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1 **Seasonal characteristics of biogenic secondary organic aerosols over Chichijima Island in**
2 **the western North Pacific: Impact of biomass burning activity in East Asia**

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18 Key Points:

- 19 1. We report 3-year observations of biogenic secondary organic aerosols (BSOAs) at
20 Chichijima Island in the western North Pacific.
- 21 2. Monoterpene oxidation products are the significant sources for BSOAs, followed by
22 isoprene and β -caryophyllene oxidation products in Chichijima aerosols.
- 23 3. High-NO_x BSOA tracers (2-MGA, 3-HGA, and 3-MBTCA) are influenced by a long-
24 range transport of anthropogenic air masses and low-NO_x BSOA tracers (2-MTLs and C5-
25 alkene triols) are produced mainly by the oxidation of locally emitted isoprene.
- 26 4. Biomass burning aerosols contribute to β -caryophyllene-derived BSOA tracer by
27 atmospheric oxidation during long-range transport from the Asian continent over the
28 western North Pacific.

29

30 Abstract

31 To better understand the formation processes of biogenic secondary organic aerosols (SOAs)
32 over remote oceanic regions, aerosol samples were collected from 2010 to 2012 at Chichijima
33 Island in the western North Pacific (WNP). The samples were analyzed by gas
34 chromatography-mass spectrometry for SOA tracers, which are produced by the photochemical
35 oxidation of biogenic volatile organic compounds (BVOCs), including isoprene, monoterpene
36 and sesquiterpene. Although no seasonal trend was identified for the isoprene-derived SOA
37 tracers, we observed higher levels of the monoterpene-derived and sesquiterpene-derived SOA
38 tracers in winter/spring and lower levels in summer/autumn. We found a significant correlation
39 ($r = 0.87$) of β -caryophyllinic acid with levoglucosan, the latter being a specific tracer of
40 biomass burning (BB). This suggests that the β -caryophyllene accumulated in higher plants is
41 evaporated by BB followed by atmospheric oxidation during long-range transport from the
42 Asian continent over the WNP. The biogenic secondary organic carbon concentration
43 estimated using a tracer-based approach ranged from 0.11–174 ngC m⁻³ (avg. 34.8±38.2 ngC
44 m⁻³), accounting for 0.02–32.0% (avg. 6.11±6.42%) of the measured organic carbon. Our
45 results indicate that SOAs are formed by the photooxidation of BVOCs. The backward
46 trajectories of air masses further support their transport from the central Pacific during mid-
47 spring to mid-autumn, whereas BB aerosols are transported from the Asian continent during
48 mid-autumn to mid-spring over the WNP. Positive matrix factorization analyses of the SOA
49 tracers suggest that organic aerosols of Chichijima are mostly related to BVOC emissions, with
50 BB's additional contributions especially in winter and spring. (248)

51 **Keywords:** Biogenic SOA tracers, biomass burning, continental influence, remote marine
52 aerosols.

53

54 1. Introduction

55 Atmospheric aerosols are derived from various natural and anthropogenic sources
56 (Robinson et al., 2006; de Gouw and Jimenez, 2009). Primary aerosols are directly emitted
57 from continents, oceans, arid regions, volcanic eruptions, fossil fuel combustion, and biomass
58 burning (BB). Conversely, secondary aerosols are formed by photochemical reactions via gas-
59 to-particle conversion in the atmosphere (Hallquist et al., 2009). Secondary organic aerosols
60 (SOAs) are abundant, representing one of the most important components of carbonaceous
61 aerosols that significantly affect the atmospheric radiation budget, both directly by scattering
62 sunlight and indirectly by acting as cloud condensation nuclei (CCN) (Kanakidou et al., 2005).
63 Considerable efforts have been devoted in recent decades to developing an understanding of
64 SOA formation by the photooxidation of volatile organic compounds (VOCs) of anthropogenic
65 and biogenic origin (Kavouras et al., 1998). Biogenic VOCs (BVOCs) are emitted from
66 terrestrial vegetation and marine biota (Guenther et al., 2006).

67 Guenther et al. (1995) estimated the annual global emission of BVOCs to be 1150
68 TgC yr⁻¹, of which isoprene and monoterpenes accounted for 44% and 11%, respectively.
69 Similarly, Piccot et al. (1992) reported the emission of 110 TgC yr⁻¹ of anthropogenic VOCs
70 (AVOCs), which is one order of magnitude lower than that of BVOCs. Hallquist et al. (2009)
71 reported the global production of SOAs from BVOCs to be 9–910 TgC yr⁻¹. The contribution
72 of BVOCs to SOA formation is much greater (8–40 Tg yr⁻¹) than that of AVOCs (0.3 to 1.8 Tg
73 yr⁻¹) (Intergovernmental Panel on Climate Change, 2001). The emissions of BVOCs followed
74 by SOA formation are expected to have a significant impact on the chemical composition and
75 physical properties of tropospheric aerosols and thus climate change (Fowler et al., 2009).
76 Although the AVOC contribution to SOA formation frequently exceeds 50% in urban areas
77 due to the influence of human activities (Ding et al., 2012; von Schneidmesser et al., 2009), it
78 is likely much smaller in the remote marine atmosphere.

79 The global production of SOAs from marine sources has been considered less
80 important than from terrestrial sources. Meskhidze and Nenes (2006) suggested that marine
81 phytoplankton could be an emission source of BVOCs and SOA formation. However, studies
82 of the oxidation products of BVOCs in the remote marine atmosphere are limited in number.
83 We note that remote marine aerosols would provide a unique opportunity to examine the
84 atmospheric chemistry of BVOCs due to their being so far away from the anthropogenic
85 sources on the continent. A potential source of SOAs in the free troposphere has been reported

86 to be the atmospheric oxidation of long-lived VOCs (Heald et al., 2005). Isoprene was included
87 as an SOA precursor in a global model developed by Henze and Seinfeld (2006). Studies on
88 SOA formation are essential for understanding the aerosol-cloud-climate system over the
89 remote oceans (Meskhidze and Nenes, 2006).

90 The authors of several chamber studies have reported the anthropogenic influence on
91 the formation of biogenic SOAs (BSOAs). Ding et al. (2014) found NO_x levels to significantly
92 influence the concentrations of BSOA tracers in the atmosphere. Surratt et al. (2006) and
93 Zhang et al. (2011) demonstrated that 2-methyltetrols are most likely generated under low- NO_x
94 and high relative humidity (RH) conditions, whereas 2-methylglyceric acid is generated under
95 high- NO_x and low RH conditions. Surratt et al. (2010) proposed that high- NO_x and low RH
96 levels affected the formation of C_5 -alkene triols. The results of chamber experiments conducted
97 by Claeys et al. (2007) and Szmigielski et al. (2007) demonstrated the formation of 3-
98 hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid under UV-radiation in the
99 presence of NO_x . Similarly, it is assumed that the anthropogenic NO_x emitted from the Asian
100 continent is transported together with anthropogenic aerosols to Chichijima Island in the
101 western North Pacific (WNP) (Boreddy et al., 2015). Under favorable meteorological
102 conditions, NO_x may affect the seasonal concentrations and formation mechanisms of BSOA
103 tracers over the remote ocean.

104 The vehicular emissions and BB in the East Asian countries are the primary sources of
105 NO_x , which might be significantly transported to the downwind regions. The anthropogenic
106 nitric oxide (NO) reacts with O_3 to form NO_2 and subsequently converts to nitrate (NO_3)
107 radicals. The long lifetime of VOCs and their oxidation by photolabile NO_3 provide additional
108 pathways for SOA formation, which is enhanced under high- NO_x conditions (Hoyle et al.,
109 2011). Hoyle et al. (2007) reported a global modeling study where oxidation of SOA
110 precursors by NO_3 in nighttime increases up to 21% of the global average SOA burden. Brown
111 et al. (2009) reported that NO_3 initiated isoprene oxidation process increased up to 17% of
112 SOA formation in the northeastern US. Ng et al. (2008) estimated that ~ 2 to $3 \text{ Tg of SOA yr}^{-1}$
113 result from isoprene reaction with NO_3 . Moreover, in the industrialized region, the average
114 percentage increased to around 50–60%, suggesting the significance of anthropogenic
115 emissions for the SOA formation pathway (Hoyle et al., 2007).

116 The East Asian monsoon significantly affects the regional climate and air quality of the
117 outflow regions in the WNP (Yamamoto et al., 2011). Over Chichijima in the WNP, pristine

118 air masses usually travel from the Pacific Ocean in summer and autumn by easterly winds,
119 whereas polluted air masses from the Asian continent are transported over the WNP in winter
120 and spring by westerly winds (Chen et al., 2013). Verma et al. (2015) reported high
121 concentrations of BB tracers in total suspended particulate (TSP) samples collected from
122 Chichijima during winter and spring. Verma et al. (2018) discussed the influence of long-range
123 atmospheric transport on the seasonal distributions of sugar components in Chichijima aerosols.
124 A long-term (2001–2012) study of TSP samples from Chichijima found NO_3^- to be more
125 abundant in winter and spring than summer and autumn over the WNP (Boreddy et al., 2015).
126 The above studies demonstrate that atmospheric circulation and wind patterns control
127 atmospheric aerosols seasonal sources and compositions over the Pacific Ocean.

128 In addition to continental emissions, followed by long-range atmospheric transport the
129 marine atmosphere is also affected by oceanic emissions. Therefore, it is essential to
130 investigate the SOA tracers in remote marine aerosols to determine their origin and impacts on
131 the regional and global climates. In this study, we analyzed TSP samples collected from
132 Chichijima to determine the molecular characteristics of the SOA tracers, and their abundances
133 and sources over the WNP. Here, we discuss the influence of the local meteorology,
134 atmospheric circulations, and long-range atmospheric transport of BVOCs and pollutants on
135 the abundance of SOAs in Chichijima aerosols. We performed a diagnostic mass concentration
136 ratio analysis, a tracer-based approach, and a positive matrix factorization (PMF) analysis at
137 annual and seasonal scales to explore the variations in SOA tracers concentrations and sources
138 over the WNP.

139 **2. Materials and Methods**

140 **2.1. Sampling Site and Aerosol Sample Collection**

141 The sampling site (Chichijima: 27.06°N and 142.21°E) is located at the Ogasawara
142 Downrange Station of the Japan Aerospace Exploration Agency (JAXA) on Chichijima Island
143 (Figure 1). A detailed description of the sampling site is given in Kawamura et al. (2003).
144 Briefly, Chichijima is a small remote island located in the WNP approximately 2000 km east
145 of the Asian continent and 1000 km south of Tokyo, Japan. The total area of the island is 24
146 km^2 , and its population is about 2000. The climate of Chichijima is classified as subtropical.
147 The island is too far away from the Asian continent to receive monsoonal rainfall on the
148 equator ward side of the Siberian High and too far south to be influenced by the Aleutian Low.

149 Figure 2 shows the monthly average values of the meteorological parameters over
150 Chichijima Island during the campaign. Its climate is a humid year around. The monthly mean
151 RH was found to be lowest in January 2011 (62%) and highest in June 2012 (89%), with an
152 average of 77% during the study period. The monthly mean temperatures ranged from 7.8 °C
153 in January to 34.1 °C in August (avg. 23.5 °C). More precipitation events were recorded at the
154 sampling site between April and July and September and October. The total precipitation
155 amounts were 1393, 942, and 1229 mm, respectively, in 2010, 2011, and 2012. A broad-leaved
156 evergreen forest covers a large part of the island. The vegetation of Chichijima is characterized
157 by rich endemic flora (75%) and short trees with sclerophyllous leaves on the ridge sites. The
158 plants typically experience severe drought in July and early summer, especially on the ridge
159 sites, due to low precipitation levels, high temperatures, and shallow volcanic soil. Typhoons
160 also affect the climate and vegetation of Chichijima as these frequently occur from mid-
161 summer to mid-autumn.

162 Detailed descriptions of the TSP samples collected at Chichijima Island are given in
163 Mochida et al. (2010) and Chen et al. (2013). Briefly, a high-volume air sampler (Kimoto
164 AS810A) was placed at JAXA's Ogasawara Downrange Station on Chichijima. The samples
165 were collected on precombusted (450 °C for 6 h) quartz fiber filters at a flow rate of 1.0 m³
166 min⁻¹ on a weekly basis from January 2010 to December 2012. After sample collection, to
167 prevent microbial activity and the loss of semi-VOCs from the samples, the individual filters
168 were placed in a precombusted glass jar with a Teflon-lined screw cap and stored in a dark,
169 cold room at -20 °C until analysis. In this study, a total of 171 filter samples were analyzed,
170 including 17 field blanks.

171 **2.2. Extraction and Derivatization of Samples**

172 Approximately 21 cm² of each of the sample filters were extracted with a
173 dichloromethane and methanol mixture (2:1) under ultrasonication. The extracts were filtered
174 through a Pasteur pipette packed with precombusted quartz wool to remove filter debris and
175 then concentrated in a rotary evaporator under vacuum and dried by nitrogen blowdown. To
176 convert the hydroxy groups into corresponding trimethylsilyl (TMS) ethers and the carboxyl
177 groups into TMS esters, the extracts were then derivatized with N,O-
178 bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% TMS chloride in the presence of 10 µL
179 of pyridine in a 1.5 mL precombusted glass vial sealed with a Teflon-lined screw cap at 70 °C

180 for three hours. More details regarding the extraction and derivatization procedures are
181 reported in Fu et al. (2008).

182 2.3. Gas Chromatography–Mass Spectrometry Determination of SOA Tracers

183 Before injection into a gas chromatograph-mass spectrometer (GC-MS), the derivatized
184 fraction was diluted with *n*-hexane containing an internal standard of *n*-C₁₃ alkane (1.43 ng
185 μL^{-1}). GC-MS analyses of samples were performed on an Agilent model 7890 GC coupled to
186 an Agilent model 5975 mass selective detector (MSD). The mass spectrometer was operated in
187 the electron ionization (EI) mode at 70 eV and scanned in the *m/z* range 40–650 Da. The GC
188 was equipped with a split/splitless injector and a DB-5MS fused silica capillary column (30 m
189 \times 0.25 mm in diameter, 0.25 μm film thickness). The GC oven temperature was programmed
190 to be 50 °C for 2 min at a rate of 15 °C min^{-1} from 50 to 120 °C, then from 120 to 305 °C at
191 5 °C min^{-1} . The final isotherm holds at 305 °C for 15 min. Helium was used as the carrier gas
192 at a flow rate of 1.0 mL min^{-1} . The sample was injected on a splitless mode at 280 °C injector
193 temperature. GC-MS data were acquired and processed with an Agilent GC/MSD ChemStation
194 software.

195 The compound masses were also compared using the relative response factors
196 determined by the injection of authentic standards and those reported in the literature and
197 library texts. The average response factors of internal standard calibration for the surrogates
198 were average of 2.18. In total 11 BSOA tracers including 2-methylthreitol (2-MTL₁), 2-
199 methylerythritol (2-MTL₂), 2-methylglyceric acid (2-MGA), *cis*-2-methyl-1,3,4-trihydroxy-1-
200 butene, 3-methyl-2,3,4-trihydroxy-1-butene, *trans*-2-methyl-1,3,4-trihydroxy-1-butene (C₅-
201 alkene triols), *cis*-pinonic (PNA), pinic acids (PA), 3-methyl-1,2,3-butanetricarboxylic acid (3-
202 MBTCA), 3-hydroxyglutaric acid (3-HGA) and β -caryophyllinic acid were detected in
203 Chichijima aerosol.

204 2.4. Quality Assurance and Quality Control

205 A total ion chromatogram (TIC) provides a reliable approach for tracer quantification in
206 the absence of authentic standards. Kleindienst et al. (2007) used TMS derivatives of ketopinic
207 acid for quantitative estimation of SOA tracers because no standards were available for the
208 majority of the compounds. In this study, GC-MS response factors were determined using
209 authentic standards of PNA, PA, 3-HGA and meso-erythritol to quantify SOA tracers. The
210 concentrations of 2-MTLs (2-MTL₁ and 2-MTL₂), 2-MGA, and C₅-alkene triols were

211 estimated using the response factor of meso-erythritol (Wang et al., 2008; Kourtchev et al.,
 212 2008), whereas the response factor of PA was used to quantify 3-MBTCA and β -
 213 caryophyllinic acid (Jaoui et al., 2007; Ding et al., 2011) due to the unavailability of
 214 commercial standards. The EI spectrum and TIC with the retention time, observed MS
 215 fragments and relative ratio of fragments of each tracers compounds were presented in Figures
 216 S1 and S2a–S2k, which supported a correct identification of the SOA tracers. The ionization
 217 and mass fragmentation of target SOA tracers are different from the surrogate standards.
 218 Therefore, the substantial uncertainties caused by different surrogate standards were estimated
 219 based on the method described in Stone et al. (2012).

220 The recoveries of authentic standards or surrogates that were spiked onto a
 221 precombusted quartz fiber filters ($n = 3$) were $90 \pm 5\%$ for 3-HGA, $93 \pm 4\%$ for meso-
 222 erythritol, $89 \pm 3\%$ for PNA, and $78 \pm 4\%$ for PA. Based on the duplicate analysis, the
 223 analytical errors in the detected compounds concentrations were determined to be within 10%.
 224 Field blanks were collected every two months during the campaign at the observation site,
 225 which was analyzed as the real samples. The measured SOA tracers were not detected in these
 226 field blanks. The method detection limits (MDL) for 3-HGA, meso-erythritol, PNA acid and
 227 PA were 3.2, 4.3, 1.2 and 2.6 pg m^{-3} , respectively, under a typical sampling volume of 4500
 228 m^3 .

229 2.5. Estimation of Measurement Uncertainty

230 The standards for PNA, PA and 3-HGA are available commercially among all the
 231 measured SOA tracers in this study. Hence, the additional error introduces for the
 232 quantification while using surrogate standards in the analytical measurements. The
 233 uncertainties in the measurements of SOA tracers were calculated by the following equation
 234 developed by Stone et al. (2012):

$$235 \quad E_A = \sqrt{E_{FB}^2 + E_R^2 + E_Q^2} \quad (\text{Eqn. - 01})$$

236 where E_A is an error in analyte measurement, E_{FB} is the standard deviation of the field blank,
 237 E_R is the error in spike recovery, and E_Q is the error from surrogate quantification. E_{FB} was 0 in
 238 this study because no target compounds were detected in the field blanks. The spike recoveries
 239 of surrogate standards were used to estimate the E_R of SOA tracers, ranging from 2 to 23%. An
 240 empirical approach was developed by Stone et al. (2012) to estimate E_Q based on the

241 homologous series of atmospherically relevant compounds. The relative error introduced by
 242 each carbon atom (E_n) was estimated to be 15%, each oxygenated functional group (E_f) to be
 243 10%, and alkenes (E_d) to be 60%. The errors introduced from surrogate quantification are
 244 treated as an additive and are calculated with Eqn. - 02,

$$245 \quad E_Q = E_n \Delta n + E_f \Delta f + E_d \Delta d \quad (\text{Eqn. - 02})$$

246 where Δn is the difference in carbon atom number between a surrogate and an analyte, Δf is the
 247 difference in the oxygen-containing functional group between a surrogate and an analyte, Δd is
 248 the difference in alkene functionality between a surrogate and an analyte. The quantification
 249 errors (E_Q) were then propagated with the other source of measurement uncertainty using Eqn.
 250 - 01 were ranged from 15% (2-MTLs) to 140% (β -caryophyllinic acid) in this study. The
 251 quantification errors (E_Q) yield the following uncertainties (E_A) for SOA tracers in this study
 252 were 20% for 2-MTLs, 25% for 2-MGA, 83% for C_5 -alkene triols, 50% for 3-MBTCA, and
 253 145% for β -caryophyllinic acid.

254 **2.6. Air-mass Circulation and Back Trajectories**

255 The five-day air-mass backward trajectories (AMBTs) arriving over the sampling site
 256 500 m above ground level were computed for each sample using the Hybrid Single-Particle
 257 Lagrangian Integrated Trajectory (HYSPLIT) model developed by the National Oceanic and
 258 Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (Draxler and Rolph,
 259 2013). Figure 3 shows the seasonal AMBTs for the samples collected at Chichijima. These
 260 trajectory-based observations show two significant pathways for the air masses that arrived in
 261 Chichijima, which indicate that the observation site is strongly affected by seasonal changes in
 262 the wind system. Trade winds, which are dominant from mid-spring to mid-autumn, transport
 263 clean and pristine marine air masses from the central Pacific. The westerly winds dominate
 264 from mid-autumn to mid-spring, bringing continental air masses enriched with pollutants
 265 including NO_x , dust, and anthropogenic aerosols emitted from East Asia and Eurasia
 266 (Kawamura et al., 2003; Simoneit et al., 2004; Wang et al., 2009).

267 Bourgeois and Bey (2011) reported global lifetimes of aerosol in the air are about five
 268 days by estimating the loss rate constant of tracers as $2.3 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at OH levels of
 269 $1 \times 10^6 \text{ molecules cm}^{-3}$. According to the above study, five days lifetime was also assumed for
 270 SOA tracers in Chichijima aerosols; however, it may vary for a different environment.
 271 Therefore, considering the lifetime of SOA tracers is five days, we compute the five-day air-

272 mass backward trajectories arriving over the sampling site 500 m above ground level. Apart
 273 from the above study, detailed research is needed about the stability, degradation, and lifetime
 274 of the SOA tracers during long-range transport.

275 **2.7. Positive Matrix Factorization (PMF) Analysis**

276 Positive matrix factorization (PMF) is a powerful statistical tool for resolving the
 277 potential sources contributing to atmospheric particles (Paatero and Tapper, 1994). The
 278 uncertainties were calculated by using the measured ambient concentrations and method
 279 detection limits (MDLs). The measured concentrations of SOA tracers below or equal to the
 280 MDLs were replaced by half of the MDL, and associated uncertainties were set at five-sixths
 281 of the MDL $[(5/6) \times \text{MDL}]$ values of each sample. The geometric mean of the concentrations
 282 replaced missing concentrations, and the calculation of uncertainty for the concentrations
 283 greater than the MDL is based on the following equation 03

$$284 \quad \text{Uncertainty} = \sqrt{(\text{error fraction} \times \text{concentration})^2 + (0.5 \times \text{MDL})^2} \quad (\text{Eqn. - 03})$$

285 The error fraction is a user-provided estimation of the analytical uncertainty of the
 286 measured concentration or flux. For example, Xie et al. (2014) and Han et al. (2017) used an
 287 error fraction of 0.2-0.3 and 0.2 for organics, respectively. In this work, the error fraction was
 288 set to be 0.2 for all species. The detailed discussions of the determination and application of
 289 PMF are reported by Paatero et al. (2002) and Zhou et al. (2004).

290 **3. Results and Discussion**

291 **3.1. Concentrations of Biogenic SOA Tracers**

292 Figure 4 shows the temporal trends in the concentrations of BSOA tracers in the
 293 Chichijima samples (Figures 4a–4n), and Table 1 presents their annual and seasonal
 294 concentration ranges and average values, together with the standard deviations. The
 295 concentrations of BSOA tracers in the Chichijima aerosols ranged from 0.03–14.1 ng m^{-3} (avg.
 296 $2.35 \pm 2.71 \text{ ng m}^{-3}$), which are lower than those reported for Okinawa Island (0.09-15.5 ng m^{-3} ,
 297 avg. 4.53 ng m^{-3}) (Zhu et al., 2016) and the East China Sea (1.1-135 ng m^{-3} , 22.9 ng m^{-3})
 298 (Kang et al., 2018). The East China Sea is closer to the Asian continent than the Okinawa and
 299 Chichijima Islands. The lower concentrations of BSOA tracers suggest that continental air
 300 masses influence is weakened over in remote Chichijima due to aerosol aging, dry/wet
 301 deposition during long-range atmospheric transport, and dilution of pristine air masses.

302 3.1.1. Isoprene-derived SOA Tracers

303 Isoprene (2-methyl-1,3-butadiene, C₅H₈) is a volatile unsaturated hydrocarbon that is
304 mainly emitted from terrestrial vegetation, maritime phytoplankton, seaweed (Shaw et al.,
305 2003) and microorganisms, including cyanobacteria. The production of isoprene is
306 temperature-dependent (Sharkey and Singaas, 1995; Kurihara et al., 2010; Li et al., 2011).
307 Although the oceanic emissions of isoprene are much smaller than the terrestrial emissions,
308 they significantly impact the atmospheric chemistry and cloud properties in the remote marine
309 boundary layer because of the short lifetime (1–2 h) and high reactivity (Bonsang et al., 1992;
310 Hackenberg et al., 2017). Hence, due to the short lifetime, isoprene cannot be transported long
311 distances after the emission in source regions. Therefore, the isoprene-derived SOA (*i*SOA)
312 tracers detected in the remote marine atmosphere are formed by the oxidation of the maritime-
313 emitted isoprene or transported to the marine site from the adjacent continent after the
314 formation of *i*SOA (Fu et al., 2016; Kang et al., 2018). Accordingly, the *i*SOA tracers abundant
315 in winter and spring were mostly long-range transported from the Asian continent. In contrast,
316 summertime higher *i*SOA tracers were formed by the oxidation of isoprene emitted in the
317 remote marine atmosphere.

318 Six *i*SOA tracers including 2-MGA, three C₅-alkene triols, and two 2-MTLs were
319 identified in the Chichijima aerosol samples (Figures 4b–4h). The total concentrations of the
320 *i*SOA tracers varied from 0.007–3.98 ng m⁻³, with a mean of 0.69 ± 0.67 ng m⁻³ (Table 1). The
321 mean concentration of the *i*SOA tracers at Chichijima is comparable to those reported for the
322 North Pacific to the Arctic (Ding et al., 2013) and the North Pacific (Fu et al., 2011), but much
323 lower than those reported for the South and East China Sea (Ding et al., 2012; Kang et al.,
324 2018).

325 We found 2-MTLs to be the dominant *i*SOA tracer in Chichijima aerosols. The
326 concentrations of 2-MTL₂ were twice those of 2-MTL₁ with concentrations ranging from
327 0.005–2.07 ng m⁻³ (avg. 0.29 ± 0.33 ng m⁻³) and 0.003–0.97 ng m⁻³ (0.14 ± 0.15 ng m⁻³),
328 respectively. The concentrations of 2-MTLs ranged from 0.007–3.04 ng m⁻³ (0.43 ± 0.47 ng
329 m⁻³), which are several times lower than those (0.05–7.22 ng m⁻³, avg. 1.58 ± 1.50 ng m⁻³)
330 reported in the aerosols from Okinawa Island in the WNP (Zhu et al., 2016). 2-MGA is formed
331 by the oxidation of methacrolein and methacrylic acids derived from isoprene (Surratt et al.,
332 2006). The average concentration of 2-MGA was determined to be 0.15 ± 0.14 ng m⁻³ (0.005-
333 0.79 ng m⁻³). C₅-alkene triols are a photooxidation product of isoprene. Its concentrations were

334 detected in the range from 0.006–1.28 ng m⁻³, with an average of 0.12 ± 0.16 ng m⁻³ in
335 Chichijima aerosols.

336 3.1.2. Monoterpene-derived SOA Tracers

337 Four monoterpene-derived SOA tracers (*m*SOA tracers), including PNA, PA, 3-HGA,
338 and 3-MBTCA were detected in the Chichijima aerosols (Figures 4i–4m). Monoterpenes are
339 photooxidation products of α/β-pinene with O₃ and OH radicals, mainly emitted from the
340 needle leaves of the higher plants and trees (Hoffmann et al., 1997; Glasius et al., 2000; Iinuma
341 et al., 2004). These components have been utilized to estimate the role of monoterpene
342 oxidation in SOA formation (Griffin et al., 1999). The concentrations of *m*SOA tracers in
343 Chichijima samples ranged between 0.005 to 11.1 ng m⁻³, with an average of 1.14 ± 1.93 ng
344 m⁻³ (Table 1). This average concentration is higher than those reported from remote sites in the
345 North Pacific and Indian Ocean (Fu et al., 2011), but lower than those reported from coastal
346 sites in the South China (Ding et al., 2012) and East China Sea (Kang et al., 2018).

347 A very low level of first-generation products such as PNA (avg. 0.05 ± 0.08 ng m⁻³)
348 and PA (0.19 ± 0.28 ng m⁻³), were detected in the Chichijima aerosols. The vapor pressure of
349 PNA is higher than that of PA (Bhat and Fraser, 2007), so PNA is not as easily saturated in the
350 atmosphere nor does it nucleate as readily as PA. Therefore, PNA is expected to have a smaller
351 fraction in the aerosol phase than PA. 3-HGA was found to be the most abundant among the
352 SOA tracers detected in the Chichijima aerosols. The concentration range of 3-HGA was
353 0.002–8.04 ng m⁻³ with an annual average of 0.71 ± 1.26 ng m⁻³. Both 3-HGA and 3-MBTCA
354 are novel *m*SOA tracers that have been reported to generate in α-pinene smog-chamber
355 experiments under UV-radiation in the presence of NO_x (Claeys et al., 2007). In addition, PNA
356 can be further photochemically oxidized to a higher-generation product 3-MBTCA in the
357 presence of oxidants (Szmigielski et al., 2007).

358 Interestingly, we found a substantial amount of 3-MBTCA in Chichijima aerosols. The
359 concentrations of 3-MBTCA ranged from 0.001–2.51 ng m⁻³, with an average of 0.29 ± 0.49
360 ng m⁻³. This 3-MBTCA concentration in Chichijima is lower than that reported at Okinawa
361 Island, which is very close to the Asian continent (Zhu et al., 2016), but comparable to those
362 reported in remote marine aerosols over the Pacific and Atlantic Oceans (Fu et al., 2011). The
363 concentration of 3-MBTCA in the atmosphere has noted to be significantly enhanced by high
364 levels of NO_x (Claeys et al., 2007), which is abundant at urban sites compared to remote
365 marine sites. Kang et al. (2018) found higher concentrations of 3-MBTCA at a coastal site in

366 the East China Sea, which is highly influenced by the continental outflows of anthropogenic
367 emissions. These findings indicate that the low concentration of 3-MBTCA in the western
368 North Pacific is associated with the lesser impact of anthropogenic sources than the East China
369 Sea. However, it is also evidence for the aging effect of 3-MBTCA during long-range transport
370 from the continental source region to the remote site.

371 **3.1.3. β -Caryophyllene-derived SOA Tracer**

372 β -Caryophyllinic acid can rapidly form in the atmosphere by the ozonolysis or
373 photooxidation of β -caryophyllene (Jaoui et al., 2007). With relatively low vapor pressure, β -
374 caryophyllinic acid is highly reactive and thus is usually the least reported SOA component in
375 atmospheric aerosols. Sesquiterpenes and isoprenoids are stored in plant tissues such as glands
376 or resin ducts in the form of liquid micelles due to their lesser volatility (Fall, 1999). They play
377 protective roles against pathogens and insects (Keeling and Bohlmann, 2006). BB (i.e.,
378 smoldering, charring, and flaming) may induce the emissions of different VOC classes
379 including β -caryophyllene into the atmosphere (de Lillis et al., 2009). BB not only stimulates
380 the emissions of sesquiterpene but also substantially impacts the formation yields of SOAs in
381 the air (Mentel et al., 2013).

382 Interestingly, an abundant presence of the β -caryophyllene-derived SOA tracer (β -
383 caryophyllinic acid or *c*SOA tracer) was detected in the Chichijima aerosols (Figure 4n). The
384 concentrations of this β -caryophyllinic acid ranged range from 0.002–2.81 ng m⁻³, with an
385 average of 0.60 ± 0.72 ng m⁻³ (Table 1). This value is lower than those reported for the marine
386 aerosols of Okinawa (Zhu et al., 2016) and the coastal aerosols of the East China Sea (Kang et
387 al., 2018). This comparison further suggests that the continental emissions of β -caryophyllene
388 profoundly influence the formation of *c*SOA in the marine atmosphere, which is discussed later
389 in section 3.2.3.

390 **3.2. Possible Sources and Factors Affecting the BSOA Tracers Over Chichijima Island**

391 Our previous studies found that atmospheric circulations significantly affect the
392 composition and seasonal variations of aerosol particles in the WNP (Verma et al., 2015; 2018).
393 Moreover, meteorological conditions also play a significant role in producing BSOA tracers
394 (Szmigielski et al., 2007). The chlorophyll-a is a good tracer of marine biological activities,
395 which affects the production of marine BVOCs (Ooki et al., 2015). Boreddy et al. (2015)
396 reported higher chlorophyll-a concentrations in winter and spring than in summer and autumn

397 in the WNP. However, the lower biological activities and, subsequently, lesser VOC emissions
398 might not be so significant for the SOA emissions over the WNP region. Moreover, the
399 photochemical processing of BVOCs, followed by their atmospheric circulation over the WNP
400 and gas-to-particle conversion of BVOCs via atmospheric oxidation, may another important
401 factor controlling the seasonal variations of BSOA tracers, which follow changes in the
402 ambient temperature and precipitation.

403 Supplementary Figures S3a and S3b show the temporal trends and monthly mean
404 variation of the NO_3^- concentrations in the Chichijima aerosols from 2010 to 2012. The
405 seasonal distributions of NO_3^- showed higher concentrations in winter and spring, while they
406 are lower in summer and autumn. Similar temporal and seasonal variations were found
407 between NO_3^- concentrations and high- NO_x SOA tracers (2-MGA, 3-HGA, and 3-MBTCA). In
408 contrast, trends were opposite for low- NO_x SOA tracers (2-MTLs, C_5 -alkene triols) in the
409 Chichijima aerosols (Figures 4b–4m and 5b–5m), which indicates a possible role of NO_3
410 radicals in the formation and seasonal variations of SOA tracers in the Chichijima aerosols.
411 Kang et al. (2018) reported a correlation between NO_3^- and high- NO_x *i*SOA tracers and *m*SOA
412 tracers. They suggested that this kind of relationship indicates the influence of NO_3 in the
413 formation of high- NO_x *i*SOA tracers and *m*SOA traces in the marine aerosol samples.
414 Therefore, the abundance and seasonal variations of BSOA tracers in the Chichijima aerosols
415 might be significantly affected by several parameters, i.e., long-range transported
416 anthropogenic and pristine air masses, NO_3 radicals, and chlorophyll-a concentrations, which
417 we discuss in the next section.

418 **3.3. Seasonal Variations of SOA Tracers**

419 Table 1 shows a summary of the seasonal concentrations of SOA tracers in the
420 Chichijima aerosols. The overall concentrations of SOA tracers were found to be higher in
421 winter (avg. $3.40 \pm 2.18 \text{ ng m}^{-3}$) and spring (avg. $3.35 \pm 3.83 \text{ ng m}^{-3}$) than summer ($1.05 \pm$
422 1.12 ng m^{-3}) and autumn ($1.68 \pm 2.17 \text{ ng m}^{-3}$). The monthly variations of biogenic SOA tracer
423 concentrations were at their maximum in spring, followed by autumn (Figure 5a). SOA tracers
424 are highly water-soluble because they contain multiple hydroxy and carboxyl groups, and
425 therefore they can be easily scavenged by precipitation and act as CCN. In Chichijima,
426 significant rainfall occurs in early summer (June) to mid-autumn (October) (Figure 2), which
427 would lead to the scavenging of SOA tracers in summer/autumn by the occasional rain events
428 in Chichijima and its surrounding areas.

429 3.3.1. Seasonal Variations of Isoprene-derived SOA Tracers

430 The *i*SOA tracers concentrations in the Chichijima aerosols exhibited no significant
431 seasonal variation (Figure 5b). Their average concentrations are comparable over the four
432 seasons i.e. winter (avg. $0.78 \pm 0.56 \text{ ng m}^{-3}$), summer ($0.73 \pm 0.90 \text{ ng m}^{-3}$), spring (0.71 ± 0.52
433 ng m^{-3}), and autumn ($0.56 \pm 0.67 \text{ ng m}^{-3}$) (Table 1). This insignificant seasonal variation
434 suggests that although the contribution of *i*SOA tracers to organic aerosols (OA) is significant
435 in the Chichijima, their production seems to occur almost irrespective of their source regions,
436 except for 2-MGA, which shows a clear winter maximum. Surratt et al. (2006) noted that total
437 concentrations of *i*SOA tracers are affected by the emission and reaction rates of BVOCs under
438 different meteorological conditions such as the ambient temperature and RH. The atmospheric
439 levels of NO_x significantly influence the production of *i*SOA tracers (Ding et al., 2014). A
440 significant amount of *i*SOA tracers in winter suggest that enhanced long-range atmospheric
441 transport of pollutants such as NO_x controls the production of *i*SOA tracers over the remote
442 island.

443 2-MTLs are formed by the photooxidation of isoprene initiated by OH radicals, which
444 was observed first time in the aerosols collected from the Amazonian rain forest (Claeys et al.,
445 2004). Based on laboratory experiments, Zhang et al. (2011) proposed that the production of 2-
446 MTLs is enhanced under low- NO_x and high RH conditions. Apparently, the remote marine
447 atmosphere is characterized by low- NO_x with high-RH, supporting the formation of MTLs
448 instead of 2-MGA. The insignificant correlation of 2-MTLs with NO_3^- ($r = 0.03$) also suggests
449 their formation in the low- NO_x condition. We observed insignificant seasonal variations of 2-
450 MTLs in the Chichijima aerosols. The monthly mean concentrations of 2-MTLs were elevated
451 from June to August (Figures 5c and 5d). The seasonally averaged concentrations of 2-MTLs
452 were $0.58 \pm 0.73 \text{ ng m}^{-3}$ in summer, $0.41 \pm 0.30 \text{ ng m}^{-3}$ in winter, $0.38 \pm 0.30 \text{ ng m}^{-3}$ in spring,
453 and $0.37 \pm 0.42 \text{ ng m}^{-3}$ in autumn (Table 1). The predominance of 2-MTLs among *i*SOA
454 tracers was also reported for the Okinawa aerosols together with higher loadings in summer
455 (Zhu et al., 2016). The long-range atmospheric transport of anthropogenic pollutants (e.g.,
456 NO_x) may contribute to a decline in the production of low- NO_x *i*SOA tracers (2-MTLs) during
457 winter and spring over Chichijima Island.

458 The isoprene emission rates might be much higher in summer than in spring, autumn
459 and winter due to the change of leafage, temperature, and light. These factors also affect the
460 isoprene reactions, causing a higher production of 2-MTLs in the summer season (Xia and

461 Hopke et al., 2006). The summertime maximum of 2-MTLs is probably associated with the
462 enhanced emission of isoprene from terrestrial and marine biota, followed by its atmospheric
463 oxidation. This occurs because isoprene emissions can increase by a factor of 10 with a 10 °C
464 increase in the leaf temperature (Sharkey and Singsaas, 1995; Rasulov et al., 2010; Li et al.,
465 2011). Moreover, phytoplankton and marine biota are unique sources for isoprene emissions in
466 the remote marine atmosphere (Bonsang et al., 1992; Broadgate et al., 1997). If the *i*SOA
467 tracers were formed over the marine atmosphere, the seasonal and spatial distribution of 2-
468 MTLs could be assumed to correlate with the mass of phytoplankton in the marine site. The
469 trade winds from the central Pacific to Chichijima might transport the isoprene emitted from
470 marine biota in summer (Figure 3). In addition, summertime low-NO_x and high RH conditions
471 may enhance the production of 2-MTLs in a pristine environment over the WNP (Zhang et al.,
472 2011). It also suggests that the formation of 2-MTLs was highly influenced by the local
473 emissions and meteorological conditions in the pristine environment of the WNP (Ding et al.,
474 2013).

475 The insignificant correlations of 2-MTLs with BB tracer (levoglucosan) during winter
476 ($r = 0.04$, $n = 37$) and spring ($r = 0.26$, $n = 40$) (Figures 6a and 6b) imply that the isoprene
477 emissions from BB are negligible. The higher levels of 2-MTLs from January to March may be
478 associated with the isoprene emissions from marine phytoplankton. A high level of
479 chlorophyll-a was observed near Chichijima Island from January to March, which is in good
480 agreement with the wintertime isoprene oxidations into 2-MTLs in the marine atmosphere over
481 Chichijima and its surrounding areas. 2-MTLs are the acid-catalyzed hydrolysis products of
482 isoprene epoxydiols (IEPOX) in the aerosol aqueous-phase (Riva et al., 2016). Chichijima
483 Island is highly influenced by anthropogenic aerosols from East Asia in winter and spring, with
484 higher levels of SO₄²⁻ and NO₃⁻ (Boreddy et al., 2015), which likely increase the acidity of
485 aerosols and the formation of 2-MTLs.

486 In a chamber experiment, Surratt et al. (2006) reported the formation of 2-MGA by the
487 photooxidation of isoprene under high-NO_x conditions. 2-MGA is an oxidation product of
488 methacrolein and methacrylic acid, which are formed by the gas-phase oxidation of isoprene at
489 high-NO_x levels (Claeys et al., 2004). We found that 2-MGA is the second most abundant
490 *i*SOA tracer at Chichijima with different seasonal patterns than low-NO_x products (i.e.,
491 2MTLs). Its concentration was higher in winter (avg. $0.22 \pm 0.15 \text{ ng m}^{-3}$) followed by spring
492 ($0.19 \pm 0.16 \text{ ng m}^{-3}$) and lower in summer ($0.07 \pm 0.08 \text{ ng m}^{-3}$). 2-MGA is most abundant in
493 mid-winter (January), to early spring (March) (Figure 5e). Surratt et al. (2006) and Zhang et al.

494 (2011) reported an enhancement of 2-MGA in low RH conditions. The wintertime maximum
495 of 2-MGA at Chichijima may be associated with the wintertime low RH and high-NO_x
496 conditions via the long-range transport of pollutants from East Asia. The lowest concentrations
497 of 2-MGA in June may be partly associated with its washout by rain at Chichijima and its
498 surroundings (Figure 2).

499 *i*SOA tracers were comprised of effectively nonvolatile material that could be allowed
500 *i*SOA to be long-lived in the atmosphere (Lopez-Hilfiker et al., 2016). In a NO₃ initiation
501 experiment, Hoyle et al. (2011) reported a significant yield of *m*SOA and *i*SOA tracers by the
502 reaction of isoprene and monoterpene with nitrate radical (NO₃), a nighttime product of NO₂
503 and O₃. Kang et al. (2018) also found the correlation of high-NO_x *i*SOA tracers (2-MGA and
504 C₅-alkene triols) with NO₃⁻ and suggested the close connections between the formation of SOA
505 tracers and NO₃ in marine aerosols. Although 2-MGA, a high-NO_x *i*SOA tracer, showed
506 seasonal variation similar to NO₃⁻ we did not find significant correlations of 2-MGA with NO₃⁻
507 ($r = 0.55$). This suggests that 2-MGA likely formed at upwind in the Asian continental region
508 and subsequently transported to the Chichijima Island in the WNP. The SOA tracers were
509 transported to long distances, but its impact gradually decreased because of the dilution and
510 deposition effects during long-range atmospheric transport.

511 The diagnostic mass concentration ratios of *i*SOA tracers can provide valuable
512 information about their sources and formation processes as well as their photochemical aging
513 and the impact of long-range transported anthropogenic aerosols on *i*SOA formation. We
514 determined the ratio of low-NO_x products (2-MTLs) to the high-NO_x product (2-MGA) to
515 understand the biogenic emissions of *i*SOA tracers and the influence of NO_x and local
516 meteorological conditions on their formation (Lewandowski et al., 2013). The average seasonal
517 ratio of 2-MTLs/2-MGA shows a maximum in summer (5.22) and autumn (4.12) and a
518 minimum in winter (2.02) and spring (2.80) (Table 2). A significantly high annual average of
519 2-MTLs/2-MGA ratio (3.43) in Chichijima aerosols suggest a decrease in the concentration of
520 2-MGA due to a dilution effect during long-range transport from the continental region to
521 Chichijima Island. The lower ratios in winter and spring are in good agreement with the
522 enhanced levels of NO_x in these seasons.

523 C₅-alkene triols are mainly formed by the reactive uptake of the isoprene epoxydiols
524 (IEPOX) produced by the reaction of isoprene with OH and HO₂ radicals in low-NO_x
525 conditions. The insignificant seasonal variation of C₅-alkene triols indicates the importance of

526 regional or local sources during the sampling campaign. C₅-alkene triols and 2-MTLs show
527 excellent linearity and a significant correlation coefficient in all seasons (Figures 7a–7d). These
528 results suggest that C₅-alkene triols and 2-MTLs are derived from the same sources via an
529 identical formation mechanism. In addition, the insignificant correlations of C₅-alkene triols
530 and NO₃⁻ ($r = 0.20$), indicates their formation by isoprene photooxidation in the low-NO_x
531 environment of the western North Pacific. The monthly mean concentrations of C₅-alkene
532 triols showed a prominent peak in mid-winter (January) to early spring (March) (Figures 5f–
533 5h), which are in good agreement with the higher chlorophyll-a concentrations during similar
534 periods, suggesting that the significant isoprene emissions from the oceanic phytoplankton in
535 the marine atmosphere of the WNP .

536 The concentration ratio of C₅-alkene triols (low-NO_x) and 2-MTLs (high RH) can be
537 used to understand the influence of anthropogenic emissions on the formation of BSOA tracers.
538 The C₅-alkene triols/2-MTLs ratio was reported to be <0.1 in aerosol samples collected over
539 the remote ocean, whereas ratio >0.6 was reported over the coastal ocean (Fu et al., 2011). The
540 seasonal mean C₅-alkene triols/2-MTLs ratios in the Chichijima samples were higher in spring
541 (0.37) and winter (0.34) than in summer (0.15) and autumn (0.22) (Table 2). The lower ratios
542 in summer and autumn are in good agreement with a laboratory experiment of Kleindienst et al.
543 (2009), in which a lower ratio was obtained for the photooxidation of isoprene in the absence
544 of NO_x. Furthermore, C₅-alkene triols can be transformed into 2-MTLs through acid-catalyzed
545 hydrolysis in summer and autumn seasons suggested the intra-transformation of *i*SOA tracers
546 under suitable atmospheric conditions.

547

548 3.3.2. Seasonal Variations of Monoterpene-derived SOA Tracers

549 The monoterpene-derived SOA (*m*SOA) tracers in the Chichijima aerosols presented
550 the highest concentration in spring (avg. $1.96 \pm 2.96 \text{ ng m}^{-3}$) followed by winter (1.45 ± 1.42
551 ng m^{-3}), autumn ($0.83 \pm 1.39 \text{ ng m}^{-3}$), and summer ($0.20 \pm 0.39 \text{ ng m}^{-3}$) (Table 1 and Figure
552 5i). The first-generation monoterpene product (PA) showed a clear seasonal trend with higher
553 levels in winter and spring, whereas low levels were observed in summer and autumn. The
554 PNA showed a similar seasonality with low concentrations (Figures 5j and 5k). Bud formation
555 and elongation are maximized in spring, along with the emission rates of terpenes (Kim, 2001).
556 3-HGA and 3-MBTCA were found to be the dominant *m*SOA tracers detected in the
557 Chichijima aerosols, and thus their seasonal variations significantly affect the seasonal trends
558 of those *m*SOA tracers. 3-HGA showed a high level in spring (avg. $1.31 \pm 2.0 \text{ ng m}^{-3}$)

559 followed by winter ($0.86 \pm 0.90 \text{ ng m}^{-3}$), whereas 3-MBTCA is equally distributed in winter
560 ($0.32 \pm 0.36 \text{ ng m}^{-3}$), spring ($0.40 \pm 0.69 \text{ ng m}^{-3}$), and autumn ($0.31 \pm 0.57 \text{ ng m}^{-3}$) (Table 1
561 and Figures 5l and 5m). A high- NO_x level in spring may enhance the formation of 3-HGA and
562 3-MBTCA (Surratt et al., 2006). 3-HGA and 3-MBTCA show good correlations in each season,
563 which suggests that the formation mechanisms of both *m*SOA tracers in the WNP are similar
564 (Figures 7e–7h).

565 In addition, the monthly mean concentrations of 3-HGA and NO_3^- were found to
566 increase from late autumn (November) and peaked in early spring (May), which prolonged up
567 to mid-spring (March). The concentrations started to decrease from early summer (May) to
568 mid-autumn (October). In the preceding periods, emissions of anthropogenic gases (NO_x and
569 SO_x) are usually high in the East Asian countries, which might initiate the oxidation of
570 monoterpenes and isoprene followed by subsequent formation of *m*SOA tracers (3-HGA and 3-
571 MBTCA) and *i*SOA tracers (2-MGA), respectively. Although the seasonal trends of 3-HGA
572 and NO_3^- are similar in the Chichijima aerosols, the negative correlation of NO_3^- with 3-HGA (r
573 $= -0.20$) and 3-MBTCA ($r = -0.09$) suggest that both *m*SOA tracers might be formed in the
574 continental region and transported to the downwind region in the WNP during winter and
575 spring (Figures 7i and 7j). The previous study also reported a long-range transport of *m*SOA
576 tracers from the East Asian continent to the remote marine region (Kang et al., 2018).

577 The lower levels of 3-HGA and 3-MBTCA in summer may be associated with
578 summertime lower emissions of monoterpenes, which decline the formation of *m*SOA tracers
579 over the remote Chichijima Island. The meteorological parameters may significantly influence
580 the formation of *m*SOA tracers in the WNP. We note that the seasonal concentration of 3-HGA
581 is slightly different from that of 3-MBTCA, suggesting an additional formation process for 3-
582 MBTCA via the photochemical oxidation of PNA in the presence of oxidants (Szmigielski et
583 al., 2007). The significant level of 3-MBTCA and low concentrations of PNA in the
584 Chichijima aerosols might indicate aerosol aging during long-range atmospheric transport.

585 3-MBTCA is an oxidation product of PNA and PA (Claeys et al., 2007). Therefore, the
586 3-MBTCA/(PNA+PA) ratios can be used to better understand the aging of *m*SOA tracers in the
587 atmosphere (Kulmala et al., 2011). Ratios greater than unity indicate the photochemical aging
588 of SOA, whereas ratios <1 indicate relatively fresh SOA. The average 3-MBTCA/(PNA+PA)
589 ratios in the Chichijima aerosols were 1.26, 1.37, 1.13, and 1.40 in winter, spring, summer, and
590 autumn, respectively (Table 2). According to the results, we hypothesized the possibilities of

591 the aging effect in the Chichijima aerosol during long-range atmospheric transport. However,
592 further research is needed to better evaluate the photochemical formation or aging of aerosol
593 during long-range transport from Asian continent to the WNP.

594 3.3.3. Seasonal Variation of β -Caryophyllene-derived SOA Tracer

595 The *c*SOA tracer showed a clear winter maximum that is differed from those of the
596 *i*SOA and *m*SOA tracers (Figures 5b, 5i and 5n). The *c*SOA tracer exhibited the highest
597 concentration in winter (avg. $1.23 \pm 0.68 \text{ ng m}^{-3}$) followed by spring ($0.66 \pm 0.73 \text{ ng m}^{-3}$),
598 autumn ($0.37 \pm 0.61 \text{ ng m}^{-3}$), and summer ($0.12 \pm 0.21 \text{ ng m}^{-3}$) (Table 1). Sesquiterpenes,
599 including β -caryophyllene, can accumulate in plant leaves and be emitted to the atmosphere.
600 However their global emission (36 Tg C yr^{-1}) is less than those of isoprene (634 Tg C yr^{-1}) and
601 monoterpenes (89 Tg C yr^{-1}) (Acosta Navarro et al., 2014). They can evaporate and emit into
602 the atmosphere substantially via the BB of higher plants (Ciccioli et al., 2014; Sekimoto et al.,
603 2018).

604 The *c*SOA tracer concentrations in Chichijima aerosols (avg. $0.60 \pm 0.72 \text{ ng m}^{-3}$) are
605 notably lower than those reported for coastal site and Marine Island in the WNP, which are
606 significantly influenced by continental outflows from East Asia. Kang et al. (2018) reported
607 high levels of the *c*SOA tracer (2.9 ng m^{-3}) in the coastal East China Sea, strongly influenced
608 by BB aerosols in winter. Zhu et al. (2016) also reported relatively high concentrations of the
609 *c*SOA tracer (1.63 ng m^{-3} in winter and 0.82 ng m^{-3} in spring) at Okinawa Island, located in
610 the east of the East China Sea and is influenced by westerly winds from the Asian continent.
611 The comparisons of *c*SOA tracer of Chichijima with those from the East China Sea and
612 Okinawa Island reveal that the significant decline in the *c*SOA tracer concentrations in the
613 Chichijima aerosols is largely caused by dry/wet scavenging along the atmospheric transport
614 pathway over the WNP.

615 As seen in Figure 4n, the concentrations of β -caryophyllinic acid substantially increase
616 from 2010 to 2012. Monthly composite images of the Moderate Resolution Imaging
617 Spectroradiometer (MODIS) active fire spots were obtained to identify the geographically
618 active fire areas as possible source regions of BB tracers (<https://earthdata.nasa.gov/data/near-real-time-data/firms/>). Three years of monthly MODIS active fire spot detections in Siberia,
619 East Asia, and Southeast Asia indicate a significant increase of fire activity in mid-autumn to
620 late spring (Figure S4). The BB for cooking and space heating is common in the East Asian
621

622 countries during the cold seasons (mid-autumn to mid-spring), which might be a significant
623 source to the downwind regions. Interestingly, concentrations of levoglucosan and β -
624 caryophyllinic acid also increased during mid-autumn to mid-spring, suggesting that *c*SOA
625 tracer is strongly associated with BB in East Asia (Figure 8). The BB activities in the Asian
626 continent significantly impact on the concentration of *c*SOA tracers in the remote marine
627 atmosphere over the WNP during the mid-autumn to mid-spring. Air mass trajectories also
628 support the transport of air parcels from East Asia, Siberia, and Russian Far East over
629 Chichijima Island (Figure 3).

630 The concentration ratios of the *i*SOA/*c*SOA tracers in the Chichijima aerosols are much
631 higher in summer (avg. 14.6) and autumn (9.64) than in spring (4.17) and winter (0.85) (Table
632 2). This indicates the enhanced emissions of isoprene and subsequent formation of *i*SOA
633 tracers in warmer seasons and the enhanced emission of β -caryophyllene in colder seasons by
634 BB in East Asia followed by atmospheric transport and oxidation over the WNP. The isoprene
635 emissions are known to increase with an increase in ambient temperature in summer and
636 autumn (Ding et al., 2014). In Chichijima, higher concentrations of *i*SOA tracers were recorded
637 during the warmer periods when biogenic emissions increase due to the higher temperatures.
638 These results also indicate a significant contribution of *i*SOA tracers from local vegetation and
639 marine phytoplankton in the Pacific. The winter minima of *i*SOA/*c*SOA ratios are amplified by
640 a greater contribution of *c*SOA tracer associated with BB in East Asia.

641 **3.4. Contributions of Oxidation Products of BVOCs to Organic Carbon (OC)**

642 In this study, we applied a tracer-based method proposed by Kleindienst et al. (2007) to
643 roughly estimate the loading of biogenic secondary organic carbon (SOC) using the SOA tracer
644 concentrations measured in the Chichijima aerosols and the mass fractions (f_{SOC}) of laboratory-
645 derived tracers: 0.155 ± 0.039 for isoprene, 0.231 ± 0.111 for monoterpene, and $0.0230 \pm$
646 0.0046 for β -caryophyllene. The SOC concentrations derived from each type of precursor were
647 calculated using the following equation: $f_{\text{SOA}} = \Sigma_i[\text{tri}]/[\text{SOA}]$, where [tri] is concentrations of
648 tracer, *i*, in ng m^{-3} and [SOA] is the mass concentrations of SOA. We note that the tracer-
649 based method simplifies the truly complex system of the real atmosphere (Stone et al., 2010).
650 Kleindienst et al. (2007) applied the total of 3 and 9 tracers to derive f_{SOC} of isoprene and α -
651 pinene, respectively. In contrast, we detected six compounds (i.e., 2-MGA, three C₅-alkene
652 triols, and two diastereoisomeric 2-MTLs) derived from isoprene and four compounds (i.e., 3-
653 HGA, PNA, PA, and 3-MBTCA) from monoterpene, whose concentrations were used to

654 estimate the f_{SOC} derived from the precursors.

655 We consider that the uncertainties associated with the differences between the tracers
656 used for the SOC estimation to be within the range of those of the tracer-based approach itself
657 (25%, 48% and 22% for isoprene-, monoterpene-, and β -caryophyllene-derived SOA,
658 respectively), based on the standard deviation in the f_{SOC} mentioned above. Although the
659 estimation of biogenic SOC is associated with some uncertainty due to the difference in the
660 number of SOA tracers used for calculation, this is a widely accepted approach for estimating
661 the SOC in atmospheric aerosols (Lewandowski et al., 2013). Kleindienst et al. (2009) reported
662 that the f_{SOC} derived for isoprene (range 0.117–0.231, ave. 0.156) in the absence of NO_x is
663 similar to that obtained under high- NO_x (0.11–0.65 ppm) conditions, although the NO_x
664 influence of the f_{SOC} for other VOCs is not clear. Hence, we emphasize that this tracer-based
665 method is highly applicable to the present study.

666 Table 3 shows the seasonal concentrations of the total SOC and their contributions to
667 OC concentrations in the Chichijima aerosols. These OC data are available in Boreddy et al.
668 (2018). The total SOC concentrations ranged from 0.11–174 ngC m^{-3} (avg. $34.8 \pm 38.2 \text{ ngC}$
669 m^{-3}), which accounts for 0.02–32.0% ($6.11 \pm 6.42\%$) of the OC in the Chichijima samples.
670 These levels are comparable to those ($0.25\text{--}157 \text{ ngC m}^{-3}$, 35.8 ngC m^{-3}) reported for the
671 Okinawa aerosols (Zhu et al., 2016). We found the highest average concentration of biogenic
672 SOC ($64.6 \pm 34.5 \text{ ngC m}^{-3}$) and contribution to OC ($12.4 \pm 6.95\%$) in winter, followed by
673 spring ($41.3 \pm 42.6 \text{ ngC m}^{-3}$, $5.48 \pm 5.41\%$), autumn ($17.3 \pm 25.8 \text{ ngC m}^{-3}$, $3.17 \pm 3.83\%$), and
674 summer ($10.7 \pm 12.5 \text{ ngC m}^{-3}$, $2.67 \pm 2.98\%$). More oxidants (NO_x , O_3 , and SO_2) are likely
675 transported over the WNP from the Asian continent due to the strong westerly winds in winter
676 (Figure 3), resulting in more SOAs from VOC precursors. Therefore, higher biogenic SOC
677 concentrations and their higher contributions to OC are reasonable in the winter season.

678 The average concentrations of isoprene-derived SOC ($i\text{SOC}$) were found to be almost
679 equally distributed in winter (avg. $5.00 \pm 3.60 \text{ ngC m}^{-3}$), summer ($4.70 \pm 5.77 \text{ ngC m}^{-3}$), and
680 spring ($4.52 \pm 3.33 \text{ ngC m}^{-3}$), with slightly lower concentration observed in autumn ($3.49 \pm$
681 4.48 ngC m^{-3}). These $i\text{SOC}$ levels in Chichijima are comparable to those reported for marine
682 aerosols over Okinawa Island ($3.86 \pm 3.86 \text{ ngC m}^{-3}$) (Zhu et al., 2016), which are significantly
683 lower than those from the East China Sea ($39.8 \pm 55.4 \text{ ngC m}^{-3}$) (Kang et al., 2018). The
684 average contribution of $i\text{SOC}$ to OC in the Chichijima aerosols was maximum in summer (1.16
685 $\pm 1.24\%$), followed by winter ($1.02 \pm 0.95\%$). Interestingly, the highest contribution of $i\text{SOC}$

686 to total SOC concentration was observed in summer ($45.0 \pm 24.9\%$), followed by autumn (35.5
687 $\pm 21.5\%$) (Table 3). This result indicates that significant amounts of isoprene are emitted from
688 terrestrial vegetation and marine phytoplankton and oxidized to SOC over the WNP under
689 higher ambient temperatures and solar radiation during the warmer seasons (Goldstein et al.,
690 2007).

691 The seasonal mean concentration of monoterpene-derived SOC (*m*SOC) in the
692 Chichijima aerosols was found to be higher in spring (avg. $8.53 \pm 12.9 \text{ ngC m}^{-3}$) and winter
693 ($6.30 \pm 6.15 \text{ ngC m}^{-3}$) than in autumn ($2.49 \pm 4.30 \text{ ngC m}^{-3}$) and summer ($0.86 \pm 1.69 \text{ ngC}$
694 m^{-3}) (Table 3). These concentration levels are much lower than those reported for coastal
695 aerosols over the East China Sea ($50.2 \pm 72.0 \text{ ngC m}^{-3}$) (Kang et al., 2018). Although the
696 *m*SOC concentrations at Chichijima were found to be several times lower than those at
697 Okinawa ($5.57 \pm 4.74 \text{ ngC m}^{-3}$) (Zhu et al., 2016), the seasonal trends are very similar in both
698 islands. The westerly winds influence the atmospheric aerosols over the Okinawa and
699 Chichijima Islands because both are situated on the transport pathways of continental aerosols
700 and their precursors from the Asian continent. Thus, we hypothesized that the SOC
701 contribution in Chichijima was significantly affected by the monoterpene emissions and *m*SOA
702 tracers formation in the upwind continental regions.

703 We found β -caryophyllene-derived SOC (*c*SOC) to be a significant contributor to the
704 total BSOC in the Chichijima aerosols. β -Caryophyllinic acid is the photooxidation product of
705 β -caryophyllene, which has an endocyclic C=C bond. Because β -caryophyllene ($\text{C}_{15}\text{H}_{24}$)
706 contains more carbon atoms than isoprene (C_5H_8) and monoterpene ($\text{C}_{10}\text{H}_{16}$), the oxidation
707 products of β -caryophyllene generally have less vapor pressure than those of isoprene and
708 monoterpenes. Consequently, the differences in the formation processes of SOA and the
709 emission strength of their precursors, and the gas-to-particle conversion of different BVOCs
710 may be a potential factor in controlling the levels of *c*SOC in the Chichijima aerosols. The
711 seasonal mean concentration of *c*SOC was found to be highest in winter ($53.6 \pm 29.6 \text{ ngC m}^{-3}$),
712 followed by spring ($28.6 \pm 31.6 \text{ ngC m}^{-3}$), autumn ($11.4 \pm 20.3 \text{ ngC m}^{-3}$), and summer ($5.20 \pm$
713 9.33 ngC m^{-3}) (Table 3). Interestingly, these *c*SOC concentrations are much higher than *i*SOC
714 and *m*SOCs throughout the study period.

715 The higher *c*SOC concentration in winter indicates an enhanced contribution of β -
716 caryophyllinic acid, which is associated with BB in the Asian continent. We note that westerly
717 winds can deliver significant amounts of BB-derived OA from the Asian continent to the WNP

718 (Verma et al., 2015). A similar seasonal trend (Figure 8) and the significant correlation
719 (Figures 6c–6g) of *c*SOA tracer with levoglucosan demonstrate that BB in East Asia likely
720 contributes significantly to *c*SOC in Chichijima aerosols. BB-derived OC (BB-OC) was found
721 to be highest in winter ($0.97 \pm 0.76 \text{ ngC m}^{-3}$), followed by spring ($0.39 \pm 0.51 \text{ ngC m}^{-3}$),
722 autumn ($0.16 \pm 0.29 \text{ ngC m}^{-3}$), and summer ($0.08 \pm 0.14 \text{ ngC m}^{-3}$) (Table 3). BB is considered
723 to affect the concentration levels of *c*SOA tracer and *c*SOC because the seasonal trend of BB-
724 OC (calculated from levoglucosan) was similar to that of *c*SOC. The above considerations
725 emphasize the contribution of SOC from BB and the production of β -caryophyllinic acid in the
726 continental region, followed by the atmospheric transports to the WNP.

727

728 3.5. Sources Apportioned of SOA Tracers by PMF Analysis

729 PMF is a powerful statistical tool for resolving the potential sources contributing to
730 atmospheric particles (Paatero and Tapper, 1994). PMF analysis was performed for
731 quantitative estimation of sources for the collected samples using tracer compounds for *i*SOA,
732 *m*SOA and *c*SOA. Based on a given understanding of sources of SOA tracers, 3 to 5 sources
733 were examined and total three interpretable factors were characterized by the enrichment of
734 each tracer compound, which reproduced more than 95% of SOA tracers. These factors were
735 selected on a basis of minimum robust and true Q values (goodness of fit parameters). The
736 PMF analysis results showed a good correlation between the predicted and observed
737 concentrations of SOA tracers and levoglucosan, which supported the excellent rationality of
738 the source apportionment (Figure S5). We also included the levoglucosan in the Chichijima
739 SOA tracer data sets in the PMF analysis to better understand the possible sources and
740 contributions of anthropogenic activities to the formation of BSOA tracers. Figure 9 shows the
741 factor profiles resolved by the PMF analysis of biogenic SOA tracers detected in the
742 Chichijima aerosols. Based on a PMF analysis of BB tracer (levoglucosan) and biogenic SOA
743 tracers, we detected three biogenic sources. Interestingly, we found that some factors represent
744 a combined influence of biogenic and BB sources as discussed below.

745 The first factor is characterized by β -caryophyllinic acid (95.4%) and levoglucosan
746 (92.9%) followed by 2-MGA (14.8%), C_5 -alkene triols (11.9%), and 2-MTLs (7.35%). The
747 higher values of β -caryophyllinic acid and levoglucosan in factor 1 suggest the substantial
748 influence of BB on the production of β -caryophyllinic acid. Although *i*SOA tracers such as 2-
749 MGA, C_5 -alkene triols, and 2-MTLs were detected as minor contributors to factor 1, they are
750 characterized as major contributors in factor 3. Due to the higher abundances of levoglucosan

751 and β -caryophyllinic acid, we conclude that factor 1 is influenced by β -caryophyllene
752 emissions and BB (Figure 9a). Here, we propose a hypothesis that β -caryophyllene is largely
753 emitted from plant tissues by evaporation during BB events in East Asia and oxidized in the
754 atmosphere during long-range transport of air masses to the remote Pacific Ocean.

755 Four *m*SOA tracers, including 3-MBTCA, PNA, PA, and 3-HGA, were found to have
756 contributed 96.8%, 96.6%, 88.5%, and 87.5%, respectively to factor 2. Due to the higher scores
757 of this factor, we conclude that factor 2 is characterized by monoterpene emissions from
758 terrestrial higher plants (Figure 9b). In factor 3, C₅-alkene triols, 2-MTLs, and 2-MGA
759 contributed 82.8%, 81.5%, and 76.1%, respectively. Hence, factor 3 is dominated by biogenic
760 isoprene oxidation products (Figure 9c). Overall, the average contributions of each factor to the
761 measured BSOA tracer concentrations were estimated by PMF analyses (Figure 10), where
762 *m*SOA tracers accounted for 44%, followed by *i*SOA tracers (29.6%) in the Chichijima
763 aerosols. The contribution of the *c*SOA and BB tracers accounts for 26.3% of the total SOA
764 tracer concentration. Levoglucosan and β -caryophyllinic acid in factor 1 indicate the
765 involvement of biogenic and BB sources. The PMF results show that biogenic emission
766 sources significantly contributed to the formation of BSOA tracers but were largely
767 superimposed by BB during the emissions of β -caryophyllene and the subsequent formation of
768 *c*SOA tracer.

769

770 **4. Summary and Conclusions**

771 In this study, atmospheric concentrations, seasonal distributions, and source
772 apportionments of biogenic isoprene, monoterpene, and sesquiterpene SOA tracers were
773 studied in aerosol samples collected at remote Chichijima Island in the western North Pacific.
774 The predominance of *m*SOA tracers, followed by *i*SOA and *c*SOA tracers were found in
775 Chichijima aerosol. The seasonal distributions of SOA tracers in Chichijima Island were
776 characterized by higher concentrations in winter and spring, and lower concentrations in
777 summer and autumn. *i*SOA tracers were formed with isoprene emissions from phytoplankton
778 in the Pacific region. In contrast, *m*SOA tracers were formed by the oxidation of monoterpenes
779 emitted at the continental region, consequently transported to Chichijima Island. The
780 contributions of β -caryophyllene oxidation products and BB-derived OC were dominant in
781 winter and spring due to long-range transport of continentally derived BB aerosols. The high-
782 NO_x BSOA tracers (2-MGA, 3-HGA, and 3-MBTCA) were aged and influenced by the long-

783 range transport of anthropogenic air masses. In contrast, the low-NO_x BSOA tracers (2-MTLs
784 and C₅-alkene triols) were mostly produced by the oxidation of locally emitted isoprene.

785 The biogenic emissions of β -caryophyllene contributed to more formation of secondary
786 organic carbon, followed by monoterpene and isoprene. A higher ratio of 2-MTLs/2-MGA
787 resulted in the formation of *i*SOA tracers by isoprene emissions from marine phytoplankton. In
788 contrast, the high 3-MBTCA/(PA+PNA) ratio indicated the aging of aerosols during long-
789 range transport from the Asian continent. The meteorological parameters such as RH,
790 temperature, and precipitation also influence the formation of biogenic SOA tracers over
791 Chichijima. PMF analysis illustrates that monoterpene oxidation products could be the major
792 sources for BSOA, followed by isoprene and β -caryophyllene in Chichijima aerosols over the
793 WNP. This study demonstrates that the biogenic and anthropogenic emissions from the
794 continental region significantly impact the formation and chemistry of BSOA over the WNP.
795 Because previous model studies have not considered the emission of *c*SOA by BB, it is
796 important to estimate how BB impacts the secondary formation of OA from the low volatility
797 terpenoids accumulated in terrestrial vegetation at regional and global scales, which are easily
798 emitted to the air on biomass burning.

799 The oxidation of isoprene emitted from phytoplankton could significantly influence the
800 cloud droplet number and affect marine cloud condensation nuclei (CCN) in the remote marine
801 atmosphere. In addition, the oxidation process of maritime BVOCs is significantly influenced
802 by the long-range transport from the continent. The SOA tracers are highly water-soluble due
803 to –OH and –COOH groups. Therefore, the chemical and physical properties of cloud
804 condensation nuclei (CCN) and gas to particle conversion could be elucidated by the
805 atmospheric compositions and seasonal studies of SOA tracers in the remote marine
806 atmosphere.

807

808 **Data Availability Statement**

809 The data set of processed absorption coefficients is available at
810 <https://data.mendeley.com/datasets/jnfsk4xbvr/1>.

811

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825 **References**

- 826 Acosta Navarro, J. C., Smolander, S., Struthers, H., Zorita, E., Ekman, A. M. L., Kaplan, J. O.,
827 Guenther, A., Arneth, A., & Riipinen, I. (2014). Global emissions of terpenoid VOCs from
828 terrestrial vegetation in the last millennium. *Journal of Geophysical Research: Atmosphere*,
829 *119*, 6867–6885. <https://doi.org/10.1002/2013JD021238>
- 830 Bhat, S., & Fraser, M. P. (2007). Primary source attribution and analysis of α -pinene
831 photooxidation products in Duke Forest, North Carolina. *Atmospheric Environment*, *41*,
832 2958–2966. <https://doi.org/10.1016/j.atmosenv.2006.12.018>
- 833 Bonsang, B., Polle, C., & Lambert, G. (1992). Evidence for marine production of isoprene,
834 *Geophysical Research Letter*, *19*, 1129–1132. <https://doi.org/10.1029/92GL00083>
- 835 Boreddy, S. K. R., & Kawamura, K. (2015). A 12-year observation of water-soluble ions in
836 TSP aerosols collected at a remote marine location in the western North Pacific: an
837 outflow region of Asian dust. *Atmospheric Chemistry and Physics*, *15*, 6437–6453.
838 <https://doi.org/10.5194/acp-15-6437-2015>
- 839 Boreddy, S. K. R., Haque, M., & Kawamura, K. (2018). Long-term (2001-2012) trends of
840 carbonaceous aerosols from remote island in the western North Pacific: an outflow region
841 of Asian pollutants and dust. *Atmospheric Chemistry and Physics*, *18*, 1291–1306.
842 <https://doi.org/10.5194/acp-18-1291-2018>
- 843 Bourgeois, Q., & Bey, I. (2011) Pollution transport efficiency toward the Arctic: Sensitivity to
844 aerosol scavenging and source regions. *Journal of Geophysical Research: Atmospheres*,
845 *116*, D08213. <https://doi.org/10.1029/2010JD015096>
- 846 Broadgate, W. J., Liss, P. S., & Penkett, S. A. (1997). Seasonal emissions of isoprene and other
847 reactive hydrocarbon gases from the ocean. *Geophysical Research Letter*, *24*, 2675–2678.
848 <https://doi.org/10.1029/97GL02736>
- 849 Brown, S. S., deGouw, J. A., Warneke, C., Ryerson, T. B., Dube', W. P., Atlas, E., Weber, R.
850 J., Peltier, R. E., Neuman, J. A., Roberts, J. M., Swanson, A., Flocke, F., McKeen, S. A.,
851 Brioude, J., Sommariva, R., Trainer, M., Fehsenfeld, F. C., & Ravishankara, A. R. (2009).
852 Nocturnal isoprene oxidation over the Northeast United States in summer and its impact
853 on reactive nitrogen partitioning and secondary organic aerosol. *Atmospheric Chemistry*
854 *and Physics*, *9*, 3027–3042. <https://doi.org/10.5194/acp-9-3027-2009>
- 855 Chen, J., Kawamura, K., Liu, C. Q., & Fu, P. Q. (2013). Long-term observations of saccharides
856 in remote marine aerosols from the western North Pacific: A comparison between 1990-
857 1993 and 2006-2009 periods. *Atmospheric Environment*, *67*, 448-458.
858 <https://doi.org/10.1016/j.atmosenv.2012.11.014>
- 859 Ciccioli, P., Centritto, M., & Loreto, F. (2014). Biogenic volatile organic compound emissions
860 from vegetation fires. *Plant, Cell and Environment*, *37*, 1810–1825.
861 <https://doi.org/10.1111/pce.12336>
- 862 Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J.,
863 Guyon, P., Andreae, M. O., Artaxo, P., & Maenhaut, W. (2004). Formation of secondary
864 organic aerosols through photooxidation of isoprene. *Science*, *303*, 1173–1176.
865 <https://doi.org/10.1126/science.1092805>
- 866 Claeys, M., Szmigielski, R., Kourtchev, I., van der Veken, P., Vermeylen, R., Maenhaut, W.,
867 Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., & Edney, E. O. (2007).
868 Hydroxydicarboxylic acids: markers for secondary organic aerosol from the
869 photooxidation of α -pinene. *Environmental Science and Technology*, *41*, 1628-1634.
870 <https://doi.org/10.1021/es0620181>
- 871 de Gouw, J., & Jimenez, J. L. (2009). Organic aerosols in the Earth's atmosphere.

- 872 *Environmental Science and Technology*, 43, 7614-7618. <https://doi:10.1021/es9006004>
- 873 de Lillis M., Bianco P.M., & Loreto F. (2009). The influence of leaf water content and
874 isoprenoids on flammability of some Mediterranean woody species. *International Journal*
875 *of Wildland Fire*, 18, 203–212. <https://doi.10.1071/WF07075>
- 876 Ding, X., He, Q.-F., Shen, R.-Q., Yu, Q.-Q., & Wang, X.-M. (2014). Spatial distributions of
877 secondary organic aerosols from isoprene, monoterpenes, β -caryophyllene, and aromatics
878 over China during summer. *Journal of Geophysical Research: Atmosphere*, 119, 11877-
879 11891. <https://doi.org/10.1002/2014JD021748>
- 880 Ding, X., Wang, X. M., Xie, Z. Q., Zhang, Z., & Sun, L. G. (2013). Impacts of Siberian
881 biomass burning on organic aerosols over the North Pacific Ocean and the Arctic: Primary
882 and secondary organic tracers. *Environmental Science and Technology*, 47(7), 3149-3157.
883 <https://doi:10.1021/es3037093>
- 884 Ding, X., Wang, X., Gao, B. Fu, X., He, Q., Zhao, X., Yu, J., & Zheng M. (2012). Tracer
885 based estimation of secondary organic carbon in the Pearl River Delta, South China.
886 *Journal of Geophysical Research*, 117, D05313. <https://doi.org/10.1029/2011JD016596>
- 887 Ding, X., Wang, X.M., & Zheng, M. (2011). The influence of temperature and aerosol acidity
888 on biogenic secondary organic aerosol tracers: observations at a rural site in the central
889 Pearl River Delta region, South China. *Atmospheric Environment*, 45, 1303-1311.
890 <https://doi.org/10.1016/j.atmosenv.2010.11.057>
- 891 Draxler, R. R., & Rolph, G. D. (2013). HYSPLIT (HYbrid Single-Particle Lagrangian
892 Integrated Trajectory) Model, access via NOAA ARL READY Website, available at:
893 https://ready.arl.noaa.gov/HYSPLIT_traj.php.
- 894 Fall R. (1999). Biogenic emissions of volatile organic compounds from higher plants. *In*
895 *Reactive Hydrocarbons in the Atmosphere* (ed C.N. Hewitt), pp. 41–86. Academic Press,
896 San Diego, CA. <https://doi.org/10.1016/B978-012346240-4/50003-5>
- 897 Fowler, D., Pilegaard, K., Sutton, M. A., Ambus, P., Raivonen, M., & Duyzer, J. (2009).
898 Atmospheric composition change: Ecosystems-Atmosphere interactions. *Atmospheric*
899 *Environment*, 43 (33), 5193–5267. <https://doi:10.1016/j.atmosenv.2009.07.068>
- 900 Fu, P. Q., Kawamura, K., & Miura, K. (2011). Molecular characterization of marine organic
901 aerosols collected during a round-the-world cruise. *Journal of Geophysical Research:*
902 *Atmosphere*, 116, D13302. <https://doi.org/10.1029/2011JD015604>
- 903 Fu, P. Q., Kawamura, K., Okuzawa, K., Aggarwal, S. G., Wang, G. H., Kanaya, Y., Wang, Z.
904 (2008). Organic molecular compositions and temporal variations of summertime mountain
905 aerosols over Mt. Tai, North China Plain. *Journal of Geophysical Research: Atmosphere*,
906 113 D19107. <https://doi:10.1029/2008jd009900>
- 907 Fu, P., Aggarwal, S. G., Chen, J., Li, J., Sun, Y., Wang, Z., Chen, H., Liao, H., Ding, A.,
908 Umarji, G. S., Patil, R. S., Chen, Q., & Kawamura, K. (2016). Molecular markers of
909 secondary organic aerosol in Mumbai, India. *Environmental Science & Technology*, 50,
910 4659– 4667. <https://doi.org/10.1021/acs.est.6b00372>
- 911 Glasius, M., Lahaniati, M., Calogirou, A., Di Bella, D., Jensen, N. R., Hjorth, J., Kotzias, D., &
912 Larsen, B. R. (2000). Carboxylic acids in secondary aerosols from oxidation of cyclic
913 monoterpenes by ozone. *Environmental Science & Technology*, 34, 1001–1010.
914 <https://doi.org/10.1021/es990445r>
- 915 Goldstein, A. H., & Galbally, I. E. (2007). Known and unexplored organic constituents in the
916 earth's atmosphere. *Environmental Science and Technology*, 41, 1514-1521.
917 <https://doi:10.1021/es072476p>
- 918 Griffin, R. J., Cocker, D. R., Seinfeld, J. H., & Dabdub, D. (1999). Estimate of global

- 919 atmospheric organic aerosol from oxidation of biogenic hydrocarbons. *Geophysical*
920 *Research Letters*, 26, 2721–2724. <https://doi.org/10.1029/1999GL900476>
- 921 Guenther, A., Hewitt, N. C., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger,
922 L., Lerday, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R.,
923 Taylor, J., & Zimmerman, P. (1995). A global model of natural volatile organic compound
924 emissions. *Journal of Geophysical Research: Atmospheres*, 100, 8873–8892.
925 <https://doi:10.1029/94JD02950>
- 926 Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P., & Geron, C. (2006). Estimates
927 of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and
928 Aerosols from Nature). *Atmospheric Chemistry and Physics*, 6, 3181–3210.
929 <https://dx.doi.org/10.5194/acp-6-3181-2006>
- 930 Hackenberg, S. C., Andrews, S. J., Airs, R., Arnold, S. R., Bouman, H. A., Brewin, R. J. W.,
931 Chance, R. J., Cummings, D., Dall’Olmo, G., Lewis, A. C., Minaeian, J. K., Reifel, K. M.,
932 Small, A., Tarran, G. A., Tilstone, G. H., & Carpenter, L. J. (2017). Potential controls of
933 isoprene in the surface ocean. *Global Biogeochemical Cycle*, 31, 644–662.
934 <https://doi.org/10.1002/2016GB005531-2017>
- 935 Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., & Claeys M. (2009).
936 The formation, properties and impact of secondary organic aerosol: current and emerging
937 issues. *Atmospheric Chemistry and Physics*, 9, 5155–5236. [https://doi:10.5194/acp-9-](https://doi:10.5194/acp-9-5155-2009)
938 [5155-2009](https://doi:10.5194/acp-9-5155-2009)
- 939 Han, F., Kota, S. H., Wang, Y., & Zhang, H. (2017). Source apportionment of PM_{2.5} in Baton
940 Rouge, Louisiana during 2009–2014. *Science of the Total Environment*, 586, 115–126.
941 <https://doi.org/10.1016/j.scitotenv.2017.01.189>
- 942 Heald, C. L., Jacob, D. J., Park, R. J., Russell, L. M., Huebert, B. J., Seinfeld, J. H., Liao, H., &
943 Weber, R. J. (2005). A large organic aerosol source in the free troposphere missing from
944 current models. *Geophysical Research Letters*, 32, L18809. [https://doi:10.1029/](https://doi:10.1029/2005GL023831)
945 [2005GL023831](https://doi:10.1029/2005GL023831)
- 946 Henze, D. K., & Seinfeld, J. H. (2006). Global secondary organic aerosol from isoprene
947 oxidation. *Geophysical Research Letters*, 45, 6972–6982.
948 <https://doi.org/10.1029/2018GL078689>
- 949 Hoffmann, T., Odum, J. R., Bowman, F., Collins, D., Klockow, D., Flagan, R. C., & Seinfeld,
950 J. H. (1997). Formation of organic aerosols from the oxidation of biogenic hydrocarbons.
951 *Journal of Atmospheric Chemistry*, 26, 189–222.
952 <https://doi.org/10.1023/A:1005734301837>
- 953 Hoyle, C. R., Berntsen, T., Myhre, G., & Isaksen, I. S. A. (2007). Secondary organic aerosol in
954 the global aerosol-chemical transport model Oslo CTM2. *Atmospheric Chemistry and*
955 *Physics*, 7, 5675–5694. <http://doi:10.5194/acp-7-5675-2007>
- 956 Hoyle, C. R., Boy, M., Donahue, N. M., Fry, J. L., Glasius, M., Guenther, A., Hallar, A. G.,
957 Huff Hartz, K., Petters, M. D., Peta ja, T., Rosenoern, T., & Sullivan, A. P. (2011). A
958 review of the anthropogenic influence on biogenic secondary organic aerosol. *Atmospheric*
959 *Chemistry and Physics*, 11, 321–343, 2011. <https://doi:10.5194/acp-11-321-2011>
- 960 Iinuma, Y., Böge, O., Gnauk, T., & Herrmann, H. (2004). Aerosol-chamber study of the α -
961 pinene/O₃ reaction: influence of particle acidity on aerosol yields and products.
962 *Atmospheric Environment*, 38, 761–773. <https://doi.org/10.1016/j.atmosenv.2003.10.015>
- 963 Intergovernmental Panel on Climate Change (IPCC): Climate Change: The Scientific Basis,
964 Cambridge University Press, UK, 2001.
- 965 Jaoui, M., Lewandowski, M., Kleindienst, T. E., Offenber, J. H., & Edney, E. O. (2007). β -
966 Caryophyllinic acid: An atmospheric tracer for β -caryophyllene secondary organic aerosol.

- 967 *Geophysical Research Letters*. 34, L05816. <https://doi:10.1029/2006GL028827>
- 968 Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., & Facchini, M. C.
969 (2005). Organic aerosol and global climate modelling: A review. *Atmospheric Chemistry*
970 *and Physics*, 5, 1053–1123. <https://doi:10.5194/acp-5-1053-2005>
- 971 Kang, M., Fu, P.Q., Kawamura, K., Yang, F., Zhang, H., Zang, Z., Ren, H., Ren, L., Zhao, Y.
972 Sun, Y., & Wang, Z. (2018). Characterization of biogenic primary and secondary organic
973 aerosols in the marine atmosphere over the East China Sea. *Atmospheric Chemistry and*
974 *Physics*, 18, 13947–13967. <https://doi.org/10.5194/acp-18-13947-2018>
- 975 Kavouras, I. G., Mihalopoulos, N., & Stephanou, E. G. (1998). Formation of atmospheric
976 particles from organic acids produced by forests. *Nature*, 395, 683–686.
977 <https://doi:10.1038/27179>
- 978 Kawamura, K., Ishimura, Y., & Yamazaki, K. (2003). Four years' observations of terrestrial
979 lipid class compounds in marine aerosols from the western North Pacific. *Global*
980 *Biogeochemical Cycles*, 17(1), 1003. <https://doi:10.1029/2001gb001810>
- 981 Keeling C.I., & Bohlmann J. (2006). Genes, enzymes and chemicals of terpenoid diversity in
982 the constitutive and induced defense of conifers against insects and pathogens. *New*
983 *Phytologist*, 170, 657–675. <https://doi.10.1111/j.1469-8137.2006.01716.x>
- 984 Kim, J. C. (2001). Factors controlling natural VOC emissions in a southeastern US pine forest.
985 *Atmospheric Environment*, 35, 3279-3292. [https://doi:10.1016/S1352-2310\(00\)00522-7](https://doi:10.1016/S1352-2310(00)00522-7)
- 986 Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenber, J. H., Lewis, C. W., & Bhave, P. V.
987 (2007). Estimates of the contributions of biogenic and anthropogenic hydrocarbons to
988 secondary organic aerosol at a southeastern US location. *Atmospheric Environment*, 41,
989 8288-8300. <https://doi.org/10.1016/j.atmosenv.2007.06.045>
- 990 Kleindienst, T. E., Lewandowski, M., Offenber, J. H., Jaoui, M., & Edney, E. O. (2009). The
991 formation of secondary organic aerosol from the isoprene plus OH reaction in the absence
992 of NO_x. *Atmospheric Chemistry Physics*, 9, 6541-6558. [https://doi.org/10.5194/acp-9-](https://doi.org/10.5194/acp-9-6541-2009)
993 [6541-2009](https://doi.org/10.5194/acp-9-6541-2009)
- 994 Kourtev, I., Warnke, J., Maenhaut, W., Hoffmann, T., & Claeys, M. (2008). Polar organic
995 marker compounds in PM_{2.5} aerosol from a mixed forest site in western Germany.
996 *Chemosphere*, 73, 1308-1314. <https://doi.org/10.1016/j.chemosphere.2008.07.011>
- 997 Kulmala, M., Asmi, A., Lappalainen, H. K., Baltensperger, U., Brenguier, J.-L., Facchini, M.
998 C., Hansson, H.-C., Hov, Ø., O'Dowd, C. D., Pöschl, U., Wiedensohler, A., Boers, R.,
999 Boucher, O., de Leeuw, G., Denier van der Gon, H. A. C., Feichter, J., Krejci, R., Laj, P.,
1000 Lihavainen, H., Lohmann, U., McFiggans, G., Mentel, T., Pilinis, C., Riipinen, I., Schulz,
1001 M., Stohl, A., Swietlicki, E., Vignati, E., Alves, C., Amann, M., Ammann, M., Arabas, S.,
1002 Artaxo, P., Baars, H., Beddows, D. C. S., Bergström, R., Beukes, J. P., Bilde, M., Burkhart,
1003 J. F., Canonaco, F., Clegg, S. L., Coe, H., Crumeyrolle, S., D'Anna, B., Decesari, S.,
1004 Gilardoni, S., Fischer, M., Fjaeraa, A. M., Fountoukis, C., George, C., Gomes, L.,
1005 Halloran, P., Hamburger, T., Harrison, R. M., Herrmann, H., Hoffmann, T., Hoose, C., Hu,
1006 M., Hyvärinen, A., Hörrak, U., Iinuma, Y., Iversen, T., Josipovic, M., Kanakidou, M.,
1007 Kiendler-Scharr, A., Kirkevåg, A., Kiss, G., Klimont, Z., Kolmonen, P., Komppula, M.,
1008 Kristjánsson, J.-E., Laakso, L., Laaksonen, A., Labonnote, L., Lanz, V. A., Lehtinen, K. E.
1009 J., Rizzo, L. V., Makkonen, R., Manninen, H. E., McMeeking, G., Merikanto, J., Minikin,
1010 A., Mirme, S., Morgan, W. T., Nemitz, E., O'Donnell, D., Panwar, T. S., Pawlowska, H.,
1011 Petzold, A., Pienaar, J. J., Pio, C., Plass-Duelmer, C., Prévôt, A. S. H., Pryor, S.,
1012 Reddington, C. L., Roberts, G., Rosenfeld, D., Schwarz, J., Seland, Ø., Sellegri, K., Shen,
1013 X. J., Shiraiwa, M., Siebert, H., Sierau, B., Simpson, D., Sun, J. Y., Topping, D., Tunved,
1014 P., Vaattovaara, P., Vakkari, V., Veefkind, J. P., Visschedijk, A., Vuollekoski, H., Vuolo,

- 1015 R., Wehner, B., Wildt, J., Woodward, S., Worsnop, D. R., van Zadelhoff, G.-J., Zardini, A.
1016 A., Zhang, K., van Zyl, P. G., Kerminen, V.-M., S Carslaw, K., & Pandis, S. N. (2011).
1017 General overview: European integrated project on aerosol cloud climate and air quality
1018 interactions (EUCAARI)—integrating aerosol research from nano to global scales.
1019 *Atmospheric Chemistry Physics*, *11*, 13061–13143. [https://doi.org/10.5194/acp-11-13061-](https://doi.org/10.5194/acp-11-13061-2011)
1020 2011
- 1021 Kurihara, M. K., Kimura, M., Iwamoto, Y., Narita, Y., Ooki, A., Eum, Y.-J., Tsuda, A., Suzuki,
1022 K., Tani, Y., Yokouchi, Y., Uematsu, M., & Hashimoto, S. (2010). Distributions of short-
1023 lived iodocarbons and biogenic trace gases in the open ocean and atmosphere in the
1024 western North Pacific. *Marine Chemistry*, *118*(3–4), 156–170.
1025 <https://doi:10.1016/j.marchem.2009.12.001>
- 1026 Lewandowski, M., Piletic, I. R., Kleindienst, T. E., Offenber, J. H., Beaver, M. R., Jaoui, M.
1027 et. al. (2013). Secondary organic aerosol characterisation at field sites across the United
1028 States during the spring–summer period. *International Journal of Environmental*
1029 *Analytical Chemistry*, *93*, 1084–1103. <https://doi.org/10.1080/03067319.2013.803545>
- 1030 Li, Z., Ratliff, E. A., & Sharkey, T. D. (2011). Effect of temperature on postillumination
1031 isoprene emission in oak and poplar. *Plant Physiology*, *155* (2), 1037–1046.
1032 <https://doi/10.1104/pp.110.167551>
- 1033 Lopez-Hilfiker, F. D., Mohr, C., D’Ambro, E. L., Lutz, A., Riedel, T. P., Gaston, C. J., Iyer, S.,
1034 Zhang, Z., Gold, A., Surratt, J. D., & Lee, B. H. (2016). Molecular composition and
1035 volatility of organic aerosol in the southeastern US: Implications for IEPOX derived SOA.
1036 *Environmental Science & Technology*, *50*, 2200–2209.
1037 <https://doi.org/10.1021/acs.est.5b04769>
- 1038 Mentel, Th. F., Kleist, E., Andres, S., Maso, M. D., Hohaus, T., Kiendler-Scharr, A., Rudich,
1039 Y., Springer, M., Tillmann, R., Uerlings, R., Wahner, A., & Wildt, J. (2013). Secondary
1040 aerosol formation from stress-induced biogenic emissions and possible climate feedbacks.
1041 *Atmospheric Chemistry and Physics*, *13*, 8755–8770. [https://doi:10.5194/acp-13-8755-](https://doi:10.5194/acp-13-8755-2013)
1042 2013
- 1043 Meskhidze, N., & Nenes, A. (2006). Phytoplankton and cloudiness in the Southern Ocean.
1044 *Science*, *314*, 1419–1423. <http://doi:10.1126/science.1131779>
- 1045 Mochida, M., Kawamura, K., Fu, P. Q., & Takemura, T. (2010). Seasonal variation of
1046 levoglucosan in aerosols over the western North Pacific and its assessment as a biomass-
1047 burning tracer. *Atmospheric Environment*, *44*(29), 3511–3518.
1048 <https://doi.org/10.1016/j.atmosenv.2010.06.017>
- 1049 Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., Pye, H.
1050 O. T., Crouse, J. D., Wennberg, P. O., Flagan, R. C., & Seinfeld, J. H. (2008). Secondary
1051 organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO₃).
1052 *Atmospheric Chemistry and Physics*, *8*, 4117–4140. <https://doi:10.5194/acpd-8-3163-2008>
- 1053 Ooki, A., Nomura, D., Nishino, S., Kikuchi, T., & Yokouchi, Y. (2015). A global-scale map of
1054 isoprene and volatile organic iodine in surface seawater of the Arctic, Northwest Pacific,
1055 Indian, and Southern Oceans. *Journal Geophysical Research Oceans*, *120*, 4108–4128.
1056 <https://doi:10.1002/2014JC010519>
- 1057 Paatero, P., & Tapper, U. (1994). Positive matrix factorization: a non-negative factor model
1058 with optimal utilization of error estimates of data values. *Environmetrics*, *5*, 111–126.
1059 <https://dx.doi.org/10.1002/env.3170050203>
- 1060 Paatero, P., Hopke, P. K., Song, X. H., & Ramadan, Z. (2002). Understanding and controlling
1061 rotations in factor analytic models. *Chemometrics and Intelligent Laboratory Systems*, *60*,
1062 253–264, 2002. [https://doi.org/10.1016/S0169-7439\(01\)00200-3](https://doi.org/10.1016/S0169-7439(01)00200-3)

- 1063 Piccot, S., Watson, J., & Jones, J. (1992). A global inventory of volatile organic compound
1064 emissions from anthropogenic sources. *Journal of Geophysical Research: Atmospheric*,
1065 *97(D9)*, 9897–9912. <https://doi:10.1029/92JD00682>
- 1066 Rasulov, B., Hüve, K., Bichele, I., Laisk, A., & Niinemets, Ü. (2010). Temperature response of
1067 isoprene emission in vivo reflects a combined effect of substrate limitations and isoprene
1068 synthase activity: a kinetic analysis. *Plant Physiology*, *154* (3), 1558–1570.
1069 <https://doi:10.1104/pp.110.162081>
- 1070 Riva, M., Budisulistiorini, S. H., Zhang, Z., Gold, A., & Surratt, J. D. (2016). Chemical
1071 characterization of secondary organic aerosol constituents from isoprene ozonolysis in the
1072 presence of acidic aerosol. *Atmospheric Environment*, *130*, 5–13.
1073 <https://doi:10.1016/j.atmosenv.2015.06.027>
- 1074 Robinson, A.L., Donahue, N. M., & Rogge, W. F. (2006). Photochemical oxidation and
1075 changes in molecular composition of organic aerosol in the regional context. *Journal of*
1076 *Geophysical Research: Atmosphere*, *111*, D03302. <https://doi.org/10.1029/2005JD006265>
- 1077 Sekimoto K., Koss, A. R., Gilman, J. B., Selimovic, V., Coggon, M. M., Zarzana, K. J., Yuan,
1078 B., Lerner, B. M., Brown, S. S., Warneke, C., Yokelson, R. J., Roberts, J. M., & de Gouw,
1079 J. (2018). High- and low-temperature pyrolysis profiles describe volatile organic
1080 compound emissions from western US wildfire fuels. *Atmospheric Chemistry and Physics*,
1081 *18*, 9263–9281. <https://doi.org/10.5194/acp-18-9263-2018>
- 1082 Sharkey, T. D., & Singaas, E. L. (1995). Why plants emit isoprene. *Nature*, *374* (6525), 769–
1083 769. <https://doi:10.1038/374769a0>
- 1084 Shaw, S. L., Chisholm, S. W., & Prinn, R. G. (2003). Isoprene production by Prochlorococcus,
1085 a marine cyanobacterium, and other phyto-plankton. *Marine Chemistry*, *80*, 227–245.
1086 [https://doi.org/10.1016/S0304-4203\(02\)00101-9](https://doi.org/10.1016/S0304-4203(02)00101-9)
- 1087 Simoneit, B. R. T., Kobayashi, M., Mochida, M., Kawamura, K., Lee, M., Lim, H. J., Turpin,
1088 B. J., & Komazaki, Y. (2004). Composition and major sources of organic compounds of
1089 aerosol particulate matter sampled during the ACE-Asia campaign. *Journal of*
1090 *Geophysical Research: Atmospheres*, *109*(D19). <https://doi:10.1029/2004jd004598>
- 1091 Stone, E. A., Hedman, C. J., Zhou, J., Mieritz, M., & Schauer, J. J. (2010). Insights into the
1092 nature of secondary organic aerosol in Mexico City during the MILAGRO experiment.
1093 *Atmospheric Environment*, *44*, 312–319. <https://doi.org/10.1016/j.atmosenv.2009.10.036>
- 1094 Stone, E. A., Nguyen, T. T., Pradhan, B. B., & Dangol, P. M. (2012). Assessment of biogenic
1095 secondary organic aerosol in the Himalayas. *Environmental Chemistry*, *9*, 263–272, 2012.
1096 <https://doi:10.1071/EN12002>
- 1097 Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M. N., Loza, C. L., & , A. J. (2010).
1098 Reactive intermediates revealed in secondary organic aerosol formation from isoprene.
1099 *Proceedings of the National Academy Science United States of America*, *107*(15), 6640–
1100 6645. <https://doi.org/10.1073/pnas.0911114107>
- 1101 Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A.,
1102 Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., Seinfeld, J. H.
1103 (2006). Chemical composition of secondary organic aerosol formed from the
1104 photooxidation of isoprene. *Journal of Physical Chemistry A*, *110*, 9665–9690.
1105 <https://doi:10.1021/jp061734m>
- 1106 Szmigielski, R., Surratt, J. D., Gómez-González, Y., van der Veken, P., Kourtchev, I.,
1107 Vermeylen, R., Blockhuys, F., Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenber,
1108 J. H., Edney, E. O., Seinfeld, J. H., Maenhaut, W., & Claeys, M. (2007). 3-methyl-1,2,3-
1109 butanetricarboxylic acid: An atmospheric tracer for terpene secondary organic aerosol.
1110 *Geophysical Research Letters*, *34*(24), L24811. <https://doi:10.1029/2007GL031338>

- 1111 Verma, S. K., Kawamura, K., Chen, J., & Fu, P. Q. (2018). Thirteen years of observations on
1112 primary sugars and sugar alcohols over remote Chichijima Island in the western North
1113 Pacific. *Atmospheric Chemistry Physics*, *18*, 81–101. [https://doi.org/10.5194/acp-18-81-](https://doi.org/10.5194/acp-18-81-2018)
1114 2018
- 1115 Verma, S. K., Kawamura, K., Chen, J., Fu, P. Q., & Zhu, C. M. (2015). Thirteen years of
1116 observations on biomass burning organic tracers over Chichijima Island in the western
1117 North Pacific: an outflow region of Asian aerosols. *Journal of Geophysical Research:*
1118 *Atmospheres*, *120*, 4155-4168. <https://doi.org/10.1002/2014JD022224>
- 1119 von Schneidemesser, E., Zhou, J., Stone, E. A., Schauer, J. J., Shpund, J., Brenner, S., Qasrawi,
1120 R., Abdeen, Z., & Sarnat, J. A. (2009). Spatial variability of carbonaceous aerosol
1121 concentrations in east and west Jerusalem. *Environmental Science and Technology*, *44*,
1122 1911–1917. <https://doi:10.1021/es9014025>
- 1123 Wang, G. H., Kawamura, K., & Lee, M. (2009). Comparison of organic compositions in dust
1124 storm and normal aerosol samples collected at Gosan, Jeju Island, during spring 2005.
1125 *Atmospheric Environment*, *43*(2), 219-227. <https://doi:10.1016/j.atmosenv.2008.09.046>
- 1126 Wang, W., Wu, M. H., Li, L., Zhang, T., Liu, X.D., Feng, J. L., Li, H.J., Wang, Y. J., Sheng, G.
1127 Y., Claeys, M., & Fu, J. M. (2008). Polar organic tracers in PM_{2.5} aerosols from forests in
1128 eastern China. *Atmospheric Chemistry and Physics*, *8*, 7507-7518.
1129 <https://doi.org/10.5194/acp-8-7507-2008>
- 1130 Xia, X., & Hopke, P. K. (2006). Seasonal Variation of 2-Methyltetrols in Ambient Air Samples.
1131 *Environmental Science and Technology* *40* (22), 6934-7. <https://doi.10.1021/es060988i>
- 1132 Xie, M., Hannigan, M. P., & Barsanti, K. C. (2014). Gas/Particle partitioning of 2-
1133 methyltetrols and levoglucosan at an urban site in Denver. *Environmental Science and*
1134 *Technology*, *48*, 2835–2842. <https://doi.org/10.1021/es405356n>
- 1135 Yamamoto, S., Kawamura, K., & Seki, O. (2011). Long-range atmospheric transport of
1136 terrestrial biomarkers by the Asian winter monsoon: Evidence from fresh snow from
1137 Sapporo, northern Japan. *Atmospheric Environment*, *45*, 3553–3560.
1138 <https://doi.org/10.1016/j.atmosenv.2011.03.071>
- 1139 Zhang, J. Y., & Wu, L. Y. (2011). Land-atmosphere coupling amplifies hot extremes over
1140 China. *Chinese Science Bulletin*, *56*(31), 3328-3332. [https://doi:10.1007/s11434-011-](https://doi:10.1007/s11434-011-4628-3)
1141 4628-3
- 1142 Zhou, L., Kim, E., Hopke, P. K., Stanier, C. O., & Pandis, S. (2004). Advanced factor analysis
1143 on Pittsburgh particle size-distribution data special issue of aerosol science and technology
1144 on findings from the fine particulate matter supersites program. *Aerosol Science and*
1145 *Technology*, *38*, 118–132. <https://doi.org/10.1080/02786820390229589>
- 1146 Zhu, C., Kawamura, K., & Fu, P. (2016). Seasonal variations of biogenic secondary organic
1147 aerosol tracers in Cape Hedo, Okinawa. *Atmospheric Environment*, *130*, 113–119.
1148 <https://doi.org/10.1016/j.atmosenv.2015.08.069>

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1152 **Figure Captions**

1153 Figure 1. Geographic location of Chichijima Island (27.06°N and 142.21°E) in the western
1154 North Pacific. Sampling site is indicated by the red star.

1155 Figure 2. Monthly variation of the meteorological parameters over Chichijima Island during
1156 2010–2012 period (The error bars denote the standard deviations).

1157 Figure 3. Seasonal air-mass backward trajectories over Chichijima Island during winter
1158 (December–February), spring (March–May), summer (June–August), and autumn
1159 (September–November).

1160 Figure 4. Temporal trends of measured SOA tracers at Chichijima Island during the campaign.

1161 Figure 5. Monthly trends of measured SOA tracers at Chichijima Island during the campaign.

1162 Figure 6. Seasonal scatter plots of levoglucosan with 2-MTLs (a, b) and *c*SOA tracers (c - g).

1163 Figure 7. Seasonal scatter plots of C₅-alkene triols with 2-MTLs (a - d), 3-MBTCA with 3-
1164 HGA (e - h), NO₃⁻ with 3-HGA (i), and 3-MBTCA (j).

1165 Figure 8. Monthly average concentrations (2010–2012) of levoglucosan and β -caryophyllene-
1166 SOA tracer in the Chichijima aerosols.

1167 Figure 9. PMF analyses of the biogenic SOA tracers and levoglucosan in the Chichijima
1168 aerosols. (levoglucosan data were acquired from Verma et al. (2015) for PMF analysis).

1169 Figure 10. Contributions to biogenic SOA tracers from various sources based on PMF analyses.

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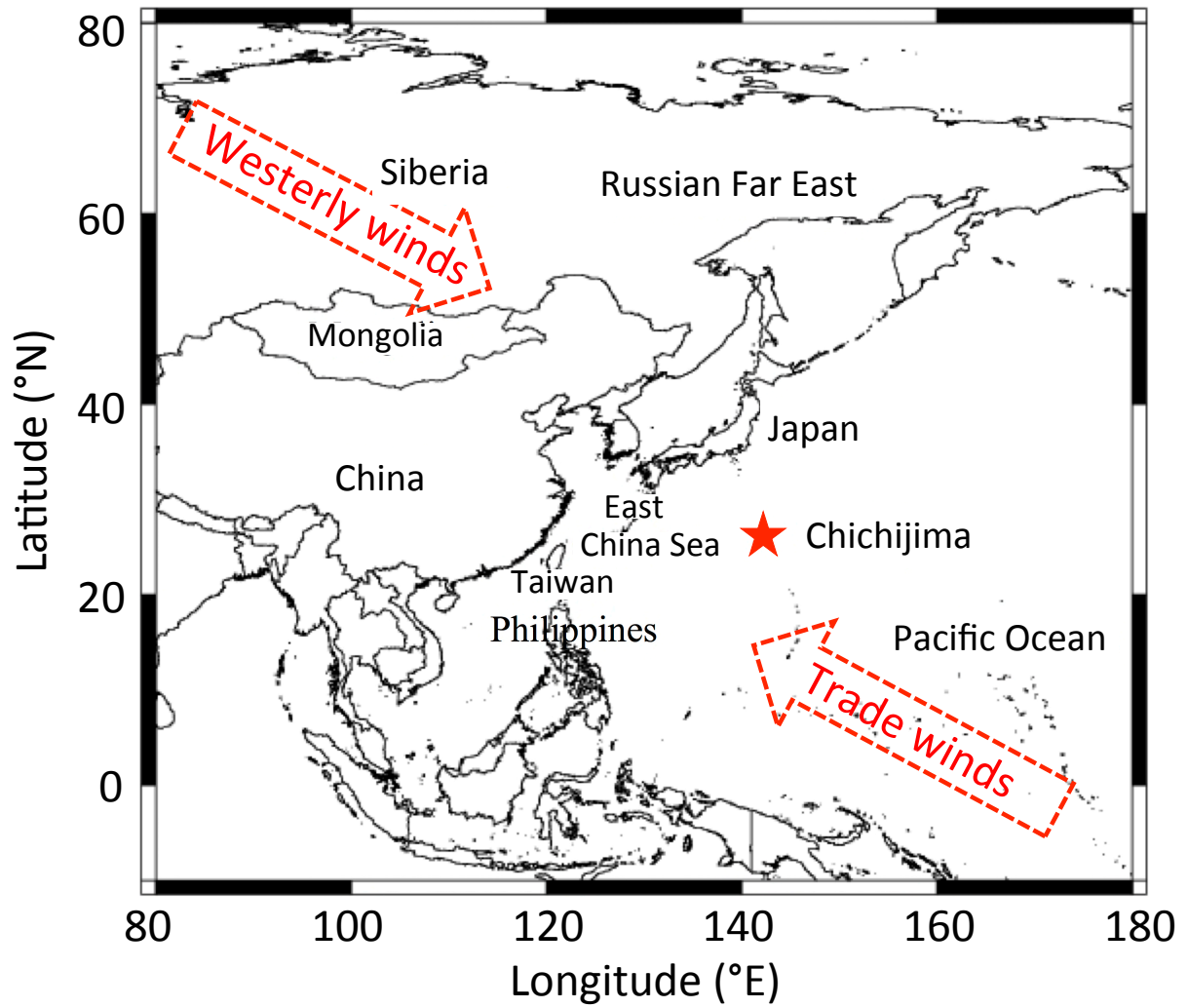
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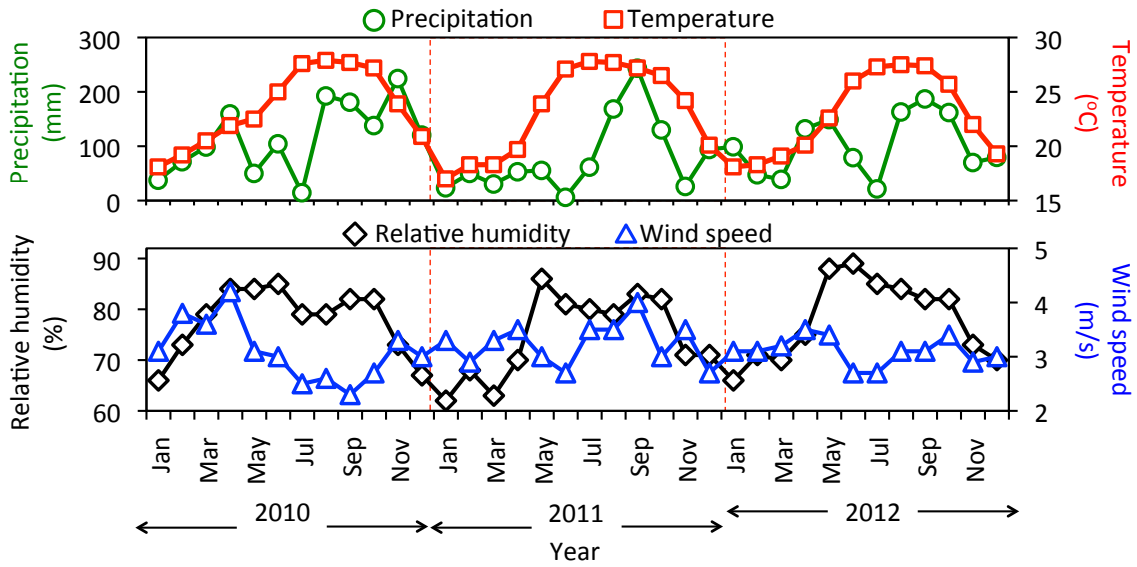
Figure 1.



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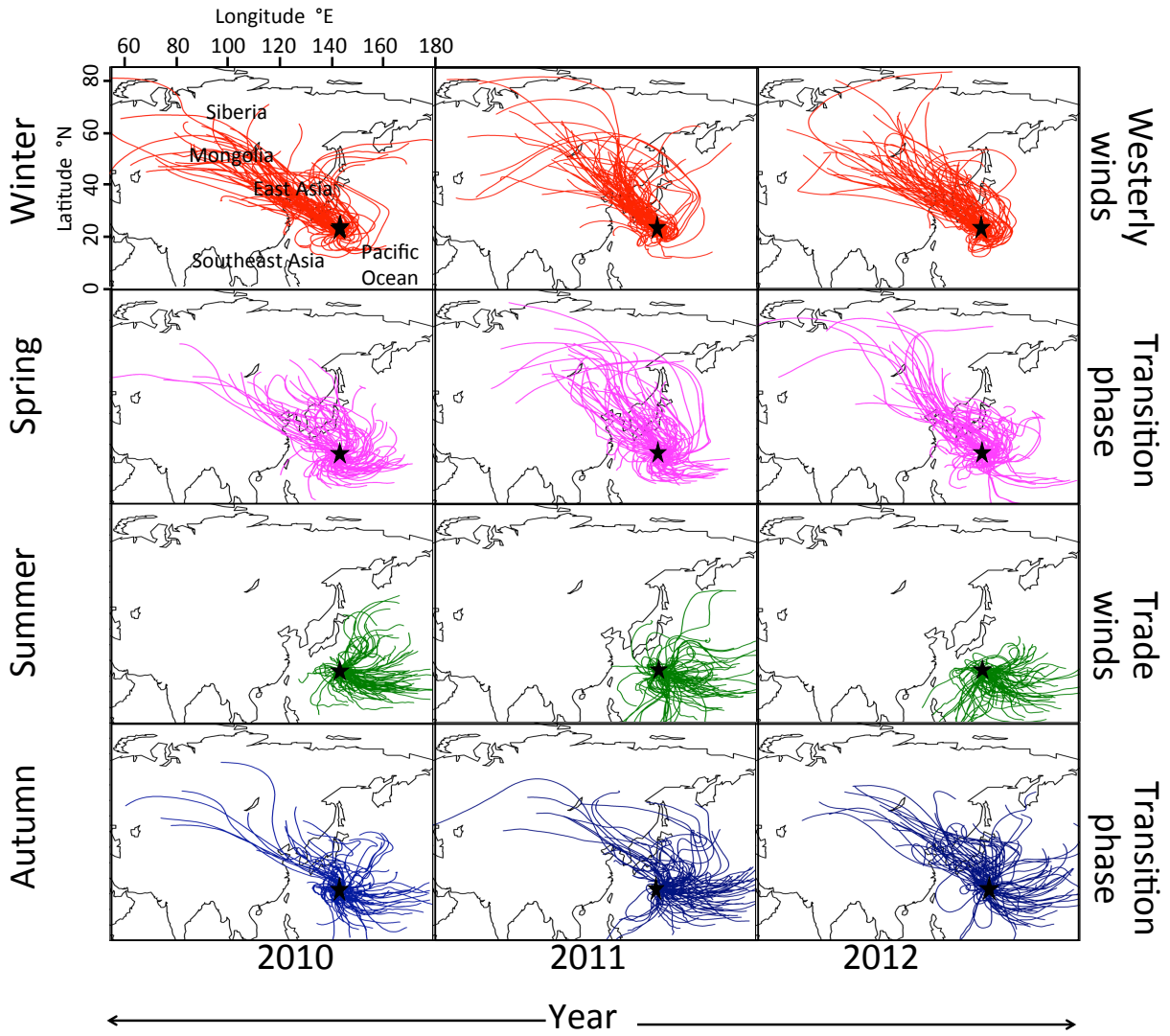
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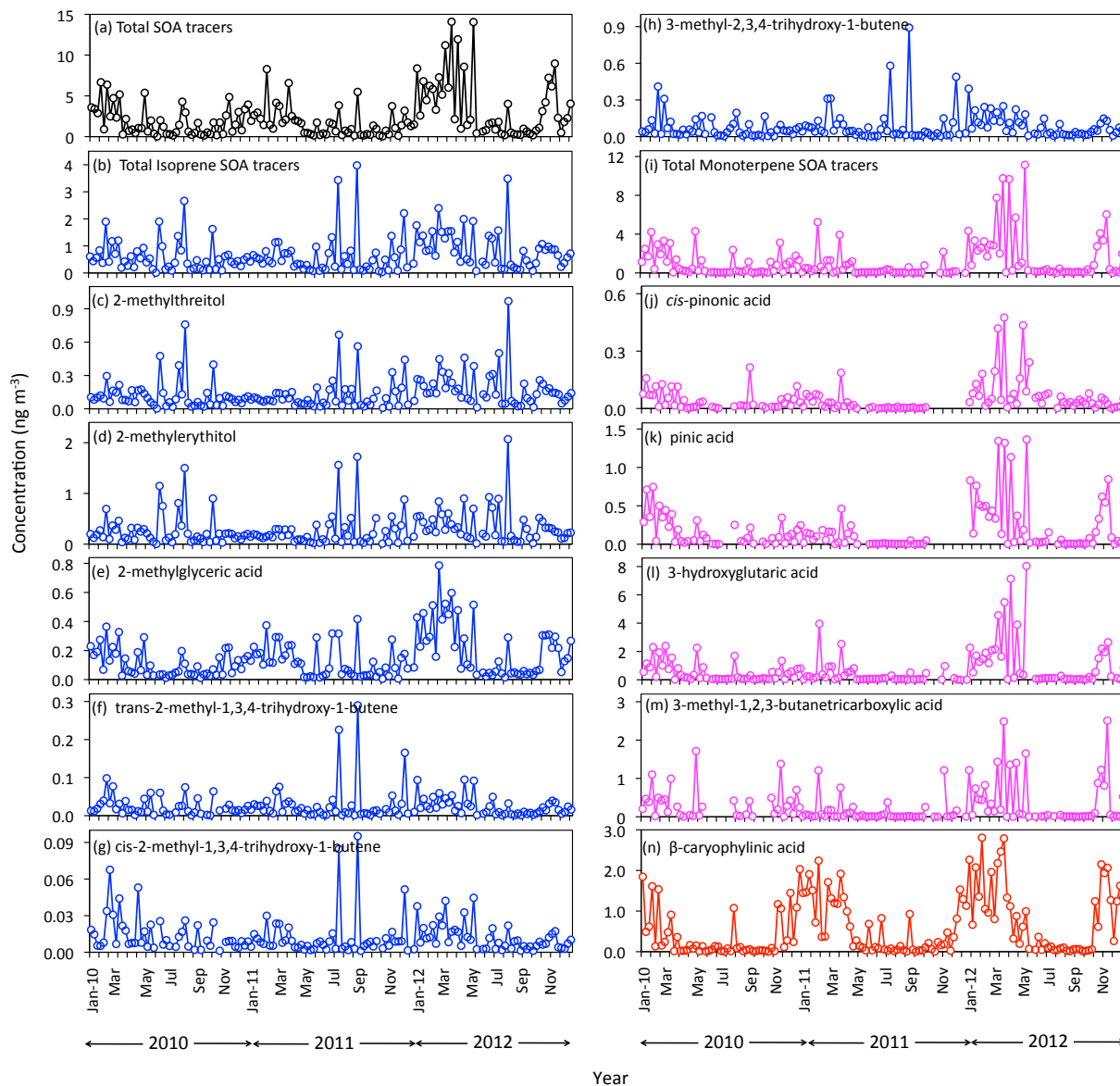
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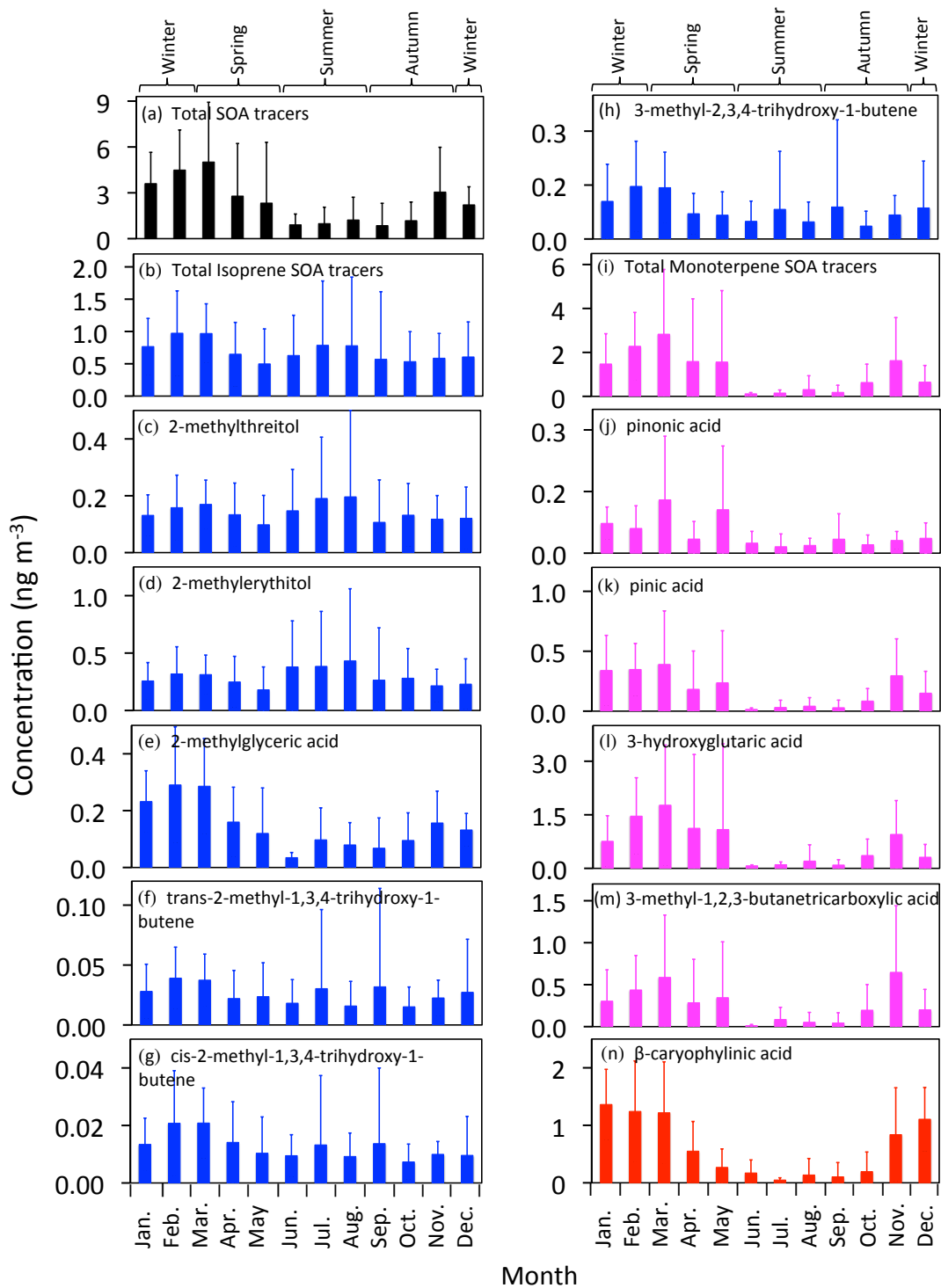
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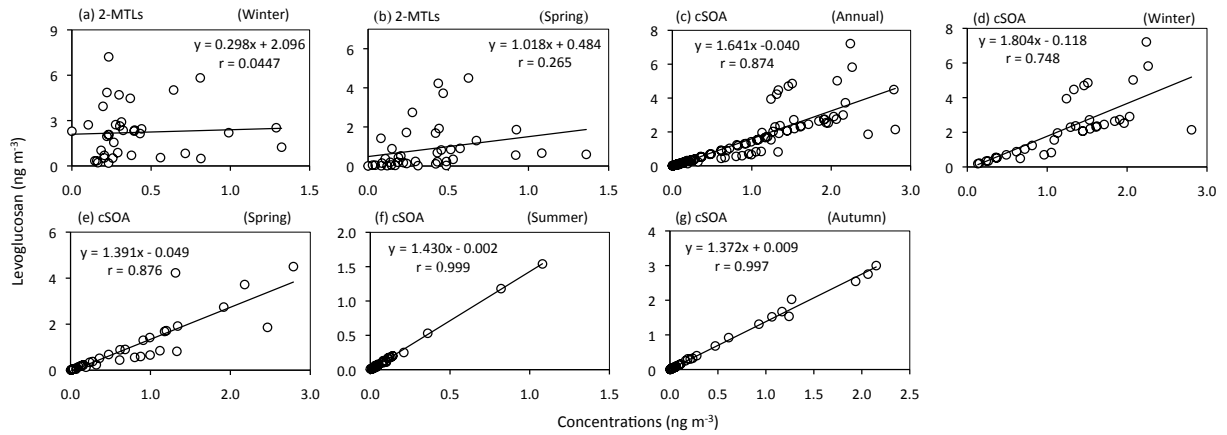
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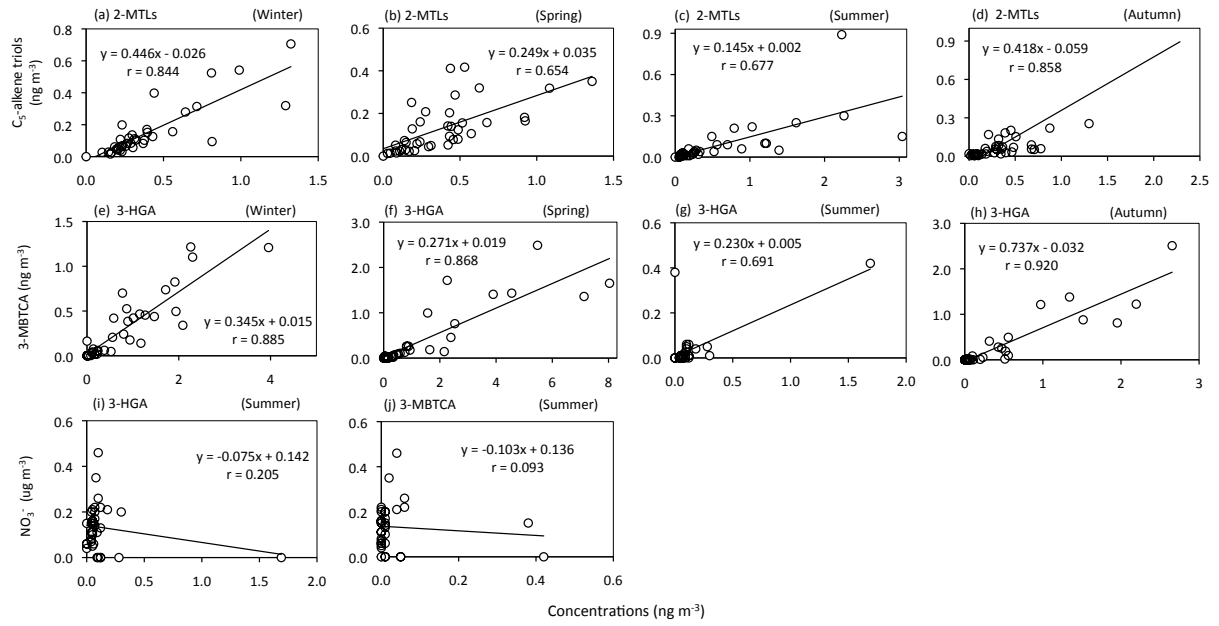
Figure 6.



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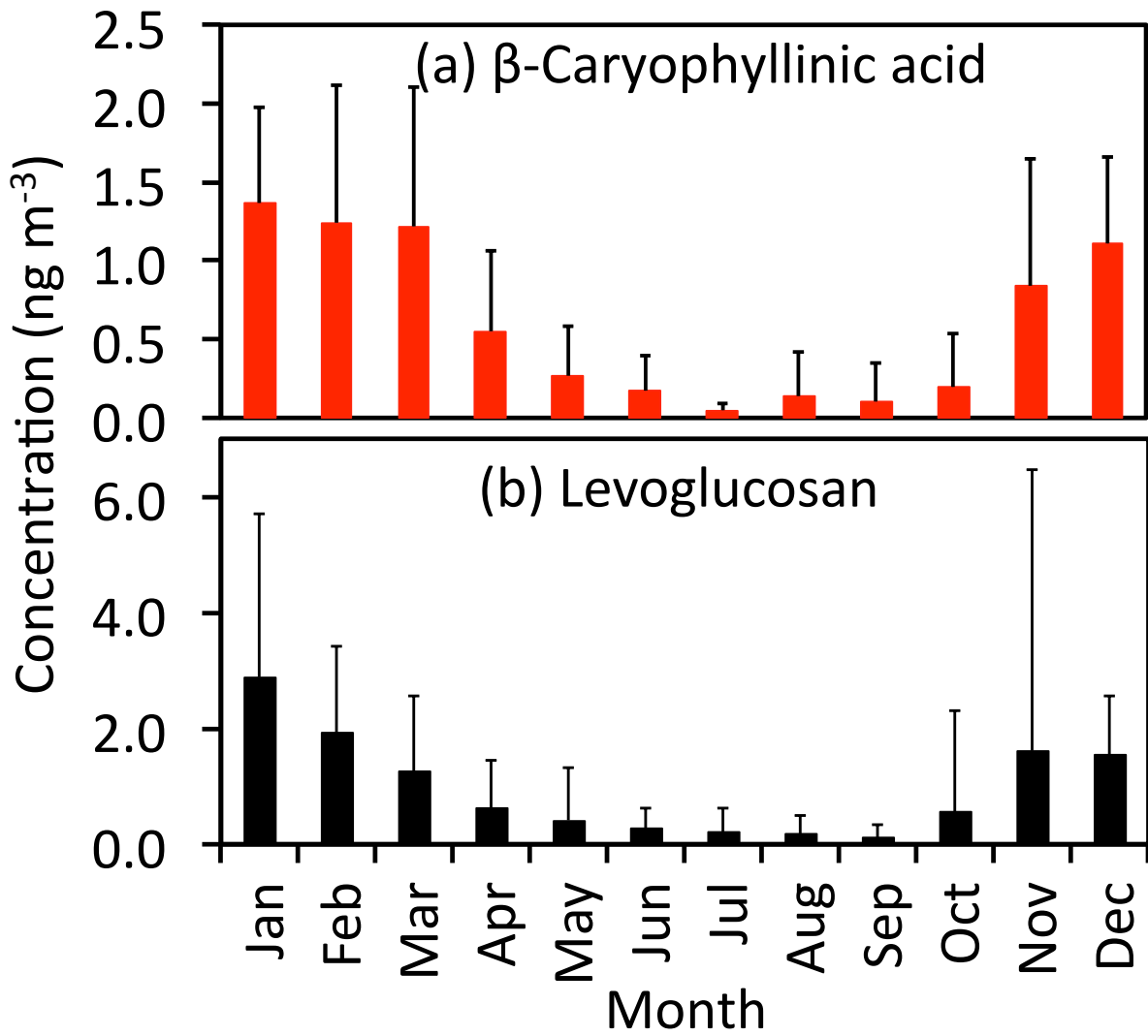
Figure 7.



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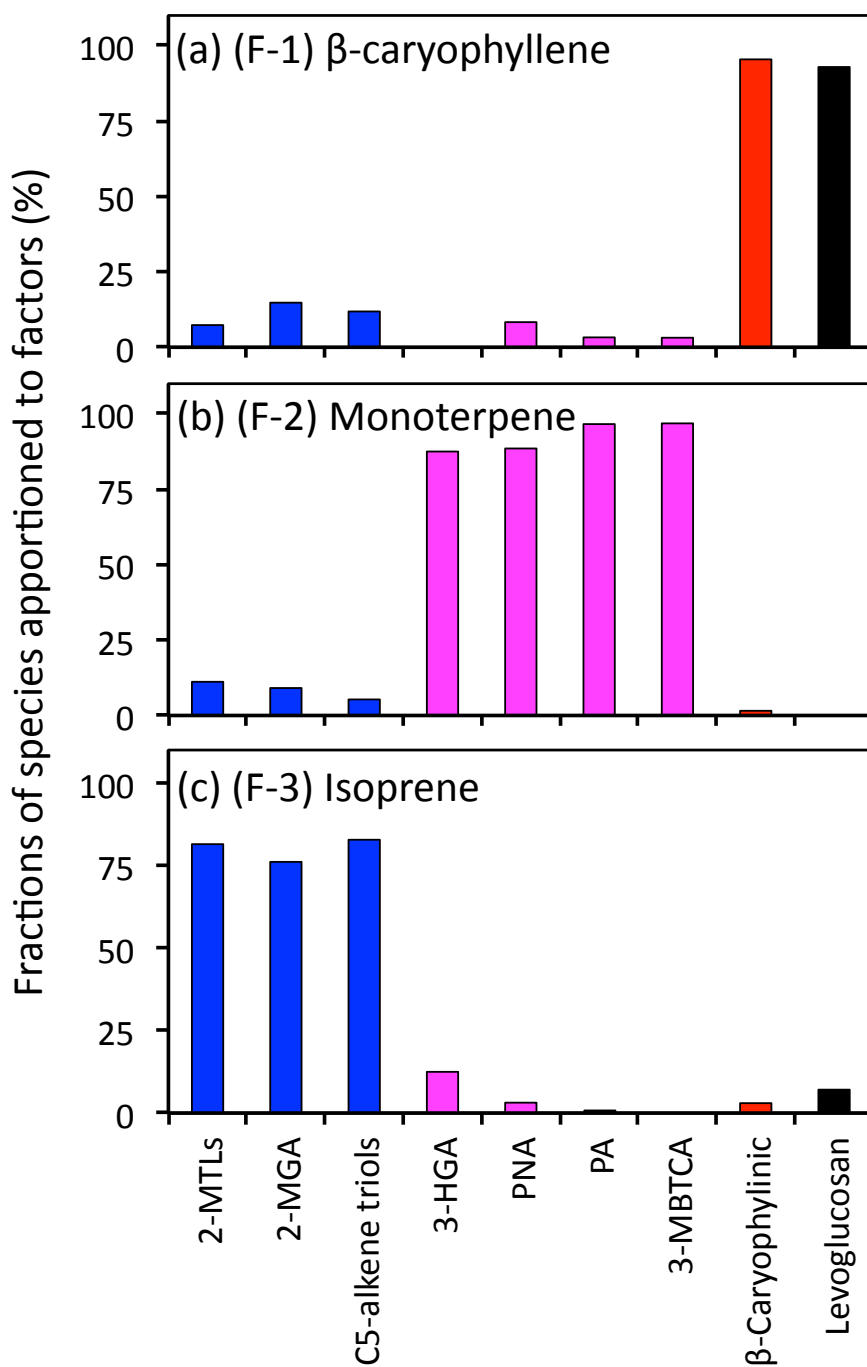
Figure 8.



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Figure 9.



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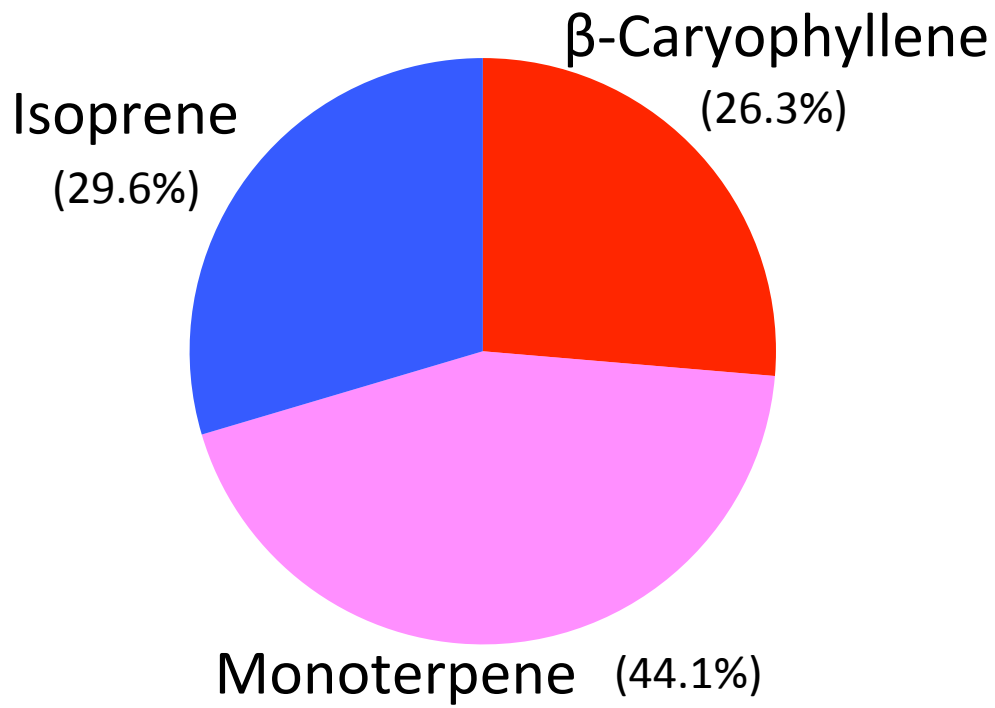
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1377 Figure 10.

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