

1 **Characterization of biogenic primary and secondary**
2 **organic aerosols in the marine atmosphere over the East**
3 **China Sea**

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5 **Mingjie Kang^{1,2,3}, Pingqing Fu^{1,2,4}, Kimitaka Kawamura⁵, Fan Yang², Hongliang**
6 **Zhang⁶, Zhengchen Zang⁷, Hong Ren^{2,8}, Lujie Ren¹, Ye Zhao³, Yele Sun^{2,8}, and**
7 **Zifa Wang^{2,8}**

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9 ¹ Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China

10 ² State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry,
11 Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

12 ³ State Key Laboratory of Water Environment Simulation, School of Environment, Beijing
13 Normal University, Beijing 100875, China

14 ⁴ Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disasters,
15 Nanjing University of Information Science & Technology, Nanjing, 210044, China

16 ⁵ Chubu Institute for Advanced Studies, Chubu University, Kasugai 487-8501, Japan

17 ⁶ Department of Civil and Environmental Engineering, Louisiana State University, Baton
18 Rouge, Louisiana 70803, USA

19 ⁷ Department of Oceanography and Coastal Sciences, Louisiana State University, Baton
20 Rouge, LA 70803, USA

21 ⁸ College of Earth and Planetary Sciences, University of Chinese Academy of Sciences,
22 Beijing 100049, China

23

24 **Correspondence:** Pingqing Fu (fupingqing@tju.edu.cn)

25

26 **Abstract**

27 Molecular composition and abundance of sugars and secondary organic aerosols (SOA) from
28 biogenic sources over the East China Sea were investigated based on gas
29 chromatography/mass spectrometry. Biogenic SOA tracers and sugars exhibit higher levels in
30 the samples affected by continental air masses, demonstrating the terrestrial outflows of
31 organic matter to the East China Sea. Glucose was the dominant sugar species (0.31–209 ng
32 m⁻³, 18.8 ng m⁻³), followed by mannitol – a fungal spore tracer. All sugar compounds show
33 generally higher average concentrations in the nighttime than in the daytime. 3-Methyl-1,2,3-
34 butanetricarboxylic acid, one higher-generation photooxidation tracer of monoterpene SOA,
35 was found to be the most abundant species among measured biogenic SOA markers,
36 suggesting the input of aged organic aerosols through long-range transport. Fungal-spore-
37 derived organic carbon (OC) was the biggest contributor to total OC (0.03–19.8%, 3.1%),
38 followed by sesquiterpene-derived secondary OC (SOC), biomass-burning-derived OC,
39 monoterpene- and isoprene-derived SOC. Larger carbon percentages of biogenic primary OCs
40 and SOCs in total OC presented in the terrestrially influenced aerosols indicate significant
41 contributions of continental aerosols through long-range transport. Positive matrix
42 factorization results illustrate that the secondary nitrate and biogenic SOA, biomass burning,
43 and fungal spores were the main sources of OC in marine aerosols over the East China Sea,
44 again highlighting the importance of Asian continent as a natural emitter of biogenic organic
45 aerosols together with anthropogenic aerosols over the coastal marine atmosphere.

46

47 **1 Introduction**

48 Oceans cover more than 70% of the Earth's surface and marine aerosols contribute
49 significantly to the global aerosol load (O'Dowd et al., 2004), playing an important role in the
50 albedo, atmospheric processes, atmospheric chemistry, climate, and biogeochemical cycling
51 of nutrients (O'Dowd and de Leeuw, 2007; Shi et al., 2011). Such influences depend on the
52 chemical composition and concentrations of marine aerosols. In recent years, significant
53 abundances of organic matter in marine aerosol and their importance to the cloud
54 condensation nuclei (CCN) formation as well as their direct and indirect radiative effects have
55 been reported (Tervahattu et al., 2002; O'Dowd et al., 2004; Facchini et al., 2008;
56 Ovadnevaite et al., 2011a; Ovadnevaite et al., 2011b; Pringle et al., 2010; Bougiatioti et al.,

57 2011; Sciare et al., 2009). However, information about marine organic aerosol remains poor
58 owing to various emission sources, complex formation mechanisms, and limited field
59 measurements regarding their chemical composition and concentrations (O'Dowd and de
60 Leeuw, 2007; Cavalli et al., 2004). Therefore, it is necessary to investigate the loadings,
61 molecular compositions and sources of marine organic aerosols, especially in coastal and
62 offshore regions where the land/ocean interaction is active.

63 In general, sources of organic compounds in marine aerosols comprise natural and
64 anthropogenic emissions. For example, surface-active organic matter of biogenic origin in the
65 ocean (e.g. bacteria, viruses and detritus) can be transferred to the marine atmosphere by
66 bubble-bursting processes (Gantt and Meskhidze, 2013; Gershey, 1983; Mochida et al., 2002;
67 Sciare et al., 2009). Terrestrial air masses also bring plentiful organic matter derived from
68 natural and/or anthropogenic activities to the oceanic atmosphere via long-range atmospheric
69 transport (Zhou et al., 1990; Uematsu et al., 2010; Kumar et al., 2012; Hawkins et al., 2010;
70 Srinivas et al., 2011; Kang et al., 2017). Sugars, important water-soluble organic constituents
71 of atmospheric particulate matter, are substantial in both continental (Pashynska et al., 2002;
72 Yttri et al., 2007; Fu et al., 2008; Jia and Fraser, 2011; Iinuma et al., 2007; Cong et al., 2015)
73 and marine aerosols (Simoneit et al., 2004b; Fu et al., 2011). Due to their ubiquity and
74 abundance, sugars can be used to elucidate sources and transport of atmospheric organic
75 aerosols. Levoglucosan along with its two isomers, mannosan and galactosan, as the primary
76 thermal alteration products by the pyrolysis of cellulose and hemicellulose, has been
77 recognized as specific tracers for biomass burning (Simoneit, 2002). Trehalose is a recognized
78 fungal carbohydrate, which can be indicative of soil dust (Fu et al., 2012; Feng and Simpson,
79 2007). Arabitol and mannitol are tracers for airborne fungal spores (Bauer et al., 2008).
80 Sucrose could serve as a marker for airborne pollen grains (Pacini, 2000; Fu et al., 2012),
81 while fructose and glucose can be emitted from plant pollen, fruits and detritus (Pacini, 2000;
82 Speranza et al., 1997; Baker et al., 1998). These sugar compounds have been detected in some
83 marine aerosols and effectively used as key tracers to assess contributions of different
84 emission sources (Simoneit et al., 2004b). Despite their importance, the knowledge about
85 molecular characterization of sugars in marine aerosols is still rare because of various sources
86 and inconvenience of sampling.

87 Apart from primary sources, atmospheric volatile organic compounds (VOCs) emitted from
88 ocean and/or continents also have significant impacts on marine aerosols. VOCs can react
89 with oxidants, such as ozone (O₃), nitrogen oxides (NO_x) and OH radicals in the atmosphere,

90 producing secondary organic aerosols (SOA) (Atkinson and Arey, 2003; Gantt and
91 Meskhidze, 2013; Meskhidze and Nenes, 2006; Hu et al., 2013; Claeys et al., 2004a; Claeys
92 et al., 2007; Jaoui et al., 2005; Hallquist et al., 2009). SOAs contribute substantially to
93 atmospheric particulate OM and strongly affects the regional and global air quality, climate
94 and human health (Zhu et al., 2016; Chen et al., 2017). Recent studies have revealed that SOA
95 is an important or even the dominant contributor to PM_{2.5} during heavy haze events in China
96 (Cao et al., 2017). Due to poor understanding of sources and formation mechanisms of SOA,
97 accurately measuring and modelling SOA concentrations remains a big issue (Zheng et al.,
98 2017). It was reported that emissions of biogenic VOCs (BVOCs) were one order of
99 magnitude larger than those of anthropogenic VOCs on a global scale (Guenther et al., 2006).
100 BVOCs emitted from terrestrial vegetation include isoprene, monoterpenes and
101 sesquiterpenes as well as other compounds (Guenther et al., 2006; Goldstein and Galbally,
102 2007), which could exert large impacts on marine aerosols through continental aerosols'
103 outflow. On the other hand, marine phytoplankton and seaweeds can release isoprene and
104 other BVOCs as well (Yokouchi et al., 1999; Shaw et al., 2010), especially during the
105 phytoplankton blooms (Hu et al., 2013). Marine-derived SOAs by oxidation of
106 phytoplankton-produced isoprene have been shown to remarkably influence the chemical
107 composition of marine CNN and cloud droplet number, forming an indirect climatic effect
108 (Gantt et al., 2009; Bikkina et al., 2014; Meskhidze and Nenes, 2006). In addition to isoprene,
109 the photooxidation products of oceanic monoterpenes (e.g. α - and β -pinene) were established
110 as well (Fu et al., 2011; Yassaa et al., 2008; Gantt et al., 2009). However, to date, the accurate
111 molecular characterisation and spatial distribution of biogenic SOAs (BSOA) in the marine
112 atmosphere are not well known due to their chemical complexity and process nonlinearity
113 (Chen et al., 2017). Consequently, there remains an urgent need for studies about marine
114 BSOA on a regional and/or global scale currently.

115 In this study, we investigated molecular compositions, abundances and spatial distributions of
116 sugars and BSOA tracers in marine aerosols over the East China Sea (ECS), which is located
117 between the east coast of Asian continent and the western North Pacific. The ECS is an
118 oceanic region susceptible to the influence from outflow of continental OM from natural and
119 anthropogenic activities in the mainland. The contributions of secondary organic carbon (SOC)
120 from isoprene, monoterpene and sesquiterpene to the total OC were estimated. Positive matrix
121 factorization (PMF) was also used to estimate the contributions of sources identified by
122 biomass burning tracers (e.g. levoglucosan), primary saccharides including fungal spore and

123 pollen tracers, BSOA tracers from oxidation of BVOCs, inorganic ions and some other
124 reliable source markers.

125

126 **2 Materials and methods**

127 **2.1 Aerosol sampling**

128 Marine total suspended particles (TSP) were collected during May 18 to June 12, 2014. The
129 sampling was performed using a high-volume air sampler (Kimoto, Japan) at an airflow rate
130 of $0.8 \text{ m}^3 \text{ min}^{-1}$ on board of the KEXUE-1 Research Vessel during a National Natural Science
131 Foundation of China (NSFC) sharing cruise. Figure 1 shows the cruise tracks and
132 concentrations of chlorophyll-a over the ECS. Detailed sampling information and map of
133 sampling sites are described elsewhere (Kang et al., 2017).

134 **2.2 Organic species analysis**

135 Filter aliquots were ultrasonically extracted for 10 min three times using
136 dichloromethane/methanol mixture (2:1, v/v). The solvent extracts were filtered through
137 quartz wool packed in a Pasteur pipette and concentrated with a rotary evaporator, and then
138 blown down to dryness with pure nitrogen gas. The extracts were reacted with 50 μL of N,O-
139 bis-(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylsilyl chloride and 10
140 μL of pyridine at 70°C for 3 hour in order to convert COOH and OH to the corresponding
141 trimethylsilyl (TMS) esters and ethers. After the reaction, 140 μL internal standard (C_{13} *n*-
142 alkane, $1.43 \text{ ng } \mu\text{L}^{-1}$) was added to the derivatives before injection into gas
143 chromatography/mass spectrometry (GC/MS).

144 **2.3 Gas chromatography/mass spectrometry**

145 Two organic species (i.e. sugars and SOA tracers) were determined on an Agilent model 7890
146 GC coupled to an Agilent model 5975C mass-selective detector (MSD). The GC instrument
147 was equipped with a split/splitless injector and a DB-5ms fused silica capillary column (30 m
148 \times 0.25 mm i.d., 0.25 μm film thickness) with the GC oven temperature programmed from
149 50°C (2 min) to 120°C at $15^\circ\text{C min}^{-1}$, and then to 300°C at 5°C min^{-1} with final isotherm
150 hold at 300°C for 16 min. Helium was used as carrier gas. The GC injector temperature was
151 maintained at 280°C . The mass spectrometer was operated in the Electron Ionization (EI)

152 mode at 70 eV and scanned in the m/z range of 50 to 650 Da. Data were processed using
153 ChemStation software. Each compound was determined through comparing mass spectra with
154 those of authentic standards or literature data. GC/MS response factors were obtained with
155 authentic standards or surrogate standards. Recoveries of the standards that were spiked onto
156 pre-combusted quartz filters and measured as the samples ($n = 3$) were generally better than
157 80%. A field blank filter was treated as the real samples for quality assurance. The present
158 data were corrected with field blanks but not for recoveries.

159 **2.4 Positive matrix factorization (PMF) analysis**

160 To further investigate the potential sources of marine organic aerosols, the positive matrix
161 factorization (PMF) analysis are used in this study. For this analysis, the measured ambient
162 concentrations less than or equal to the method detection limit (MDL) were replaced by
163 MDL/2 and associated uncertainties were $(5/6)*MDL$. For the concentrations greater than the
164 MDL, the calculation of uncertainty is based on the following equation:

$$165 \quad \text{Uncertainty} = \sqrt{(\text{error fraction} * \text{concentration})^2 + (0.5 * \text{MDL})^2} \quad (1)$$

166 where the error fraction is a user-provided estimation of the analytical uncertainty of the
167 measured concentration or flux. In the present study, the error fraction was set as 0.2 for all
168 species for receptor-oriented source apportionment analyses (Han et al., 2017).

169

170 **3 Results and discussion**

171 Concentrations of sugars and biogenic SOA tracers in marine aerosols over the ECS were
172 presented in Table 1. Total abundance of the quantified sugar compounds ranged from 1.8–
173 950 ng m^{-3} with an average of 81.5 ng m^{-3} much lower than those in urban atmosphere in
174 China (Wang et al., 2006), and the nighttime aerosols contained more sugars (average 90.1 ng
175 m^{-3}) than the daytime ones (72.6 ng m^{-3}). Individual sugar compounds also showed higher
176 nighttime concentrations, but still lower than those in urban aerosols (Wang et al., 2011). The
177 total biogenic SOA tracers were in the range of 1.1–135 ng m^{-3} (average 22.9 ng m^{-3}) with
178 lower nighttime abundance (22.2 ng m^{-3}) than daytime (23.6 ng m^{-3}). In contrast to
179 monoterpene and sesquiterpene SOA tracers, the isoprene SOA tracers presented higher levels
180 in the nighttime aerosols (9.6 ng m^{-3}) than those in the daytime samples (7.1 ng m^{-3}).

181 Generally, higher values of these organics were observed in coastal regions compared with
182 those far away from mainland (Fig. 2, Fig. 4 and Fig. S1), similar to the spatial pattern of
183 lipids, PAHs and phthalates in our previous report (Kang et al., 2017), suggesting the impact
184 from the outflow of continental OM on the basis of back trajectory analysis (Fig. S2-S6).

185 **3.1 Sugars and sugar-alcohols**

186 Sugars, a major class of water-soluble organic constituents in the atmosphere, have been
187 reported to be ubiquitous in marine aerosols (Fu et al., 2011; Chen et al., 2013; Simoneit et al.,
188 2004b; Burshtein et al., 2011). Most of them can serve as tracers of biological primary aerosol
189 particles and biomass burning (Simoneit, 2002; Bauer et al., 2008). Eleven sugar compounds
190 including anhydrosugars (levoglucosan, galactosan, mannosan), sugars (fructose, glucose,
191 sucrose and trehalose) and sugar alcohols (erythritol, arabitol, mannitol and inositol) were
192 measured in marine aerosols collected over the ECS. The concentrations of sugars are shown
193 in Table 1 and Fig. 2. Glucose ($0.31\text{--}209\text{ ng m}^{-3}$, mean 18.8 ng m^{-3}) and mannitol ($0.03\text{--}169$
194 ng m^{-3} , 16.3 ng m^{-3}) were the dominant species, followed by sucrose ($0.09\text{--}216\text{ ng m}^{-3}$, 11.7
195 ng m^{-3}), trehalose ($0.08\text{--}96.0\text{ ng m}^{-3}$, 9.4 ng m^{-3}), fructose ($0.09\text{--}106\text{ ng m}^{-3}$, 9.1 ng m^{-3}), and
196 levoglucosan ($0.09\text{--}64.3\text{ ng m}^{-3}$, 7.3 ng m^{-3}) (Fig. 3). Chen et al. (2013) also reported that
197 glucose and mannitol are the major sugar compounds detected in marine aerosols collected at
198 Chichi-Jima Island during spring and summer. Moreover, nighttime concentrations of all
199 sugars were generally higher than the daytime ones, likely due to lower height of planetary
200 boundary layer (PBL) and the land breeze carrying plentiful terrestrial OM at night.

201 Figure 2 presents the temporal variations in sugar compounds determined in the marine
202 aerosol samples collected over the ECS. The concentrations of total sugars were characterized
203 by higher levels in the regions close to continent and/or influenced by land air masses,
204 indicating substantial influence of continental outflow compared to marine air over the
205 pelagic ocean.

206 **3.1.1 Anhydrosugars**

207 Levoglucosan, a thermal degradation production of cellulose (Simoneit, 2002) and a specific
208 indicator for biomass burning (Simoneit et al., 1999), can largely modify the chemical
209 composition of atmospheric aerosols on a regional to global scale. Due to its water solubility,
210 levoglucosan contribute to water-soluble organic carbon in aerosols, significantly enhancing
211 the hygroscopic properties of atmospheric aerosols (Mochida and Kawamura, 2004). The

212 abundance of levoglucosan detected in the present study (0.09–41.2 ng m⁻³, mean 6.1 ng m⁻³
213 and 0.10–64.3 ng m⁻³, mean 8.4 ng m⁻³ for day and night, respectively) was not the highest
214 among measured sugar species (Fig. 3 and Table 1). The average concentration of
215 levoglucosan is close to those reported at Gosan, Jeju Island in summer (mean 8.0 ng m⁻³) (Fu
216 et al., 2012). During the whole sampling period, higher concentrations of levoglucosan were
217 found in the samples under the effect of continental air masses based on five-day backward
218 trajectories (Fig. S2-S6), consistent with our previous report about lipids, PAHs and
219 phthalates (Kang et al., 2017). Mannosan and galactosan, isomers of levoglucosan, are
220 produced by pyrolysis of cellulose and hemicellulose and can also act as biomass burning
221 tracers (Fabbri et al., 2009; Simoneit, 2002). Mannosan and galactosan were detected in the
222 samples with similar variation trends to levoglucosan (Table 1 and Fig. 2), further indicating
223 the strong impact of continental biomass burning activities on the marine atmosphere. As
224 shown in Table 1 and Fig. 3, the nighttime average concentrations of all three anhydrosugars
225 were higher than the daytime ones, probably attributable to enhanced biomass combustion
226 and lower height of PBL as well as the land breeze during the night.

227 In addition, hard wood tend to contain higher levels of cellulose than hemicellulose, therefore
228 the mass concentration ratios of levoglucosan to mannosan (L/M) can be utilized as a
229 diagnostic parameter for diverse biomass burning substrates (Zhu et al., 2015). Previous
230 studies found that L/M ratios from softwood are in a range of 3–10 and those from hardwood
231 are 15–25, while the ratios from crop residues are even higher (25–40) (Zhu et al., 2015). In
232 this study, the L/M ratios range from 0.71–32 with an average of 4.2, and higher values were
233 observed in the terrestrially influenced aerosols, especially coastal areas near Fujian province
234 (Fig. S7). The lower L/M ratios in our study (average 4.2) suggest that the aerosols were
235 mainly associated with the burning of softwood, consistent with the lower L/M ratios (2.1–4.8)
236 observed on Okinawa Island in May–June (Zhu et al., 2015) and Mt. Fuji (4.6–7.6, mean 5.5)
237 (Fu et al., 2014). It is worth noting that a couple of samples near Fujian Province in Southeast
238 China were characterized by a higher L/M ratio (>20) (Fig. S7), agreeing well with the values
239 of straw burning smokes (Chen et al., 2013). Zhu et al. (2015) also reported combustion of
240 agricultural residues, peat and wood could contribute to high L/M ratios. Therefore, these
241 higher values probably indicate emissions from terrestrial burning of straw residues, which
242 could affect the chemical components of aerosols in the western North Pacific via long-range
243 atmospheric transport as confirmed by backward trajectories (Fig. S5).

244 **3.1.2 Sugar alcohols**

245 Sugar alcohols detected in these samples consist of arabitol, mannitol, inositol and erythritol,
246 which had similar temporal patterns (Fig. 2e-h). Higher abundances of sugar alcohols
247 observed in the terrestrially influenced aerosol samples suggesting a significant contribution
248 from terrestrial source (Fig. S2-S6). While the marine fungi and algae, which can also release
249 fungal spores into the marine atmosphere via bubble bursting, contribute little to the sugar
250 alcohols in the coastal aerosols. Obviously, mannitol and arabitol were the most abundant
251 sugar alcohols detected in the present study (Fig. 3 and Table 1), ranging from 0.03–169 ng
252 m⁻³ (16.3 ng m⁻³) and 0.02–51.0 ng m⁻³ (5.1 ng m⁻³), respectively. A strong positive
253 correlation between arabitol and mannitol were found in marine aerosols ($p < 0.001$, $r = 0.996$,
254 $N = 51$), suggesting a similar origin. Mannitol and arabitol are very common in fungi, and are
255 the most frequently occurring sugar alcohols in plants (Burshtein et al., 2011), which can be
256 utilized to assess the contribution of fungal spores to the aerosol OC (Bauer et al., 2008). For
257 instance, mannitol is particularly abundant in algae (Burshtein et al., 2011). The peak
258 concentrations of sugar alcohols were found in the nighttime samples, which can be attributed
259 to the increased activities of yeasts and fungi at night (Graham et al., 2003). Moreover, the
260 maxima concentrations of these sugar polyols, especially arabitol and mannitol, were
261 observed in offshore regions in early summer (June) (Fig. 2e-h), likely due to the more active
262 microbial activities resulting from warmer temperature in June and more biota in coastal
263 regions (Fig. 1).

264 **3.1.3 Sugars**

265 Glucose, fructose, sucrose, and trehalose are the primary saccharides measured in marine
266 aerosols over the ECS. Glucose was the dominant sugar compound (0.31–209 ng m⁻³, 18.8 ng
267 m⁻³), followed by sucrose (0.09–216 ng m⁻³, 11.7 ng m⁻³) (Fig. 2i-l and Fig. 3). Glucose and
268 fructose originate from plant materials, such as pollen, fruits and their fragments (Fu et al.,
269 2012; Graham et al., 2003). Both glucose and fructose presented higher levels in the coastal
270 areas, demonstrating great contribution from terrestrial vegetation. Medeiros and Simoneit
271 (2007) reported that high abundance of glucose associated with lower molecular weight fatty
272 acids (mainly C₁₆) was attributed to the spring bloom of algae. In our study, glucose
273 correlated well with measured C_{16:0} fatty acid ($p = 0.001$, $r = 0.46$, $N = 51$), which mainly
274 emitted from the ocean surface via sea spray (Kang et al., 2017), suggesting that marine
275 sources also contributed to the particulate glucose in the oceanic atmosphere. It was noted that

276 fructose had a strong correlation with glucose ($p < 0.001$, $r = 0.94$, $N = 51$), indicating they
277 share similar sources. Sucrose, as a predominant sugar species in the phloem of plants as well
278 as developing flower buds, is reported to be the richest and dominant component of airborne
279 pollen grains (Graham et al., 2003). High abundance of sucrose along with fructose and
280 glucose observed in our study implies a large emission of airborne pollen grains into the
281 marine atmosphere over the ECS. Significantly, the concentration of glucose, fructose and
282 sucrose were highest at the beginning of June in early summer (Fig. 2i-l), probably
283 attributable to an enhanced pollen emission, because pollen counts tend to be highest in late
284 spring/early summer in temperate zones (Graham et al., 2003). Such peak concentrations in
285 early June are in accord with a previous study by Pashynska et al. (2002). Trehalose, a fungal
286 metabolite, is present in a variety of microorganisms (fungi, bacteria, yeast and algae), and a
287 few higher plants as well as invertebrates (Medeiros et al., 2006a). Thus, trehalose can be
288 used as a microbial biomarker and stress protectant. Furthermore, trehalose was reported to be
289 the most abundant sugar in soil (Rogge et al., 2007; Medeiros et al., 2006b; Jia and Fraser,
290 2011), thus the enrichment of trehalose in aerosols can be indicative of soil resuspension and
291 unpaved road dust (Simoneit et al., 2004a; Fu et al., 2012). The trehalose in our study was
292 positively correlated with non-sea-salt calcium (nss- Ca^{2+}) ($p < 0.01$, $r = 0.43$, $N = 51$), the
293 best tracer for soil dust (Virkkula et al., 2006), suggesting the atmospheric trehalose over the
294 ECS was mainly derived from resuspension of soil particles. Higher abundance of trehalose in
295 coastal regions (Fig. 2l), may be in connection with the outflow of Asian dust primarily
296 occurring in winter/spring (Fu et al., 2012), and inland soil resuspension/dust aerosols.

297 **3.2 Secondary organic aerosols**

298 The sum of all SOA tracers ranged from 1.1–135 ng m^{-3} (22.9 ng m^{-3}), which were higher
299 than previous report of marine aerosols (0.19–27 ng m^{-3} , 6.6 ng m^{-3}) (Fu et al., 2011), but
300 much lower than those in the continental sites (Fu et al., 2010; Ding et al., 2014). These
301 differences suggest that the major source of SOA tracers over the ECS is of terrestrial origin.
302 Specifically, the total concentrations of detected isoprene SOA-tracers ranges from 0.15–64.0
303 ng m^{-3} (8.4 ng m^{-3}), comparable to those reported in marine aerosols (mean 8.5 ng m^{-3}) (Hu et
304 al., 2013), but lower than those of urban aerosols (Ren et al., 2017; Ding et al., 2014); total
305 monoterpene SOA-tracers in the range of 0.26–87.2 ng m^{-3} (11.6 ng m^{-3}) lower than those in
306 urban aerosols as well (Ren et al., 2017); total sesquiterpene SOA-tracers ranged between
307 0.16 and 17.2 ng m^{-3} (2.9 ng m^{-3}). Such phenomena that BSOA derived from monoterpenes

308 are more abundant than those from isoprene were also reported in Chinese urban areas (Ren et
309 al., 2017). On the whole, biogenic SOA tracers exhibited higher loadings in the coastal areas
310 than those remote sampling sites, further indicating that long-range atmospheric transport of
311 terrestrial aerosols has significant influence on the chemical composition and abundance of
312 SOA over oceans. Marine VOC spatial distributions are expected to be linked to the
313 distributions of photosynthetic pigments in seawater, such as chlorophyll-a (Ooki et al., 2015).
314 The higher concentrations of chlorophyll-a in the coastal regions (Fig. 1) stand for higher
315 biological activities and more emission of VOCs, which agree well with higher SOA tracers
316 over the coastal waters. Such spatial variations in biogenic SOA tracers are in agreement with
317 a previous report about marine organic aerosols collected during a round-the-world cruise (Fu
318 et al., 2011).

319 **3.2.1 Isoprene SOA tracers**

320 Isoprene is a reactive biogenic hydrocarbon and primarily originates from terrestrial
321 photosynthetic vegetation (e.g. trees and plants). Marine phytoplankton and seaweed can also
322 emit isoprene (Yokouchi et al., 1999; Shaw et al., 2010). Moreover, bacteria produce isoprene
323 as well, and the bacterial isoprene production is temperature-dependent (Kurihara et al., 2010).
324 In spite of much lower emission strength in the ocean region, more recent researches have
325 suggested that the oceanic source of isoprene significantly impact atmospheric chemistry and
326 cloud microphysical properties in the remote marine boundary layer because of its high
327 reactivity (about 1–2 hour lifetime) (Hackenberg et al., 2017).

328 Six isoprene SOA tracers, including 2-methylglyceric acid, three C₅-alkene triols, and two 2-
329 methyltetrols (2-methylthreitol and 2-methylerythritol), were identified in the marine aerosols
330 over ECS. Isoprene SOA tracers showed diurnal variations with higher average
331 concentrations at night (Fig. 4a-c, Fig. 5, Fig. S8), consistent with the report by Fu et al.
332 (2010). The higher abundance during the night can be explained by the enhanced gas-to-
333 particle partition at cooler temperatures during the nighttime and/or increased input of
334 continent-originated isoprene-SOA into the oceanic atmosphere via land-sea breeze
335 circulations at night. However, T-test showed that the difference between daytime and
336 nighttime concentrations for 2-methyltetrols, C₅-alkene triols and 2-MGA was not that
337 significant ($p > 0.05$). As expected, much higher concentrations of isoprene tracers were
338 observed in coastal regions, where continental outflows exert larger effects from spring to
339 early summer. For the remote ocean, terrestrial sources have weak impacts because of the

340 short atmospheric lifetime of isoprene and the dilution effects during long-range atmospheric
341 transport. In addition to the effect of continental outflow, more nutrients in the coastal and
342 estuarine regions could be another factor responsible for the higher levels of isoprene SOA
343 tracers compared to the pelagic areas. Because nutrient-rich surface water can promote the
344 development of phytoplankton blooms and increases chlorophyll-a concentrations.
345 Chlorophyll-a is a measure of phytoplankton, or algal, biomass (Quinn et al., 2014) and
346 currently most widely used proxy for predicting isoprene concentrations in water
347 (Hackenberg et al., 2017). Numerous studies reported the positive relationship between
348 isoprene emission and chlorophyll-a in the surface seawater (Hackenberg et al., 2017; Zhu et
349 al., 2016). In the present study, the temporal and spatial distributions of chlorophyll-a at the
350 ECS surface during the whole sampling period are characterized by higher coastal levels, such
351 as waters near Zhejiang and Fujian provinces, but lower abundance in eastern Taiwan and the
352 remote sea (Fig. 1). Thus, high chlorophyll-a waters in coastal locations mean more isoprene
353 emissions than remote open waters. However, the isoprene in the remote ocean may mainly
354 originate in situ from biological production by marine biota at the ocean surface.

355 The low-NO_x products 2-methyltetrols with mass concentrations ranging from 0.03–41.9 ng
356 m⁻³ (4.8 ng m⁻³) were the major species among the isoprene SOA tracers, in line with early
357 report about summer aerosols in China (Ding et al., 2014). Specially, concentration ranges of
358 2-methyltetrols were 0.11–17.0 ng m⁻³ (3.8 ng m⁻³) during the daytime and 0.03–41.9 ng m⁻³
359 (5.7 ng m⁻³) at night with 2-methylerythritol being about 2.1-fold more abundant than 2-
360 methylthreitol. This ratio is similar to those calculated in previous studies (Fu et al., 2010; Ion
361 et al., 2005; Cahill et al., 2006). The atmospheric levels of 2-methyltetrols are comparable to
362 those reported in marine aerosols collected during a round-the-world cruise (0.07–15 ng m⁻³,
363 2.4 ng m⁻³) (Fu et al., 2011). However, these values are small compared to those from
364 terrestrial emissions, such as mountain (Fu et al., 2014; Cahill et al., 2006) and forest aerosols
365 (Miyazaki et al., 2012; Fu et al., 2010; Claeys et al., 2004a). A significant positive
366 relationship between 2-methyltetrols and levoglucosan ($p < 0.001$, $r = 0.87$, $N = 51$) in our
367 study suggests that biomass burning may also generate the precursors of 2-methyltetrols
368 followed by photochemical reactions (Xie et al., 2014). Besides, 2-methyltetrols correlated
369 with C₂₉ *n*-alkane (the dominant species of terrestrial higher plant waxes) as well ($p < 0.001$, r
370 = 0.74, $N = 51$), suggesting these organic tracers originate from higher plants or from similar
371 source regions as well. The correlations above illustrate that terrestrial emissions (e.g.

372 biomass burning and higher plants) contributed significantly to the levels of 2-methyltetrols in
373 the marine atmosphere.

374 C₅-Alkene triols are formed from photooxidation of isoprene under low-NO_x conditions
375 (Surratt et al., 2006; Lin et al., 2013). They were detected in all the samples ranging from
376 (0.03–14.6 ng m⁻³, 2.2 ng m⁻³), which are higher than those reported in Arctic aerosols (0.01–
377 0.15 ng m⁻³) (Fu et al., 2009) and other marine aerosols (0.002–4.6 ng m⁻³, 0.65 ng m⁻³) (Fu
378 et al., 2011); but lower than the atmospheric levels of mountain aerosols (Fu et al., 2014; Fu
379 et al., 2010) and subtropical urban aerosols from Hong Kong (Hu et al., 2008). Such a
380 difference illustrates the outflow of continental aerosols, which can be confirmed by the
381 significant positive correlations between C₅-alkene triols and tracers of terrestrial emissions,
382 such as C₂₉ *n*-alkanes ($p < 0.001$, $r = 0.78$, $N = 51$) and levoglucosan ($p < 0.001$, $r = 0.87$, $N =$
383 51). It was found that 2-methyltetrols correlated well with C₅-alkene triols in marine aerosols
384 over ECS ($p < 0.001$, $r = 0.86$, $N = 51$), suggesting a similar formation mechanism or
385 common sources. However, the mass concentration ratios of C₅-alkene triols to 2-
386 methyltetrols showed significant variation in different sampling sites (Fig. 6a), indicating
387 different formation pathways, consistent with a previous report (Fu et al., 2010).

388 Concentrations of 2-methylglyceric acid (2-MGA), formed by photooxidation of isoprene
389 under high-NO_x (NO_x = NO + NO₂) conditions (Surratt et al., 2006), were in the range of
390 0.09–8.3 ng m⁻³ (1.4 ng m⁻³) being greatly lower than those in mountain aerosols (Cahill et al.,
391 2006; Fu et al., 2010; Fu et al., 2014), implying much stronger influence of NO_x on isoprene
392 SOA formation in continental aerosols. 2-MGA is a possible further oxidation product of
393 methacrolein and methacrylic acid, which are two major gas-phase oxidation products of
394 isoprene (Claeys et al., 2004b; Edney et al., 2005; Fu et al., 2009). 2-MGA was related to C₂₉
395 *n*-alkanes ($p < 0.001$, $r = 0.84$, $N = 51$) and levoglucosan ($p < 0.001$, $r = 0.81$, $N = 51$) as well,
396 again suggesting a terrestrial input. These isoprene-SOA tracers in marine aerosols over the
397 ECS may stem from terrestrial higher plants and biomass burning, and then were oxidized
398 during the transport to the oceanic atmosphere. Similar correlations between isoprene-derived
399 SOA tracers and levoglucosan were mentioned in previous study, which reported that biomass
400 burning enhanced the isoprene-SOA formation (Li et al., 2018). Additionally, 2-methyltetrols
401 are higher generation products than 2-MGA (Fu et al., 2014), but the ratios of 2-MGA to 2-
402 methyltetrols did not vary significantly with cruise track. However, a couple of high ratios
403 were observed in the ocean-air influenced aerosols, suggesting the importance of marine
404 source for fresh isoprene-derived SOAs in the atmosphere (Fig. 6b).

405 NO_3^- was found to be related to 2-MGA, 2-methyltetrols and C_5 -alkene triols ($p < 0.001$, $r =$
406 $0.60\text{--}0.71$, $N = 51$). The ratio of 2-MGA to 2-methyltetrols was found to be negatively
407 correlated with particulate NO_3^- ($p < 0.05$, $r = -0.31$, $N = 51$). These relationships reveal that
408 there may be a close connection between formation of isoprene SOA and NO_3^- in the marine
409 boundary layer.

410 **3.2.2 Monoterpene SOA tracers**

411 The detected α/β -pinene oxidation products in the study consist of pinonic, pinic acids, 3-
412 hydroxyglutaric acid (3-HGA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). They
413 are derived from the photooxidation of α/β -pinene with O_3 and OH radicals (Hoffmann et al.,
414 1997; Yu et al., 1999; Glasius et al., 2000; Iinuma et al., 2004). Since monoterpenes account
415 for around 35% of the global biogenic VOCs' emissions, these compounds have been utilized
416 to estimate the role of monoterpene oxidation in the SOA formation (Griffin et al., 1999).
417 Monoterpenes were chiefly emitted from needle leaf trees. In this study, monoterpene-SOA
418 tracers were found to be positively correlated to levoglucosan with $p < 0.001$ (r ranges from
419 $0.68\text{--}0.82$), indicating terrestrial biomass burning made substantial contributions to the
420 formation of monoterpenes, then being transported to the oceanic atmosphere. Generally, total
421 monoterpene-SOA tracers in our study showed a major peak in spring (Fig. S1g), in
422 agreement with a previous study (Zhu et al., 2016). Pinonic and pinic acids, well-known
423 tracers for α/β -pinene, ranged from $0.02\text{--}1.6 \text{ ng m}^{-3}$ (0.47 ng m^{-3}) and $0.16\text{--}14.9 \text{ ng m}^{-3}$ (3.4
424 ng m^{-3}), respectively (Table 1). Their concentrations were higher than those in high Arctic
425 aerosols (average 69 pg m^{-3} and 514 pg m^{-3} , respectively) (Fu et al., 2009). In addition,
426 concentrations of pinic acid were 7 times higher than pinonic acid, similar to an earlier report
427 (Fu et al., 2009). The vapour pressure of pinic acid is about 2 orders of magnitude lower than
428 pinonic acid (Bhat and Fraser, 2007). Thus, pinic acid can saturate and readily nucleate, being
429 expected to have a higher fraction in the aerosol phase than pinonic acid.

430 Two novel monoterpene SOA tracers, 3-hydroxyglutaric acid (3-HGA) and 3-methyl-1,2,3-
431 butanetricarboxylic acid (MBTCA), were also detected in these marine aerosols. Both of them
432 are reported to be higher-generation products of α -pinene photooxidation (Kourtchev et al.,
433 2009; Szmigielski et al., 2007). The concentration ranges of 3-HGA in marine aerosols over
434 ECS were lower than those of aerosols in Mt. Tai, central east China (Fu et al., 2010), but
435 comparable to other studies about marine aerosols (Fu et al., 2011). The average abundance of
436 atmospheric MBTCA for all samples were 5.6 ng m^{-3} with mean concentrations of 6.8 ng m^{-3}

437 and 4.5 ng m⁻³ during the day and night, respectively, more abundant than 3-HGA (2.2 ng m⁻³)
438 ³). Interestingly, these mean values of MBTCA were comparable to those of mountain
439 aerosols (Fu et al., 2010), but still higher than the marine aerosols collected on the remote
440 seas (Fu et al., 2011). Since the ECS is adjacent to Mainland China, the atmospheric boundary
441 layer in these regions would inevitably be affected by continent-derived air masses, as
442 supported by the spatial pattern of individual SOA tracers (Fig. 4 and Fig. S1), in particular of
443 the peaks occurring in the coastal areas. Furthermore, in contrast to isoprene SOA tracers,
444 monoterpene SOA tracers commonly exhibit higher average daytime concentrations (Table 1
445 and Fig. 5), but T-test showed no significant difference ($p > 0.05$) between daytime and
446 nighttime concentrations for both total and individual monoterpene SOA tracers. The
447 concentration ratio of 3-HGA plus MBTCA to pinic acid ((3HGA+MBTCA)/pinic) showed
448 higher values in the terrestrially influenced aerosols (Fig. 6c). Besides, this mass
449 concentration ratios were basically higher during the daytime (mean 2.0) than nighttime (1.9),
450 indicating that aged aerosols are more abundant in the daytime.

451 **3.2.3 Sesquiterpene SOA tracers**

452 The analysis of sesquiterpenes is a great challenge due to their high reactivity and relatively
453 low vapour pressure. However, the aging of β -caryophyllene derived SOA has proved its
454 significant effects on all CCN-relevant properties (Asa-Awuku et al., 2009). β -caryophyllene
455 is one of the most abundant species among sesquiterpenes originating from plants (Duhl et al.,
456 2008). β -caryophyllinic acid is an ozonolysis or photooxidation product of β -caryophyllene
457 (Jaoui et al., 2007). Moreover, sesquiterpenes accumulated in leaves and woods can be
458 emitted during biomass combustion (Ciccioli et al., 2014).

459 The atmospheric levels of β -caryophyllinic acid were 0.16–17.2 ng m⁻³ (mean 2.9 ng m⁻³),
460 with 0.17–17.2 ng m⁻³ (3.5 ng m⁻³) during daytime and 0.16–9.6 ng m⁻³ (2.3 ng m⁻³) during
461 nighttime, respectively (Table 1). As expected, β -caryophyllinic acid correlated well with
462 levoglucosan ($p < 0.001$, $r = 0.61$, $N = 51$) in agreement with earlier report (Ding et al., 2016),
463 indicating substantial contribution of terrestrial biomass burning to sesquiterpenes' loading in
464 the marine atmosphere. On the other hand, biomass-burning processes (e.g. crop straw
465 combustion and forest fires) can raise ambient and/or leaf temperature to some extent,
466 consequently probably enhancing the emission of sesquiterpenes from trees and plants.

467 Many researches have proved that sesquiterpene emissions increase significantly with
468 increasing ambient temperatures (Tarvainen et al., 2005; Jaoui et al., 2007). Ambient

469 temperature seems to be the dominant factor controlling temporal variation in sesquiterpene
470 emission although other factors contribute (Duhl et al., 2008). An early study reported that
471 emission rates of sesquiterpene were 1.2–3 times higher in the daytime as well (Duhl et al.,
472 2008). All the reports described above perfectly interpret much higher concentrations of β -
473 caryophyllinic acid during daytime in our study. The abundance of β -caryophyllinic acid in
474 this study are higher than those reported in the remote marine aerosols during a round-the-
475 world cruise, but comparable to the maximum concentration of 2.5 ng m^{-3} observed at
476 California coast (Fu et al., 2011); however, the concentrations of β -caryophyllinic acid were
477 much lower than those of Mt. Tai aerosols, central east China (average 12 ng m^{-3} for both
478 daytime and nighttime aerosols) (Fu et al., 2010). The spatial distributions of β -caryophyllinic
479 acid also presented higher levels in coastal regions than other sampling sites (Fig. 4h), again
480 proving contribution of terrestrial aerosols.

481 **3.3 Contributions of biogenic primary and secondary sources**

482 To assess the relative abundances of organic aerosols from primary and secondary emission
483 sources, tracer-based methods are employed to evaluate their contributions to the marine
484 ambient OC. For example, mannitol and arabitol determined in marine aerosols were used to
485 calculate the contributions of fungal spores to OC (Bauer et al., 2008); the average mass
486 percent ratios of levoglucosan to OC (8.14%) are used to investigate the biomass burning
487 derived OC (Fu et al., 2014). Besides, biogenic SOA tracers detected in the present study are
488 utilized to evaluate the SOC formation resulting from the oxidation of isoprene, α -pinene and
489 β -caryophyllene through a tracer-based method reported by Kleindienst et al. (2007). This
490 method used the laboratory-derived mass fractions (f_{soc}) of marker species generated from
491 known precursors into SOC concentrations. Specifically, the f_{soc} values used in our study is
492 0.155 ± 0.039 for isoprene, 0.231 ± 0.111 for α -pinene and 0.023 ± 0.005 for β -caryophyllene,
493 respectively (Kleindienst et al., 2007). Through dividing the sum of tracer compounds
494 measured in these marine samples by f_{soc} , an estimate of the contribution of each SOA to the
495 total marine SOC concentration was determined and the results were presented in Table 2.

496 Biomass burning derived OC in the whole samples is in the range of $1.1\text{--}790 \text{ ngC m}^{-3}$ (89.6
497 ngC m^{-3}), with higher levels in the nighttime ($1.3\text{--}790 \text{ ngC m}^{-3}$, 103 ngC m^{-3}) compared to
498 those ($1.1\text{--}506 \text{ ngC m}^{-3}$, 75.5 ngC m^{-3}) in the daytime. Higher concentrations of biomass-
499 burning OC near the Asian continent than those over the remote oceans (Fig. 7) suggest that
500 continental biomass-burning tracers were possibly removed by dry and/or wet deposition of

501 airborne particles, photodegradation by free radicals in the atmosphere or other atmospheric
502 dilution mechanism during long-range transport to the western North Pacific. Fungal-spore-
503 derived OC for all samples ranged from 1.2–1840 ngC m⁻³ (180 ngC m⁻³), accounting for
504 0.03–19.8% (3.1%) of OC, higher than those of biomass-burning-derived OC (Table 2). The
505 nighttime fungal-spore-derived OC (1.2–1840 ngC m⁻³, 203 ngC m⁻³) is higher than those of
506 daytime ones (1.3–911 ngC m⁻³, 157 ngC m⁻³), possibly associated with intensified activities
507 of yeasts and fungi during nighttime (Fu et al., 2012). As we all known, evenings tend to have
508 higher moist content, which exerts a stronger influence on microbial activity than temperature
509 (Liang et al., 2003). Similar higher levels of fungal-spore-derived OC were also observed in
510 the aerosols collected in coastline waters, probably due to more intensified microbial
511 activities in the coastal regions as discussed previously. β -caryophyllene SOC (6.9–747 ngC
512 m⁻³, 126 ngC m⁻³, with 7.4–747 ngC m⁻³, mean 153 ngC m⁻³ during the day and 6.9–416 ngC
513 m⁻³, mean 100 ngC m⁻³ at night) is found to be dominant contributor among the measured
514 biogenic SOCs over the ECS (the average concentrations were 39.8 ngC m⁻³ and 50.2 ngC m⁻³
515 for isoprene SOC and α/β -pinene SOC, respectively). Moreover, β -caryophyllene SOC
516 account for 0.36–5.3% (2.4%) of OC, about 2–3 times as high as those of isoprene (0.13–
517 3.8%, 0.83%) and monoterpene SOC (0.08–3.5%, 0.98%). Therefore, an emission inventory
518 for sesquiterpenes in marine aerosols over the ECS will be helpful for further understanding
519 formation of biogenic SOA in this region. Zhu et al. (2016) also reported that the
520 sesquiterpene-derived SOC was more abundant than isoprene- and monoterpene-derived SOC
521 for the aerosols collected in Okinawa, Japan.

522 The higher levels of sesquiterpene-SOC than monoterpene- and isoprene-SOC may be due to
523 the differences in the gas/particle partitioning of oxidation products from different VOCs,
524 given that longer chain sesquiterpenes (C₁₅H₂₄) have more carbon atoms than monoterpenes
525 (C₁₀H₁₆) and isoprene (C₅H₈), decreasing the vapour pressures of their oxidation products (Fu
526 et al., 2016). The levels of SOCs stemmed from isoprene, monoterpenes and sesquiterpene in
527 the marine aerosols over the ECS were much lower than those of PM_{2.5} samples in Hong
528 Kong, China during summer (Hu et al., 2008) and those observed in Mt. Tai aerosols (Fu et
529 al., 2010). The sum of biogenic SOCs over the ECS is 11.3–1060 ngC m⁻³ (216 ngC m⁻³),
530 much lower than that of Mt. Fuji aerosols (227–1120 ngC m⁻³, 542 ngC m⁻³) (Fu et al., 2014)
531 and those in the Mt. Tai aerosols (420–3100 ngC m⁻³) (Fu et al., 2010), but higher than those
532 observed in marine aerosols collected during a round-the-world cruise covering most remote
533 oceans (Fu et al., 2011) and those reported in the Arctic aerosols (average 14.6 ngC m⁻³) (Fu

534 et al., 2009). Such difference between terrestrial aerosols and marine aerosols highlights the
535 outflow of continental aerosols again. In terms of spatial distributions, biogenic SOCs
536 calculated from these compounds showed higher loadings in the locations close to the
537 coastline or significantly influenced by terrestrial air (Fig. 8a-b), also validating strong
538 influence of continental origin. Generally, the total concentrations of biogenic SOC (216 ngC
539 m⁻³) are higher than those of biomass-burning-derived OC (89.6 ngC m⁻³) and fungal-spore-
540 derived OC (180 ngC m⁻³) (Table 2), presenting greater contribution from biogenic SOA to
541 the marine aerosols, in agreement with the report by Fu et al. (2014).

542 In order to compare the relative contribution of marine and continental sources to total OC in
543 the oceanic atmosphere, the whole sampling area was divided into five regions from north to
544 south according to the spatial distribution of aerosol samples, i.e. northern waters of ECS,
545 nearby waters in the ECS, seas adjacent to Fujian and Zhejiang provinces, eastern waters of
546 Taiwan. Five-day HYSPLIT back trajectory analysis showed that the atmosphere over waters
547 north of ECS were mainly controlled by marine air masses, while aerosol samples achieved
548 on June 12 showed great influence from South Korea and North China as well (Fig. S2).
549 Aerosol samples in waters of ECS were basically under the control of marine air masses,
550 except for the samples collected on May 20, which were also affected by terrestrial air from
551 the Asian mainland (Fig. S3). In general, aerosols collected off the eastern coast of Taiwan
552 Island were affected by air masses from the remote sea, but some aerosols collected on May
553 22–23 were also influenced by air masses coming from Southeast Asia (Fig. S4). In contrast,
554 air masses from Asian mainland had substantial impacts on the samples collected near Fujian
555 and Zhejiang province (Fig. S5-S6). On the whole, the aerosols strongly affected by terrestrial
556 sources (e.g. Asian mainland, Southeast Asia and South Korea) tend to own higher levels of
557 sugars and SOA tracers (Fig. 2 and Fig. 4).

558 The contributions of biomass-burning-derived OC, fungal-spore-derived OC, and biogenic
559 SOCs to OC (%) in these five sampling regions were presented in Fig. 9. Generally, the
560 average contributions of biogenic SOCs, biomass-burning OC and fungal-spore OC to OC
561 near Zhejiang and Fujian waters were higher than the other sampling areas, especially for the
562 fungal-spores-OC (7.5±6.8 for Zhejiang waters, 4.0±2.8 for Fujian waters, 2.6±3.2 for the
563 northern waters of ECS, 1.9±1.7 for eastern waters of Taiwan, and 1.5±1.4 for ECS,
564 respectively) and biomass-burning-OC (2.8±2.6 for Zhejiang waters, 2.7±1.8 for Fujian
565 waters, 1.3±0.92 for the northern waters of ECS, 0.52±0.36 for eastern waters of Taiwan, and

566 0.96±1.7 for ECS, respectively). Such spatial variations were closely associated with different
567 contributions of land and marine sources to the oceanic atmosphere.

568 Figures S2-S6 display a strong influence from land air masses in waters around Zhejiang and
569 Fujian provinces, while the atmosphere over northern waters of ECS, ECS and eastern waters
570 of Taiwan Island basically came under the influence of relatively clean marine air.
571 Interestingly, the average percentage of isoprene SOC in the eastern waters of Taiwan was
572 slightly larger compared to other regions. In light of back trajectory analysis, aerosols in this
573 region were mainly affected by terrestrial photosynthetic vegetation (e.g. trees and plants) in
574 Southeast Asia and/or marine biota (e.g. phytoplankton, seaweed and bacteria) (Fig. S4).
575 Sesquiterpene-derived SOC was found to be the most abundant SOC species in all five areas
576 (2.9±0.87 for Zhejiang waters, 3.1±1.7 for Fujian waters, 2.1±0.80 for the northern waters of
577 ECS, 2.2±1.2 for eastern waters of Taiwan, and 2.2±1.3 for ECS, respectively) in comparison
578 with other SOCs derived from isoprene and monoterpene. On the other hand, the nighttime
579 contributions of biomass-burning OC, fungal-spores OC and biogenic SOCs to OC were
580 commonly greater than the daytime ones in all five regions (Fig. S9). For instance, the
581 contributions of biomass-burning-OC and fungal-spores-OC to OC during nighttime in the
582 seas near Zhejiang (3.9±3.5 and 9.3±8.0, respectively) are significantly greater than those in
583 the daytime (1.9±1.2 and 6.0±6.3, respectively). Such enhanced contributions in the evening
584 were likely to be in connection with intensified emissions, decreased height of PBL and land-
585 sea breeze circulations at night. The downward movement of PBL does not facilitate
586 dispersion of pollutants and lead to increases in aerosol concentration in the lower PBL (Li et
587 al., 2017). The prevailing land breeze in the nighttime in coastal areas could bring plentiful
588 terrestrial particles to the clean marine atmosphere. Such difference between daytime and
589 nighttime contributions illustrates that land-sea breeze circulation and PBL can be another
590 important factor influencing organics in marine aerosols.

591 **3.4 Source apportionment by PMF**

592 **3.4.1 Analysis of source profiles**

593 After testing runs with different number of factors (5–9), eight factors were chosen on basis of
594 the minimum value of Q (goodness of fit parameters) and probable source profile expected
595 from the study region.

596 Figure 10 illustrates the first source had high loadings of Na^+ (90.8%), suggesting a
597 contribution from sea salt. This profile also contained a significant amount of SO_4^{2-} , which
598 can react with sea-salt particles and release HCl gas, leaving lower Cl^-/Na^+ ratio (0.1) than
599 that of sea water (1.8) (Boreddy et al., 2014).

600 The second source shows high loadings of levoglucosan (66.3%), arabitol (55.0%), mannitol
601 (51.1%) and trehalose (50.4%), representing mixed sources of biomass burning and fungal
602 spores (Simoneit et al., 1999; Bauer et al., 2008; Medeiros et al., 2006a). Yang et al. (2012)
603 found an enhanced abundance of fungal tracers on account of biomass burning activities,
604 during which large numbers of fungi could be dispersed into the surrounding atmosphere or
605 be carried upward with the warm plume to other fields via long-distance atmospheric
606 transport.

607 The third source can be interpreted as crustal dust because of high loadings of Mg^{2+} (66.1%)
608 and Ca^{2+} (64.2%), characteristic elements of soil/crustal dust (Xu et al., 2016). This source
609 may include airborne road dust, construction dust and windblown soil particles, which are
610 derived primarily from terrestrial source.

611 The fourth factor is characterized by dominance of NH_4^+ (58.4%) and SO_4^{2-} (49.7%), which
612 can be classified as secondary ammonium sulfate. The molar ratio of NH_4^+ and SO_4^{2-} was 2.9
613 in this profile, suggesting that $(\text{NH}_4)_2\text{SO}_4$ was the dominated sulfate form in the marine
614 atmosphere over the ECS. Due to its long lifetime in the atmosphere, terrestrial SO_4^{2-} could
615 be transported long distance to coastal areas and even to the remote sea (Itahashi et al., 2017),
616 affecting chemical composition of oceanic atmosphere.

617 The fifth factor exhibits high loadings of di-isobutyl (DiBP) and di-n-butyl (DnBP), dominant
618 species of phthalates in the marine aerosols over the ECS, which is assigned to plastic
619 materials' emission likely from industry, agriculture and domestic application in coastal
620 regions.

621 The sixth factor has high loadings from sucrose (85.3%) followed by fructose (50.9%),
622 implies a significant emission from airborne pollen grains to the marine atmosphere over the
623 ECS during late spring to early summer (Fu et al., 2012).

624 The seventh profile presents high loading of Cl, likely to be associated with coal combustion,
625 which provides significant releases of chlorine (McCulloch et al., 1999; Sun et al., 2013).
626 Another confirmation is high concentration of SO_4^{2-} from this profile, since coal consumption
627 can produce mass sulfate as well.

628 The eighth factor illustrates high loadings of NO_3^- (67.5%) and biogenic SOA tracers,
629 especially the monoterpene SOA tracers, i.e. PA (67.5%) and MBTCA (65.2%). This factor
630 could be attributed to the photochemical oxidation products stemmed from emission of
631 vehicle and biogenic VOCs. Formation of secondary nitrate depends on NO_x , which is mainly
632 produced from power plants and mobile sources (Heo et al., 2009; Kim et al., 2006).
633 Anthropogenic NO_x could also enhance biogenic SOA formation via nitrate radical oxidation
634 of monoterpenes (Xu et al., 2015). The positive correlations between NO_x and isoprene-
635 derived SOA tracers as discussed before in our study also suggest NO_3^- and BSOA may share
636 common formation and/or transport pathways. Previous studies have reported that nitrogen-
637 containing species act a pivotal part in the formation and fate of SOA through varying radical
638 and oxidant regimes and particle properties, such as volatility and hygroscopicity (Chen et al.,
639 2017), agreeing well with our results.

640 Overall, the eight sources based on PMF were sea salt, biomass burning and fungal spores,
641 crustal dust, secondary sulfate ammonia, plastic emission, pollen grains, coal combustion, and
642 secondary nitrate and BSOA, which contributed to the TSP over the ECS of 16.9%, 3.5%,
643 8.0%, 28.5%, 6.3%, 2.0%, 14.3% and 20.4%, respectively. The results of PMF present that
644 secondary origin and marine natural emissions could be the main sources for the aerosols over
645 the ECS. Figure 11 shows the contributions of different sources to OC in marine aerosols. On
646 the whole, secondary nitrate and BSOA (25.5%), and biomass burning and fungal spores
647 (19.5 %) contributed more to OC than other sources during the whole sampling periods,
648 elucidating the significant influence of biogenic primary and secondary sources on marine
649 organic aerosols.

650 **3.4.2 Temporal and spatial variation in sources**

651 Figure 12 shows the temporal and spatial variation in each profile during the day and the night.
652 The contribution of each source changes over time and varies with distance from the continent.
653 In general, higher levels contributed by biomass burning, fungal spores, crustal dust, pollen
654 grains, coal combustion, secondary nitrate and BSOA, were basically observed in coastal
655 aerosols and/or terrestrially influenced aerosols, suggesting strong influence of continental air
656 from East Asia and Southeast Asia in light of the back trajectories and wind directions during
657 the sampling periods (Fig. S2-S6 and S10). However, the contributions from sea-salt particles,
658 indicative of oceanic emission (organic components can be emitted from the ocean surface
659 together with sea-salt particles via sea spray or bubble bursting), tend to be higher in the

660 aerosols mainly affected by marine air masses. Our study demonstrates that primary and
661 secondary OM of terrestrial origin play an important role in the marine aerosol chemistry over
662 the western North Pacific through long-range atmospheric transport in addition to natural
663 emission of ocean.

664

665 **4 Conclusions**

666 In summary, atmospheric concentration, spatial distribution and source apportionment of
667 sugars and biogenic SOA tracers were studied for the coastal and remote marine aerosols.
668 Higher concentrations of sugars and BSOA tracers were observed in the atmosphere around
669 coastal waters and/or in the terrestrially influenced regions in comparison with the remote
670 oceans, suggesting that continent origin contributed a lot to the abundance of sugars and
671 BSOA tracers in the marine atmosphere. Glucose was the dominant sugar species, followed
672 by mannitol among the total identified sugar compounds. Biogenic SOC were characterized
673 by a predominance of β -caryophyllene oxidation products in comparison with isoprene and
674 α/β -pinene tracers. The contributions of biomass-burning-derived OC, fungal-spore-derived
675 OC, and biogenic SOC to OC (%) were greater in the marine aerosols affected by land air
676 masses. The results of PMF illustrate that secondary nitrate, BSOA, biomass burning, and
677 fungal spores could be the major contributors to OC in marine aerosols over the ECS. Our
678 study demonstrates that both primary and secondary organic aerosols of terrestrial origin have
679 great influences on the marine aerosol chemistry over the western North Pacific through long-
680 range atmospheric transport.

681

682 **Data availability.** The data for this paper are available upon request from the corresponding
683 author (fupingqing@tju.edu.cn).

684

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

686

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1127 **Table 1.** Concentrations (ng m⁻³) of saccharides and biogenic SOA tracers measured in the
 1128 marine aerosols collected over the East China Sea during May to June 2014.

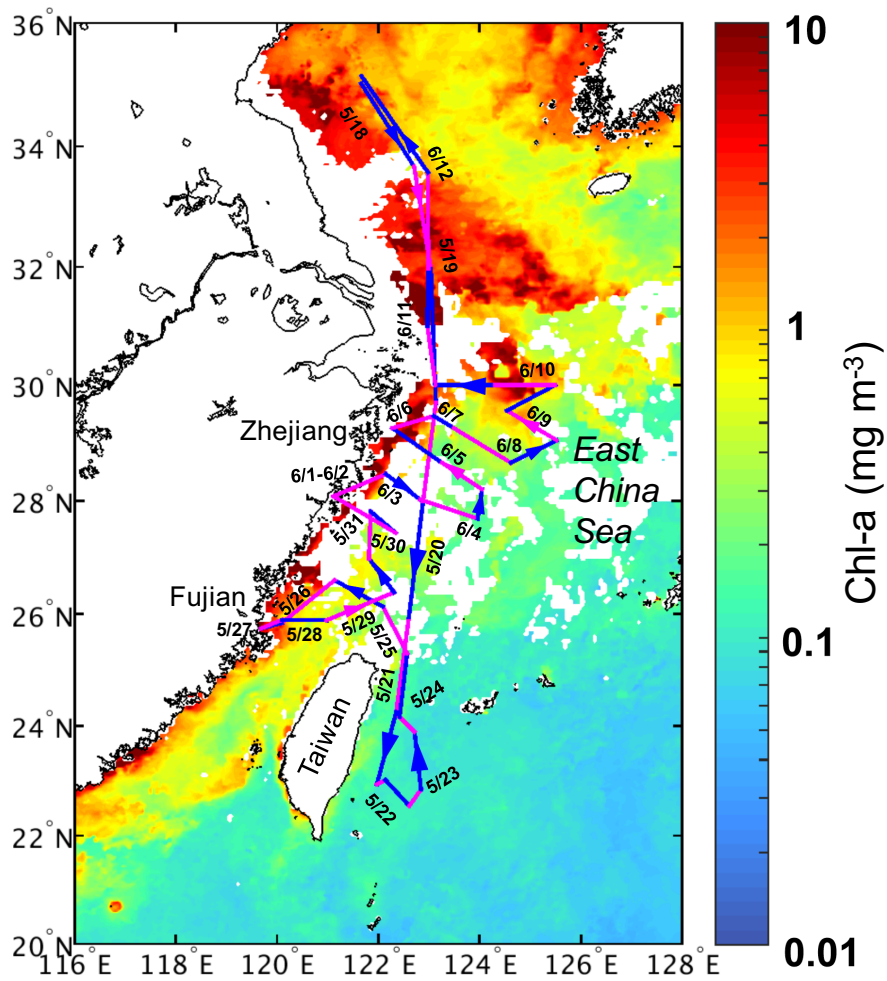
Compounds	Whole period (n = 51)		Daytime (n = 25)		Nighttime (n = 26)	
	Mean	Range	Mean	Range	Mean	Range
<i>Anhydrosugars</i>						
Galactosan	0.59	0.02–3.9	0.56	0.04–3.6	0.62	0.02–3.9
Mannosan	1.4	0.06–10.2	1.2	0.08–5.2	1.6	0.06–10.2
Levoglucozan	7.3	0.09–64.3	6.1	0.09–41.2	8.4	0.10–64.3
<i>Sugar Alcohols</i>						
Erythritol	1.3	n.d. ^a –16.9	0.87	0.02–4.60	1.6	n.d.–16.9
Arabitol	5.1	0.02–51.0	4.5	0.06–26.7	5.7	0.02–51.0
Mannitol	16.3	0.03–169	14.1	0.08–81.3	18.4	0.03–169
Inositol	0.57	0.01–7.7	0.47	0.01–2.8	0.67	0.01–7.7
<i>Sugars</i>						
Fructose	9.1	0.09–106	8.1	0.09–56.5	10.2	0.32–106
Glucose	18.8	0.31–209	17.8	0.31–106	19.7	0.47–209
Sucrose	11.7	0.09–216	9.7	0.14–136	13.5	0.09–216
Trehalose	9.4	0.08–96.0	9.1	0.08–60.7	9.7	0.10–96.0
Subtotal	81.5	1.8–950	72.6	1.0–525	90.1	1.8–950
<i>Isoprene SOA tracers</i>						
2-methylthreitol	1.5	0.01–12.7	1.2	0.04–5.2	1.9	0.01–12.7
2-methylerythritol	3.2	0.02–29.1	2.5	0.08–11.8	3.9	0.02–29.1
Sum of 2-methyltetrols	4.8	0.03–41.9	3.8	0.11–17.0	5.7	0.03–41.9
2-Methylglyceric acid (2-MGA)	1.4	0.09–8.3	1.2	0.20–3.6	1.6	0.09–8.33
C ₅ -Alkene triols ^b	2.2	0.03–14.6	2.1	0.06–14.6	2.3	0.03–13.8
Subtotal	8.4	0.15–64.0	7.1	0.42–35.2	9.6	0.15–64.0
<i>α/β-pinene (monoterpene) SOA tracers</i>						
3-Hydroxyglutaric acid (3-HGA)	2.2	0.03–14.1	2.3	0.08–14.1	2.1	0.03–7.7
Pinonic acid (PNA)	0.47	0.02–1.6	0.49	0.06–1.6	0.46	0.02–1.6
Pinic acid (PA)	3.4	0.16–14.9	3.4	0.28–14.9	3.3	0.16–13.6
MBTCA	5.6	n.d.–56.9	6.8	n.d.–56.9	4.5	n.d.–24.5
Subtotal	11.6	0.26–87.2	13.0	0.45–87.2	10.3	0.26–43.7
<i>β-caryophyllene (sesquiterpene) SOA tracers</i>						
β-Caryophyllinic acid	2.9	0.16–17.2	3.5	0.17–17.2	2.3	0.16–9.6
Total measured tracers	22.9	1.1–135	23.6	1.4–135	22.2	1.1–115

^a n.d. denotes not detected. ^b C₅-alkene triols: cis-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene and trans-2-methyl-1,3,4-trihydroxy-1-butene.

1130 **Table 2.** Concentrations of organic carbon (OC) (ngC m⁻³) from biogenic primary emission
 1131 (biomass-burning OC and fungal-spore OC) and biogenic SOC and their contributions in
 1132 aerosol OC (%) in marine aerosols over the East China Sea.

Component	Total			Daytime			Nighttime		
	Range	Mean	std	Range	Mean	std	Range	Mean	std
Concentration (ngC m ⁻³)									
Aerosol OC	424–14100	4260	3480	1030–14100	4940	3800	424–9830	3600	3080
Biomass burning OC	1.1–790	89.6	156	1.1–506	75.5	117	1.3–790	103	187
Fungal spore OC	1.2–1840	180	334	1.3–911	157	249	1.2–1840	203	403
Isoprene SOC ^a	0.78–324	39.8	55.4	2.3–133	32.1	37.6	0.78–324	47.2	68.3
Monoterpene SOC	1.1–377	50.2	72.0	1.9–377	56.1	84.3	1.1–189	44.6	58.9
Sesquiterpene SOC	6.9–747	126	153	7.4–747	153	183	6.9–416	100	114
Sum of biogenic SOC	11.3–1060	216	250	13.7–1060	241	279	11.3–824	192	222
Subtotal	16.1–3460	486	688	29.8–2480	473	600	16.1–3460	498	776
Percentage in aerosol OC (%)									
Biomass burning OC	0.05–8.5	1.5	1.8	0.05–4.4	1.1	1.2	0.13–8.5	1.8	2.3
Fungal spore OC	0.03–19.8	3.1	4.0	0.03–16.6	2.6	3.7	0.18–19.7	3.5	4.2
Isoprene SOC	0.13–3.8	0.83	0.87	0.13–2.0	0.60	0.54	0.14–3.8	1.0	1.1
Monoterpene SOC	0.08–3.5	0.98	0.90	0.10–3.3	1.00	0.95	0.08–3.5	0.96	0.87
Sesquiterpene SOC	0.36–5.3	2.4	1.2	0.36–5.3	2.5	1.4	0.87–5.1	2.4	1.1
Sum of biogenic SOC	0.67–9.3	4.2	2.2	0.67–9.3	4.1	2.2	1.8–8.8	4.4	2.2
Subtotal	1.5–37.0	8.7	6.9	1.5–27.4	7.8	6.3	2.8–37.0	9.7	7.4

^a The total mass concentrations of SOC produced by isoprene (2-methylglyceric acid and 2-methyltetrols were used), α/β -pinene, and β -caryophyllene were estimated using the tracer-based method by Kleindienst et al. (2007).

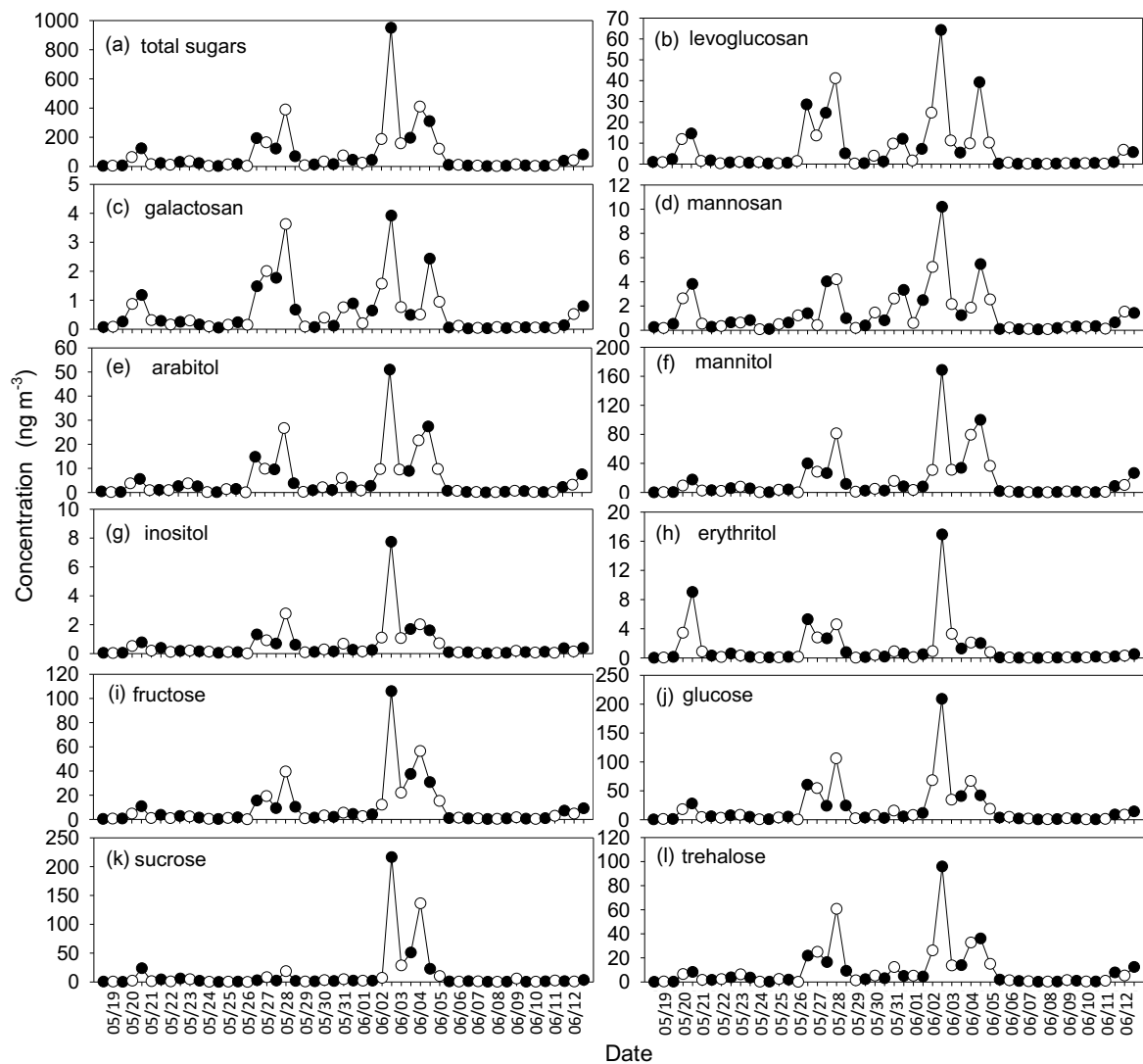


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1135 **Figure 1.** Cruise tracks of KEXUE-1 and spatial distribution of satellite-derived chlorophyll-a
 1136 concentrations (chl-a , mg m^{-3}) in surface seawater derived from MODIS L3 products during
 1137 the sampling period in the East China Sea. The purple and blue lines represent daytime and
 1138 nighttime aerosol samples, respectively.

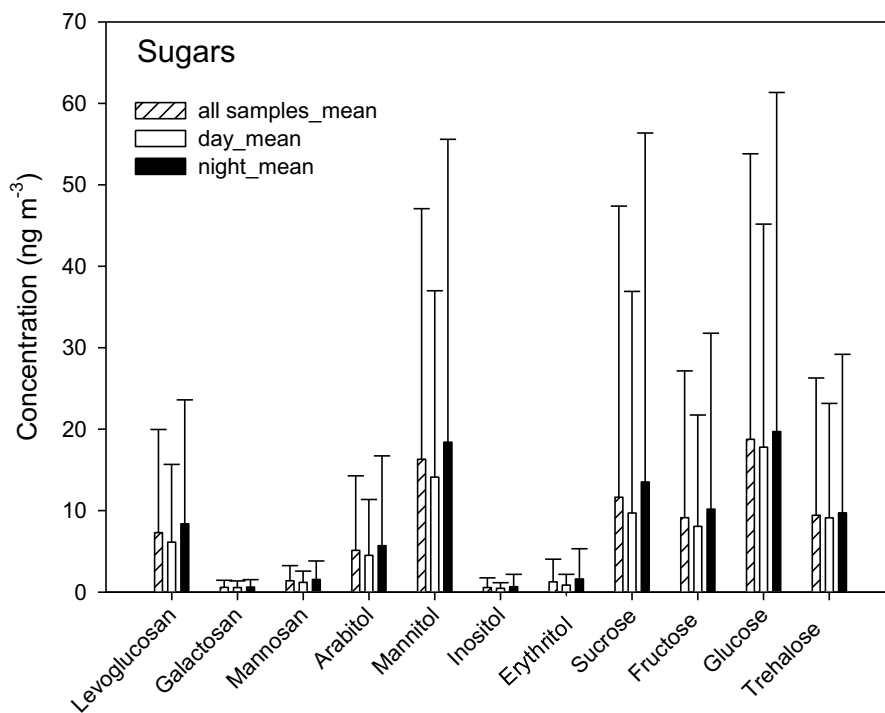
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1142 **Figure 2.** Temporal variations in sugar compounds in marine aerosols collected over the East
1143 China Sea. The open and shaded circles represent daytime and nighttime values, respectively.

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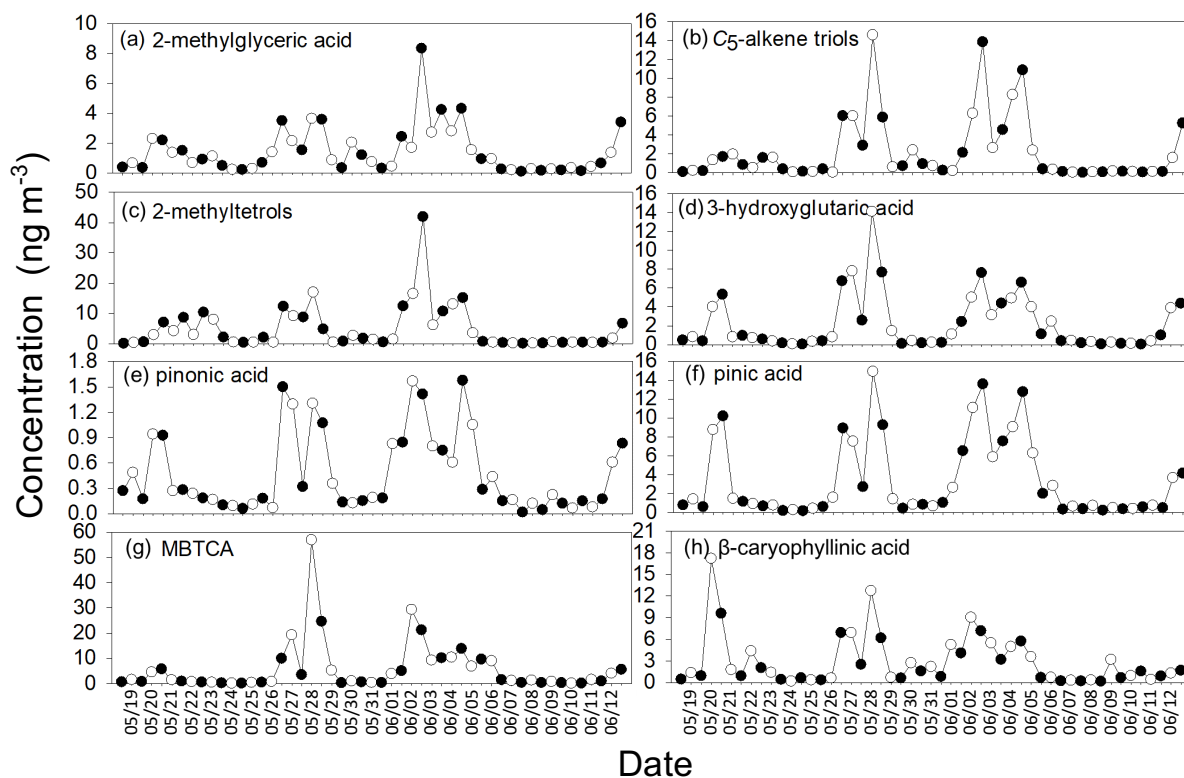
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1147 **Figure 3.** Average concentrations of sugars detected in marine aerosols over the East China

1148 Sea.

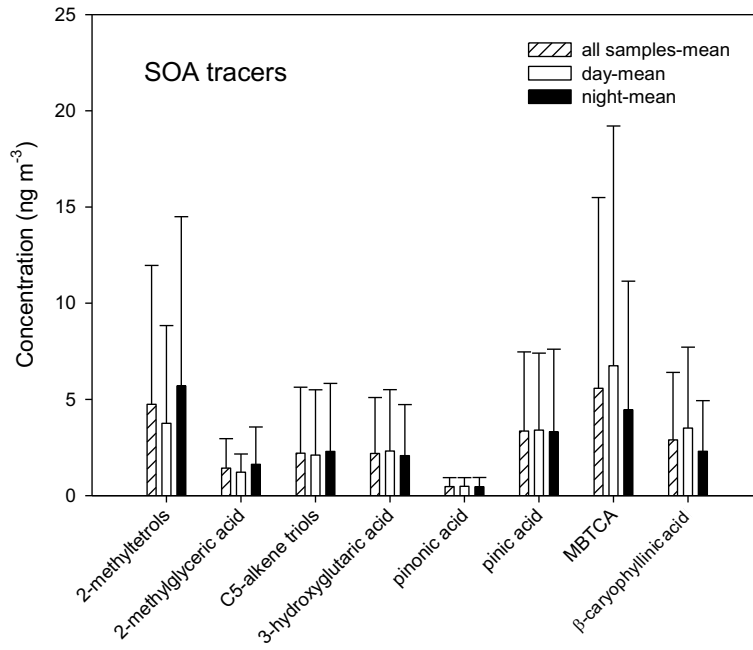
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1152 **Figure 4.** Temporal variations in biogenic SOA tracers detected in marine aerosols over the
1153 East China Sea during May to June 2014. The open and shaded circles represent daytime and
1154 nighttime values, respectively.

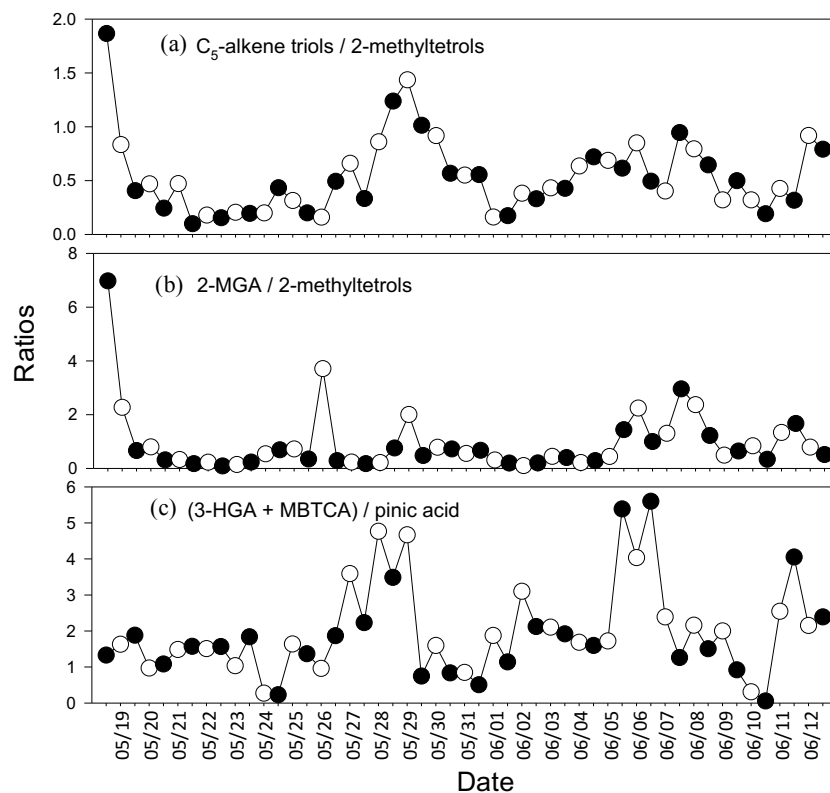
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1158 **Figure 5.** Average concentrations of SOA tracers detected in marine aerosols over the East
1159 China Sea.

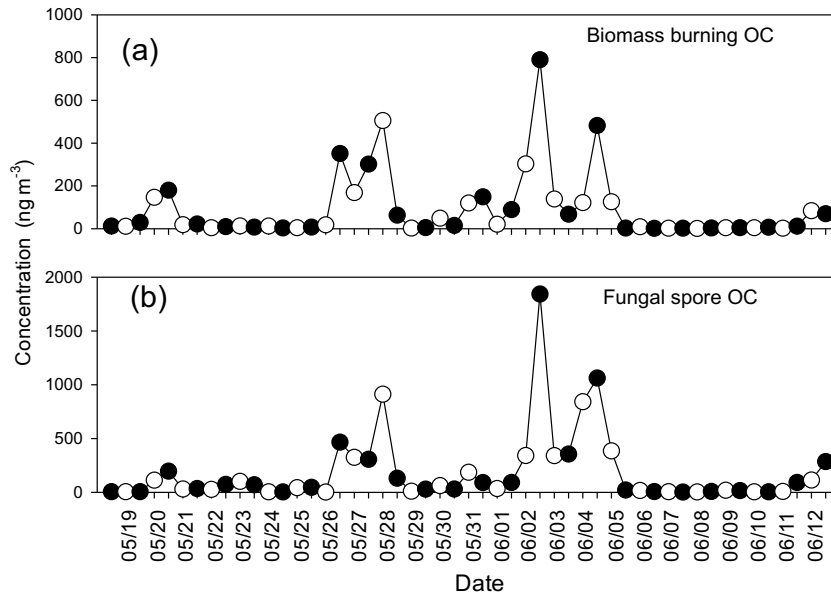
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1163 **Figure 6.** Temporal variations in the concentration ratios of isoprene and α/β -pinene oxidation
 1164 products in the marine aerosols over the East China Sea. The open and shaded circles
 1165 represent daytime and nighttime samples, respectively.

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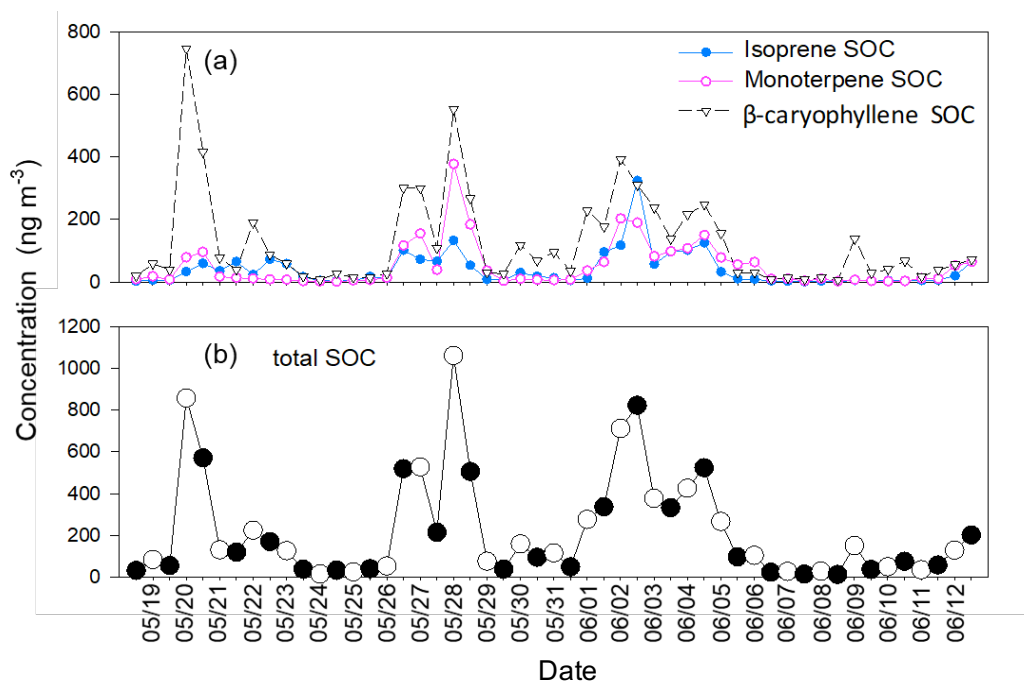


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1169 **Figure 7.** Temporal variations in (a) biomass-burning-derived OC, and (b) fungal-spore-
 1170 derived OC in the marine aerosols over the East China Sea. The open and shaded circles
 1171 represent daytime and nighttime samples, respectively.

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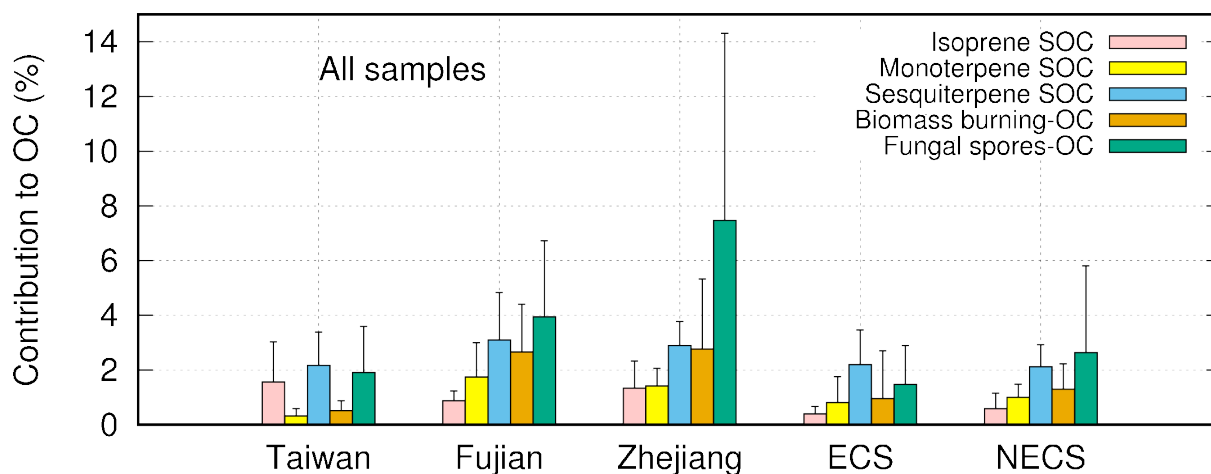


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1175 **Figure 8.** Temporal variations in (a) secondary organic carbon (SOC) derived from isoprene,
 1176 α/β -pinene and sesquiterpene and (b) the total SOC levels in the marine aerosols over the East
 1177 China Sea during May to June 2014. The open and shaded circles represent the daytime and
 1178 nighttime samples, respectively.

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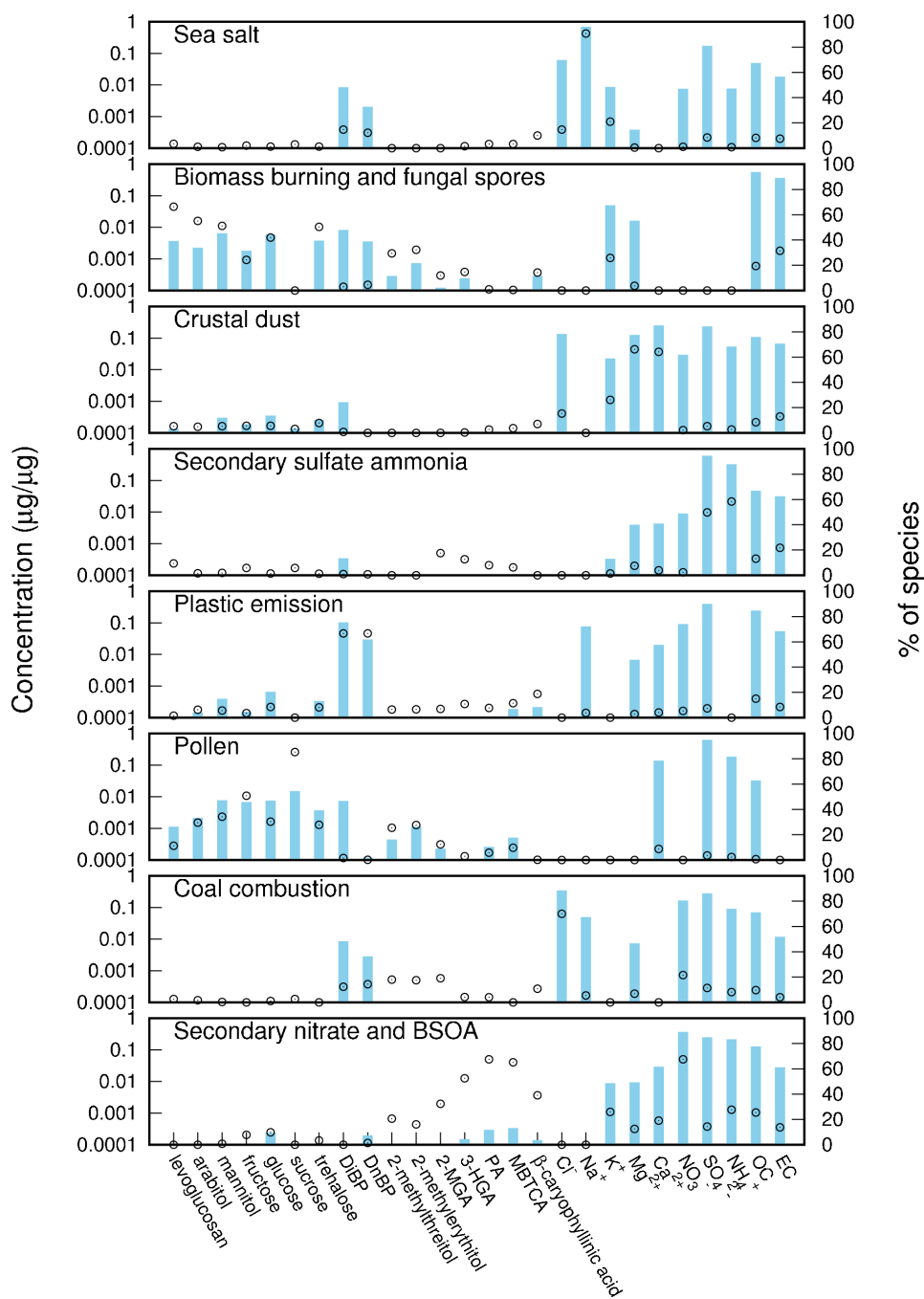


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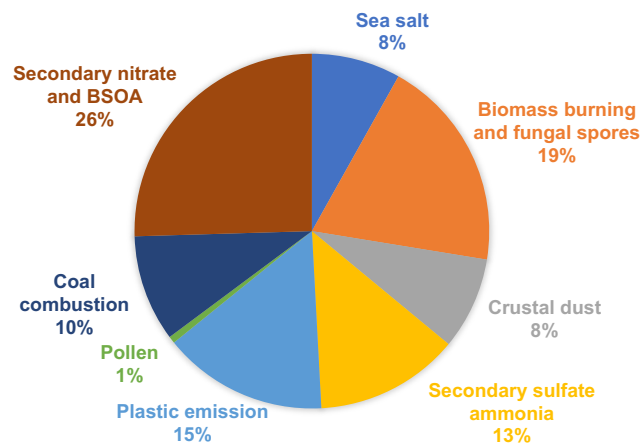
1182 **Figure 9.** Contributions of OC (ngC m⁻³) from biogenic primary emission (biomass-burning
 1183 OC and fungal-spore OC) and biogenic SOC to OC (%) in different sampling regions. Taiwan,
 1184 Fujian and Zhejiang refer to the waters around Taiwan, Fujian and Zhejiang; ECS represents
 1185 East China Sea waters; NECS represents northern waters of ECS.

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Figure 10. Source profiles identified by PMF. Blue bars represent the mass contribution with y-axis on the left, while black dots stand for the percentage of species to the sum with y-axis on the right.



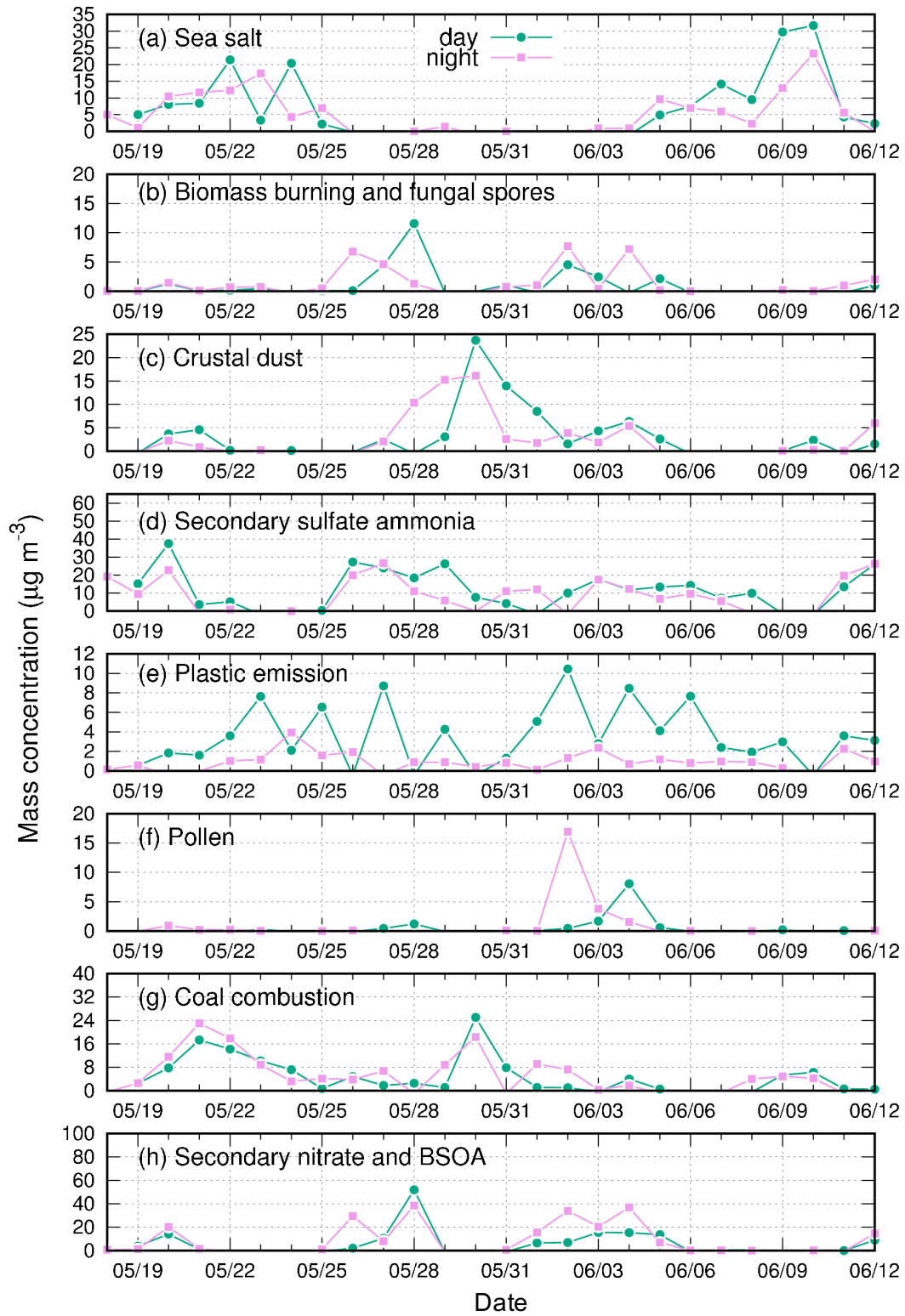
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1195 **Figure 11.** Contributions of different sources to organic carbon (OC) in marine aerosols over

1196 the East China Sea.

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1200 **Figure 12.** Temporal variation in sources contributed to marine aerosols ($\mu\text{g m}^{-3}$).