be likely

666 because $OC_{nonfossil}$ has contributions from the BB and the secondary formation process or the

667 primary biogenic sources. The contribution of primary OC generated from BB (POC_{BB}) to

668 $OC_{nonfossil}$ was taken from Zhang et al. (2016). In their study, the ^{14}C-based $EC_{nonfossil}$ levels

669 were scaled by a factor to constrain the POC_{BB} (Zhang et al., 2016). Here the conversion

670 factor is '4.5' (range: 3-10), which is a median value representing the primary OC/EC ratio

671 from BB emissions (($POC/EC)_{BB}$).

672     $POC_{BB} = EC_{nonfossil} \times (POC/EC)_{BB}$    (7)

673 *Lev*-C showed a somewhat improved linear correlation with POC_{BB} than with the $OC_{nonfossil}$

674 (Figure 10f). It is apparent from Figure 10 that the regression slopes are comparable,

675 indicating their contribution to *Lev* from both coal combustion and BB emissions over Gosan.

676 The prevailing weak linear relationship (moderate correlation) of *Lev* with nonfossil and

677 fossil carbon fractions is likely being the result of photo-degradation of *Lev* during

678 atmospheric transport. This result would mean that the higher atmospheric abundance of *Lev*

679 and its pronounced linear relationships with the nonfossil and fossil carbon fractions implies

680 a much stronger impact of both source emissions in East Asia during the continental outflow

681 in winter and spring.

682   Overall, we present a new finding on the contribution of coal combustion sources in East
683   Asia in controlling the atmospheric levels of *Lev* apart from the traditional biomass/biofuel
684   burning emissions. This is based on the prevailing linear relationship between the
685   radiocarbon based nonfossil-EC and *Lev* in the year-round TSP samples collected from the
686   KCOG site in Jeju Island. The Gosan supersite is the best location to understand how the
687   chemical composition of source-emissions from East Asia affects the outflow regions in
688   winter and spring. Recent studies have highlighted the potential contribution of *Lev* from
689   residential coal combustion in China (Yan et al., 2018), with estimated annual emission of
690   ~2.2 Gg of *Lev* from domestic coal combustion (Wu et al., 2021). Given this background
691   information, the prevailing significant linear relationship between *Lev* and nonfossil-EC (P-
692   value < 0.05) over the KCOG clearly emphasizes the need for reconsideration of the previous
693   assessments on the impact of BB in East Asian outflow to the WNP. Additionally, this
694   dataset is further compared with the molecular distributions and relative abundances of
695   organic tracers in the TSP samples collected over Gosan during 2001, a decade ago (Fu et al.,
696   2012). This comparison allows us to better understand the regional changes in the emission
697   sources (*e.g.,* fugitive dust, BB, and fossil-fuel combustion) on a decadal basis.

698   **4. Conclusions**

699   We investigated seasonal variations of primary organic components such as anhydrosugars,
700   primary sugars, and sugar alcohols and biogenic secondary organic aerosol (BSOA) tracers
701   (isoprene- and monoterpene-derived SOA products) in ambient aerosols from Gosan, Jeju
702   Island. Among the detected sugar compounds, levoglucosan was dominant in winter/fall,
703   whereas glucose and sucrose were more abundant in spring/summer. The seasonal trends
704   documented that BB impact is more significant in winter/fall and the primary bioaerosol
705   particles are important in spring/summer. Diagnostic ratios of levoglucosan, galactosan, and
706   mannosan reflect that emissions from BB are mostly dominated by hardwood. The significant
707   linear relationship of sucrose with glucose and fructose suggests their origin from airborne
708   pollen. On a similar note, trehalose showed a significant positive correlation with arabitol,
709   mannitol, and erythritol, implying their contribution from airborne fungal spores and soil
710   microbes over the KCOG.

711   Distributions of biogenic SOA tracers were characterized by a predominance of
712   monoterpene- than isoprene-derived oxidation products in Gosan aerosols. The BSOA tracers
713   were formed in summer to a greater extent, followed by fall/spring and then winter. The low
714   ratio of *cis*-pinonic acid + pinic acid to MBTCA (P/M) demonstrated that monoterpene SOA

was relatively aged over Gosan aerosols. The estimated secondary organic carbon (SOC) with the predominance in summer shows that substantial SOA formation occurred in summer due to favorable meteorological conditions. The backward air mass trajectories and source apportionment studies entirely demonstrated that BB and biogenic SOA contribution significantly dominate the ambient OA mass over KCOG. Interestingly, levoglucosan-C exhibited a significant positive correlation with nonfossil and fossil organic carbon fractions, along with the comparable regression slopes. This result reveals that BB and coal (lignite) combustion both are the prominent source for levoglucosan in the East Asian outflow.

Although there is some evidence that levoglucosan could originate from the combustion of brown coals (*e.g.,* lignite) in China; however, our observations are from the KCOG (receptor site) also hinted at the fossil source contribution of this molecular marker in the regional influx of the East Asian outflow. Therefore, attribution of ambient levoglucosan levels over the WNP to the impact of BB emission may cause large uncertainty.

Data availability

The data used in this paper are available upon request from the corresponding author.

Author contributions

KK and YLZ designed the research. ML collected the aerosol samples. MMH and SB performed the analysis of aerosol samples. MMH wrote the paper under the guidance of YLZ and KK. All authors were actively involved in the discussion of the paper.

Competing interests

The authors declare that they have no conflict of interest.

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Table 1. Concentrations of identified sugar compounds and BSOA tracers (ng m^{-3}) in the atmospheric
aerosol samples from Gosan.

Species	Annual	Summer	Fall	Winter	Spring
	Avg.[a] ± S.D.[b] Min.[c], Max.[d]	Avg. ± S.D. Min., Max.	Avg. ± S.D. Min., Max.	Avg. ± S.D. Min., Max.	Avg. ± S.D. Min., Max.
Anhydrosugars					
Levoglucosan (Lev)	17.6 ± 16.8 0.60, 45.9	2.92 ± 3.89 0.60, 9.81	21.7 ± 19.0 2.30, 43.9	39.2 ± 6.60 32.0, 45.9	12.7 ± 11.6 1.45, 33.4
Mannosan (Man)	1.57 ± 1.82 0.05, 6.74	0.18 ± 0.24 0.05, 0.61	1.69 ± 1.49 0.13, 3.66	3.63 ± 2.28 1.47, 6.74	1.31 ± 1.57 0.08, 4.08
Galactosan (Gal)	2.28 ± 2.10 0.14, 6.78	0.64 ± 0.68 0.14, 1.82	2.45 ± 2.13 0.35, 4.92	5.21 ± 1.64 3.40, 6.78	1.65 ± 1.26 0.50, 3.88
Primary Sugars					
Glucose	18.8 ± 27.1 2.45, 122	13.4 ± 18.2 2.45, 45.6	16.5 ± 15.7 2.68, 33.6	4.74 ± 3.14 2.88, 9.44	32.4 ± 41.1 4.87, 122
Fructose	10.3 ± 15.9 0.97, 74.0	4.90 ± 5.15 0.97, 13.7	7.48 ± 6.99 1.71, 16.2	3.82 ± 4.45 1.56, 10.5	19.8 ± 25.0 2.69, 74.0
Sucrose	16.1 ± 32.2 0.26, 140	1.46 ± 1.05 0.68, 3.28	9.74 ± 12.1 0.76, 27.2	8.87 ± 16.3 0.42, 33.3	35.1 ± 50.5 0.26, 140
Trehalose	2.42 ± 1.97 0.65, 7.03	2.72 ± 2.53 0.97, 6.98	3.71 ± 2.29 1.18, 7.03	1.21 ± 0.42 0.72, 1.63	1.98 ± 1.55 0.65, 5.33
Xylose	0.81 ± 0.65 0.04, 2.03	0.23 ± 0.23 0.04, 0.63	0.86 ± 0.68 0.14, 1.70	1.59 ± 0.37 1.21, 2.03	0.74 ± 0.55 0.16, 1.68
Sugar alcohols					
Arabitol	3.96 ± 4.24 0.47, 18.7	5.64 ± 7.46 1.20, 18.7	5.27 ± 3.51 2.27, 10.9	1.06 ± 0.60 0.47, 1.91	3.47 ± 2.19 1.18, 6.30
Mannitol	4.61 ± 5.54 0.25, 22.0	7.39 ± 8.65 1.71, 22.0	6.64 ± 6.03 1.69, 16.7	0.99 ± 0.45 0.55, 1.60	3.24 ± 2.67 0.25, 7.03
Erythritol	0.62 ± 0.43 0.12, 1.52	0.92 ± 0.53 0.42, 1.52	0.93 ± 0.33 0.55, 1.27	0.42 ± 0.27 0.16, 0.80	0.30 ± 0.12 0.12, 0.48
Inositol	0.34 ± 0.39 0.04, 1.53	0.29 ± 0.41 0.08, 1.03	0.56 ± 0.60 0.10, 1.53	0.13 ± 0.07 0.08, 0.23	0.35 ± 0.28 0.04, 0.73
Isoprene SOA tracers					
2-MGA	0.99 ± 0.70 0.17, 2.79	1.61 ± 1.17 0.17, 2.79	0.95 ± 0.43 0.51, 1.61	0.67 ± 0.14 0.49, 0.81	0.76 ± 0.35 0.20, 1.32
Σ2-MLTs	1.04 ± 1.40 0.05, 5.81	2.48 ± 1.98 0.51, 5.81	1.34 ± 1.16 0.33, 2.74	0.20 ± 0.05 0.15, 0.26	0.29 ± 0.25 0.05, 0.82
ΣC5-alkene triols	0.20 ± 0.25 0.02, 1.17	0.46 ± 0.44 0.02, 1.17	0.13 ± 0.05 0.05, 0.18	0.09 ± 0.03 0.05, 0.13	0.14 ± 0.11 0.02, 0.30
Monoterpene SOA tracers					
cis-pinonic acid	0.15 ± 0.14 0.02, 0.52	0.12 ± 0.13 0.03, 0.36	0.08 ± 0.06 0.02, 0.16	0.07 ± 0.03 0.02, 0.10	0.26 ± 0.17 0.08, 0.52
pinic acid	1.67 ± 1.01 0.72, 4.81	2.40 ± 1.67 0.99, 4.81	1.53 ± 0.57 0.75, 2.11	1.07 ± 0.25 0.84, 1.42	1.61 ± 0.78 0.72, 2.94
3-HGA	2.30 ± 2.38 0.19, 10.6	3.46 ± 4.39 0.19, 10.6	1.52 ± 0.77 0.76, 2.79	1.40 ± 0.39 0.94, 1.88	2.54 ± 1.83 0.38, 4.57
MBTCA	5.11 ± 4.54 0.29, 19.6	8.44 ± 6.88 3.00, 19.6	6.24 ± 3.64 1.17, 9.49	1.90 ± 0.85 0.97, 2.83	3.77 ± 2.96 0.29, 8.08

[a]Average, [b]Standard deviation, [c]Minimum, [d]Maximum. 2-MGA: 2-methylglyceric acid, 2-MLTs: 2-methyltetrols, 3-HGA: 3-hydroxyglutaric acid, MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid.

Table 2. Statistical summary of diagnostic ratios and carbonaceous components contribution in Gosan

aerosols.

Species	Annual	Summer	Fall	Winter	Spring
	Avg.[a] ± S.D.[b] Min.[c], Max.[d]	Avg. ± S.D. Min., Max.	Avg. ± S.D. Min., Max.	Avg. ± S.D. Min., Max.	Avg. ± S.D. Min., Max.
Diagnostic ratios					
Lev/Man	15.1 ± 6.76 6.81, 31.3	17.1 ± 8.21 8.58, 28.4	13.7 ± 2.51 11.1, 17.3	13.5 ± 6.24 6.81, 21.7	15.4 ± 8.76 6.98, 31.3
Man/Gal	0.55 ± 0.32 0.10, 1.07	0.28 ± 0.13 0.10, 0.42	0.64 ± 0.20 0.37, 0.90	0.66 ± 0.27 0.43, 1.05	0.61 ± 0.43 0.16, 1.07
Lev/(Man + Gal)	4.27 ± 1.23 2.18, 6.56	3.12 ± 0.78 2.18, 4.03	5.08 ± 0.32 4.71, 5.51	4.85 ± 1.35 3.49, 6.56	4.17 ± 1.33 2.50, 6.45
Lev/K^+ × 10^{-2}	5.73 ± 5.65 0.65, 23.2	1.00 ± 0.52 0.65, 1.91	3.94 ± 2.51 1.26, 6.30	12.3 ± 7.87 6.42, 23.2	6.65 ± 4.48 1.77, 15.3
Lev/OC × 10^{-2}	0.73 ± 0.66 0.08, 2.29	0.14 ± 0.10 0.08, 0.31	0.84 ± 0.61 0.12, 1.56	1.60 ± 0.67 0.99, 2.29	0.56 ± 0.40 0.11, 1.05
Lev/WSOC × 10^{-2}	1.09 ± 0.97 0.10, 3.46	0.20 ± 0.13 0.10, 0.42	1.25 ± 0.94 0.23, 2.21	2.33 ± 0.90 1.48, 3.46	0.92 ± 0.65 0.13, 1.69
MGA/MLTs	2.18 ± 1.59 0.33, 5.40	0.67 ± 0.43 0.33, 1.33	1.04 ± 0.49 0.41, 1.55	3.60 ± 1.43 1.90, 5.40	3.27 ± 1.17 1.60, 4.75
[e]P/MBTCA	0.62 ± 0.61 0.17, 5.90	3.22 ± 0.62 2.47, 3.89	3.62 ± 1.67 1.52, 5.90	1.68 ± 0.64 0.83, 2.38	1.73 ± 1.07 0.34, 3.32
Carbonaceous components					
Isoprene derived SOC (μgC m^{-3})	23.7 ± 23.9 2.26, 97.4	51.0 ± 32.4 8.08, 97.4	25.9 ± 17.9 8.54, 45.7	8.52 ± 1.07 7.46, 9.87	11.3 ± 6.80 2.26, 24.9
Isoprene SOC to OC (%)	1.45 ± 1.74 0.21, 6.40	3.56 ± 2.18 1.03, 6.40	1.46 ± 1.38 0.35, 3.48	0.35 ± 0.17 0.21, 0.57	0.57 ± 0.38 0.24, 1.35
Isoprene SOC to total SOC (%)	35.5 ± 15.5 13.5, 71.1	46.6 ± 20.3 26.0, 71.1	38.1 ± 10.4 21.1, 47.3	31.6 ± 7.05 24.0, 39.7	27.9 ± 15.5 13.5, 54.0
Monoterpene SOC (μgC m^{-3})	40.1 ± 33.3 7.18, 154	62.7 ± 56.5 19.2, 154	40.7 ± 20.0 11.8, 57.7	19.3 ± 5.61 14.0, 25.2	35.5 ± 23.5 7.18, 62.7
Monoterpene SOC to OC (%)	2.0 ± 1.47 0.37, 5.74	3.65 ± 1.58 2.44, 5.74	2.15 ± 1.45 0.48, 3.88	0.87 ± 0.58 0.37, 1.48	1.58 ± 0.84 0.54, 3.13
Monoterpene SOC to total SOC (%)	64.5 ± 15.5 28.9, 86.5	53.4 ± 20.3 28.9, 74.0	61.9 ± 10.4 52.7, 78.9	68.4 ± 7.05 60.3, 76.1	72.1 ± 15.5 46.0, 86.5

[e]P: *cis*-pinonic acid + pinic acid

Table 3. Comparisons of the ==mean== concentration (ng m^{-3}) of anhydrosugars, sugar, and sugar alcohols in Gosan aerosols with those from different sites around the world.

Sampling sites	==Sampling type==	==Sampling time==	Anhydro-sugars	Primary sugars	Sugar alcohols	References
Gosan, South Korea	**TSP**	Summer	**3.74**	**22.8**	**14.3**	**This study**
		Fall	**25.9**	**38.3**	**13.4**	
		Winter	**48.0**	**20.2**	**2.60**	
		Spring	**15.7**	**90.0**	**7.36**	
Chennai, India	PM10	Summer	127	15.5	7.44	Fu et al., 2010b
		Winter	134	11.4	4.81	
Mt. Tai, China	TSP	Summer (June)	224	61.1	125	Fu et al., 2012b
Alert, Canada	TSP	Winter	0.32	1.14	0.25	Fu et al., 2009a
		Spring	0.02	0.18	0.36	
Okinawa, western North Pacific	TSP	Summer	0.93	73.5	62.9	Zhu et al., 2015a, b
		Autumn	2.58	56.0	30.7	
		Winter	6.04	34.4	6.03	
		Spring	3.44	101	31.2	
Chichijima, western North Pacific	TSP	Summer	0.32	32.8	38.6	Verma et al., 2015, 2018
		Autumn	0.85	22.0	35.1	
		Winter	2.40	14.2	3.93	
		Spring	0.94	24.2	15.5	
Mt. Hua, China (Non-dust storm)	PM10	April	57.8	92.5	22.4	Wang et al., 2012
Mt. Hua, China (Dust storm)	PM10	April	44.5	162	25.7	Wang et al., 2012
Nanjing, China	PM2.5	Summer	151 (Lev)	59.3	11.8	Wang and Kawamura, 2005
		Winter	268 (Lev)	42.3	13.4	
Beijing, China	PM2.5	Summer	14.5	6.63	3.31	Kang et al., 2018a
		Autumn	129	17.2	13.7	
		Winter	254	41.5	17.8	
		Spring	81.4	33.9	12.3	
Belgrade, Serbia	TSP	Autumn	425 (Lev)	116	98.4	Zangrando et al., 2016
Maine, USA	PM1	May-October	13.9	28	8.31	Medeiros et al., 2006
Crete, Greece	PM10	Year-round	14.4	32.3	6.53	Theodosi et al., 2018

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Supporting information for

Regional heterogeneities in the emission of airborne primary sugar compounds and biogenic secondary organic aerosols in the East Asian outflow: Evidence for coal combustion as a source of levoglucosan

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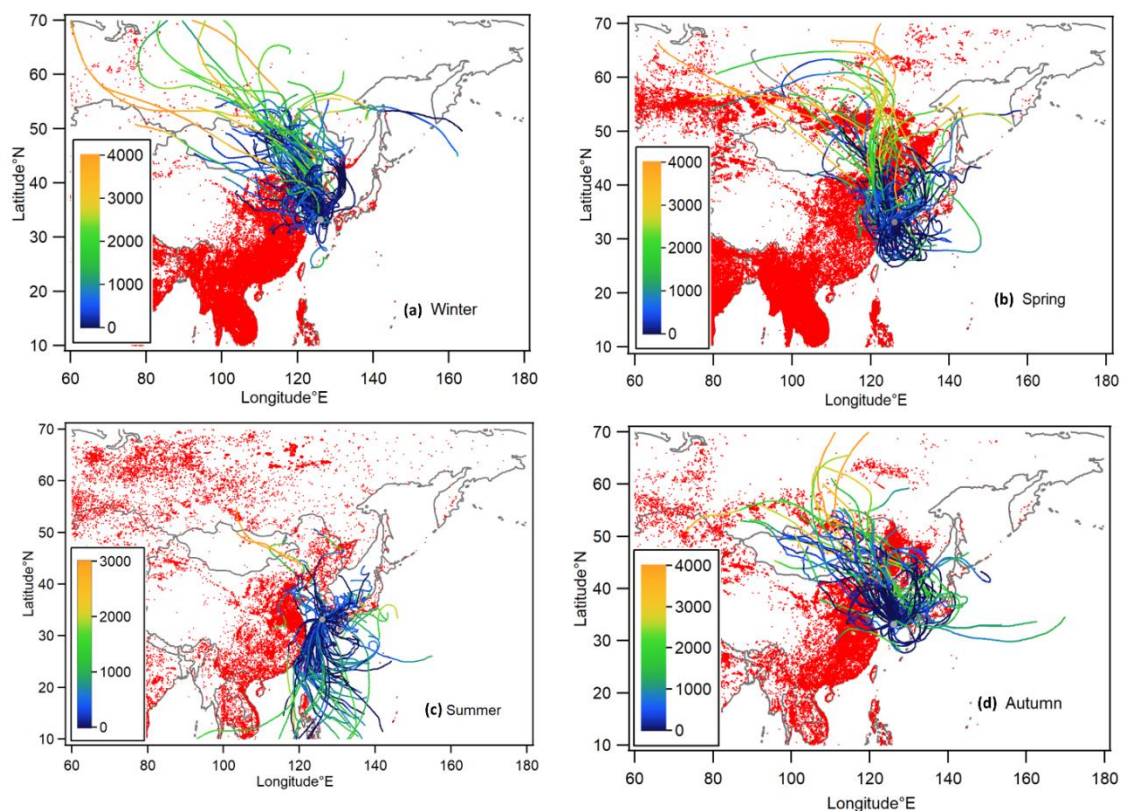
1170   **Figure S1**. HYSPLIT-based backward air mass trajectories as a function of arrival height
1171   (see color bar in each panel) and MODIS-firecounts for the TSP collected over Gosan
1172   according the four seasons, (a) winter, (b) spring, (c) summer, and (d) autumn.

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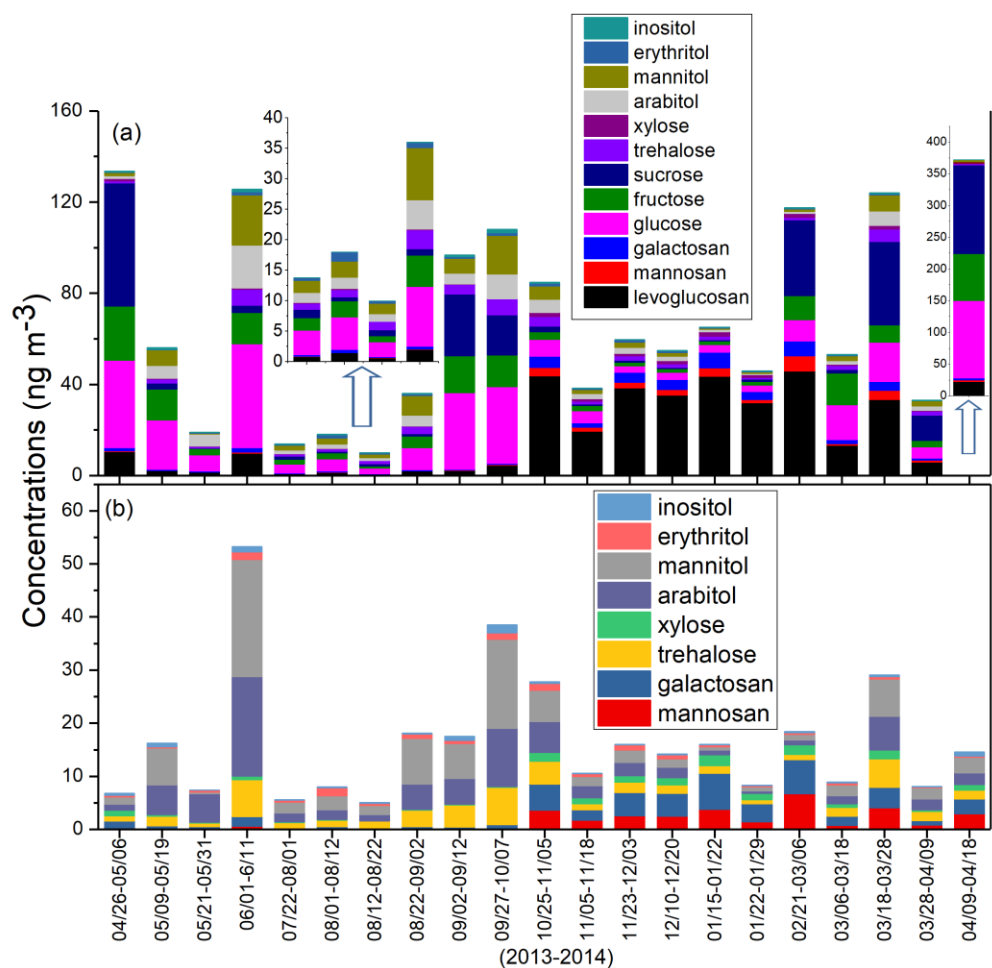
Figure S2. Time series of the concentrations of anhydrosugars, primary sugars, and sugar
alcohols during the period of study in Gosan.

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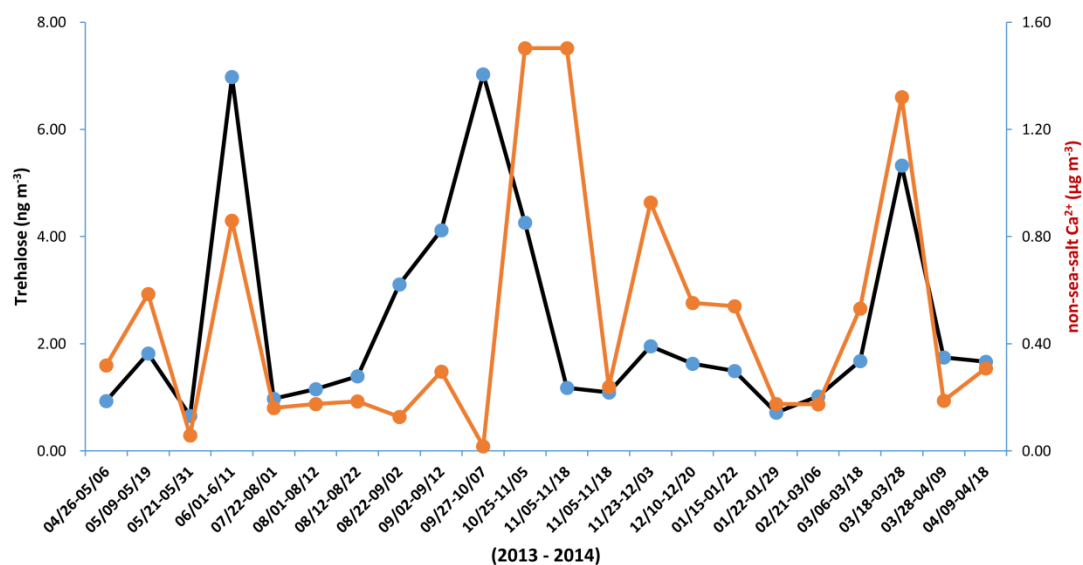
1190 **Figure S3.** Temporal variability of mass concentrations of trehalose and non-sea-salt Ca²⁺ in
1191 TSP collected over Gosan during April 203-April 2014.

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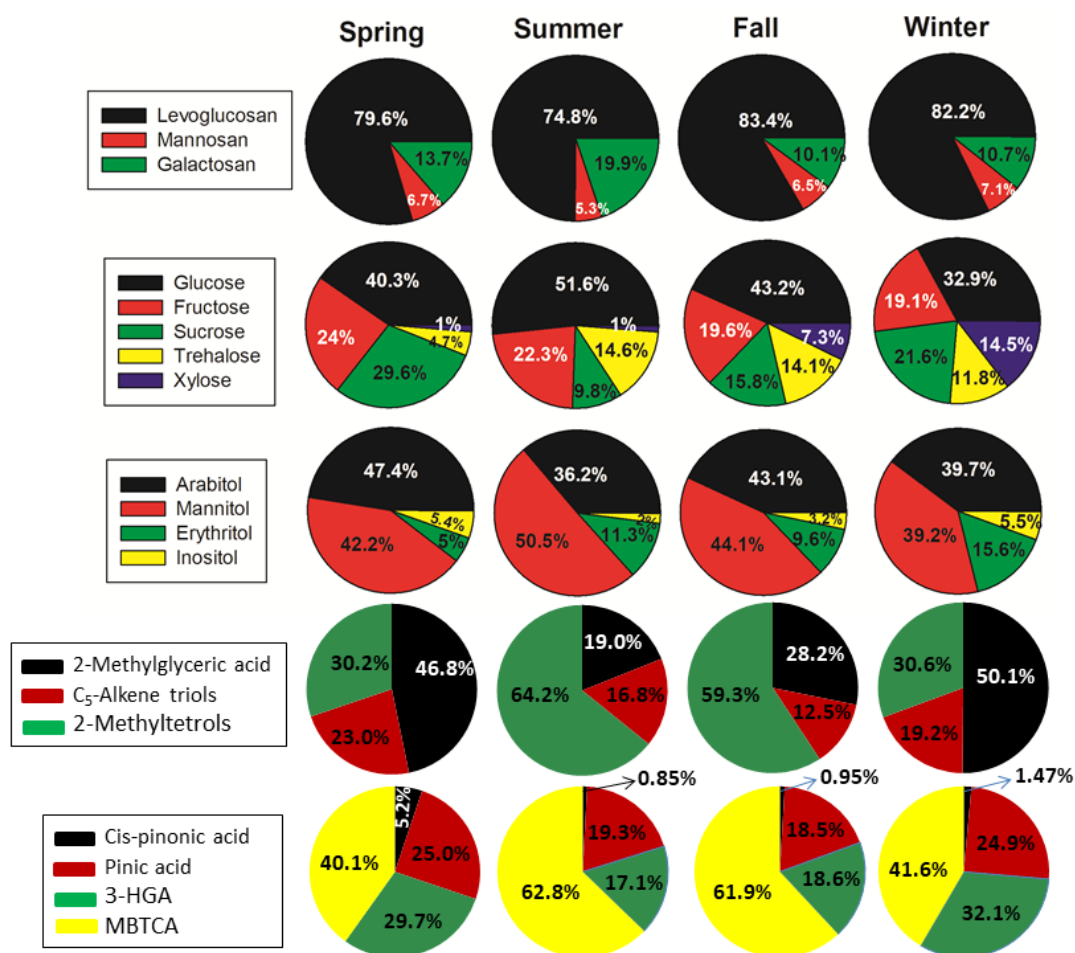
1204 **Figure S4.** Seasonal variability of molecular distributions of anhydrosugars, primary sugars,
1205 sugar alcohols, isoprene SOA tracers and monoterpene SOA tracers in their total mass
1206 concentration of respective group-types in TSP samples collected over Gosan during April
1207 2013-April 2014.

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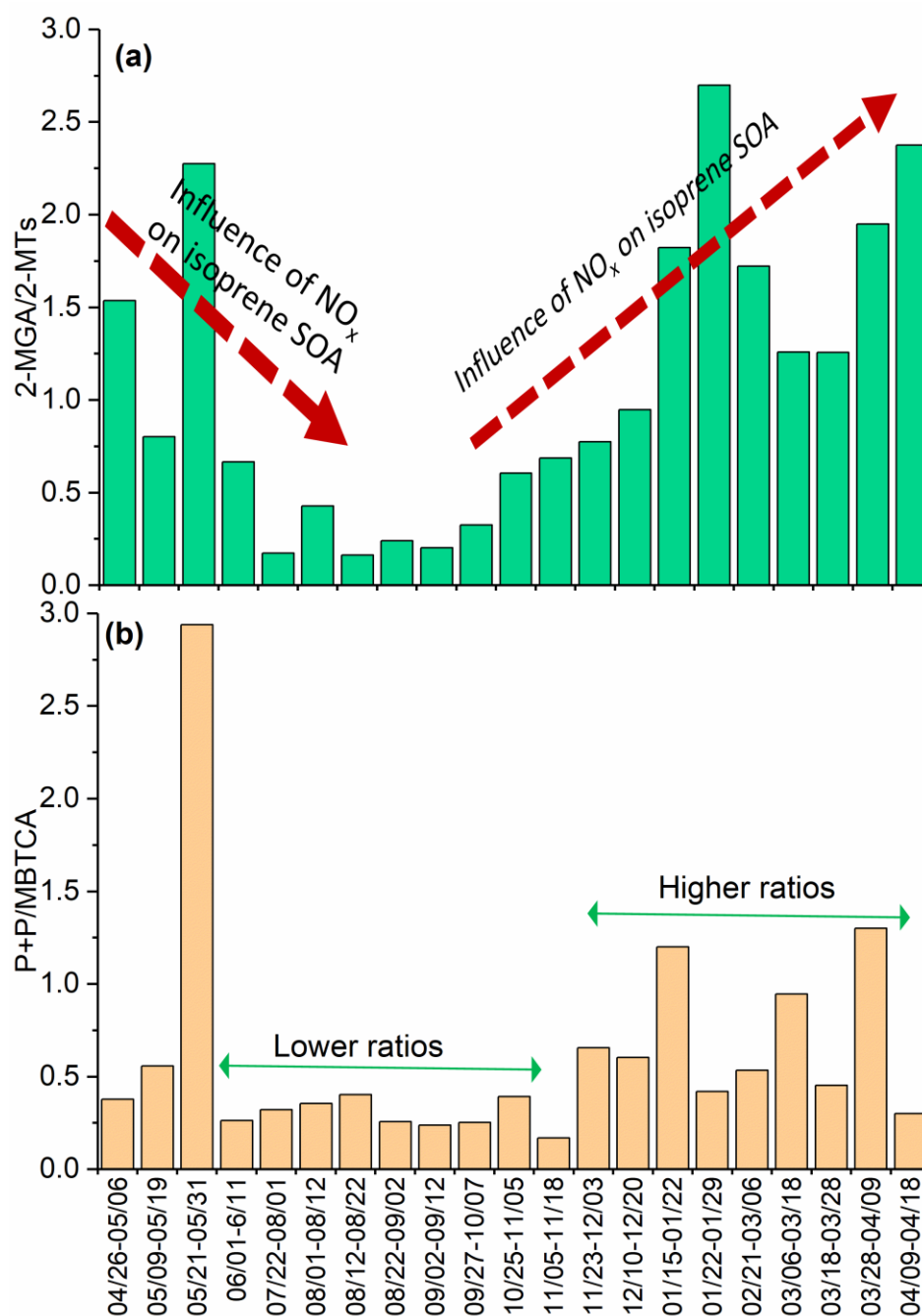
Figure S5. Diagnostic ratios of 2-methylglyceric acid/2-methyltetrols (2-MGA/2-MTs) and
cis-pinonic acid+pinic acid/3-methyl-1,2,3-butanetricarboxylic acid (P+P/MBTCA) in Gosan
TSP samples collected during April 2013-April 2014.

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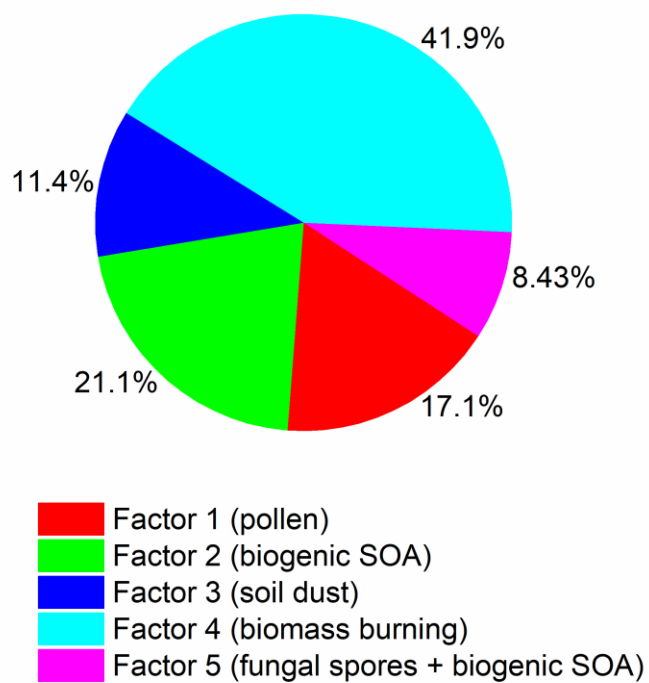
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1228   **Figure S6**. PMF- resolved source contributions to the organic carbon in Gosan aerosols.

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