

1 **Molecular distributions and isotopic compositions of organic aerosols over the western**  
2 **North Atlantic: Dicarboxylic acids, oxoacids,  $\alpha$ -dicarbonyls (glyoxal and methylglyoxal),**  
3 **lipid class compounds, sugars, and secondary organic aerosol tracers**

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**23 Abstract**

24 Marine aerosols were collected over the western North Atlantic off the coast of  
25 Boston to Bermuda in August 2012 using a high-volume air sampler. Aerosol samples were  
26 analyzed for organic and elemental carbon (OC/EC), low molecular weight dicarboxylic acids  
27 and related compounds, lipid class compounds (n-alkanes, fatty acids and fatty alcohols),  
28 sugars and various secondary organic aerosol (SOA) tracers. Homologous series (C<sub>2</sub>-C<sub>12</sub>) of  
29 dicarboxylic acids (31-335 ng m<sup>-3</sup>) were detected with a predominance of oxalic acid. Diacids  
30 were found to be the most abundant compound class followed by monoterpene-SOA tracers >  
31 isoprene-SOA tracers > sugars > oxoacids > fatty alcohols > fatty acids > α-dicarbonyls >  
32 aromatic acids > n-alkanes. The concentrations of these compounds were higher in the coastal  
33 site and decreased towards the open ocean. However, the abundance of diacids stayed  
34 relatively high even in the remote ocean. Interestingly, contributions of oxalic acid to total  
35 aerosol carbon increased from the coast (2.3%) to the open ocean (5.6%) near Bermuda.

36 Stable carbon isotope ratios of aerosol total carbon and individual diacids and  
37 oxoacids were determined using an isotope ratio mass spectrometer. The stable carbon isotopic  
38 composition of oxalic acid increased from the coast (-17.5‰) to the open ocean (-12.4‰),  
39 suggesting that photochemical aging of organic aerosols occurred during the atmospheric  
40 transport over the ocean. Stable carbon isotope ratios of bulk aerosol carbon also increased  
41 from the coast near Boston (-24.3‰) to the open ocean near Bermuda (-18.2‰), consistent  
42 with photochemical aging of organic aerosols.

43 **Keywords:** Marine aerosols, western North Atlantic, oxalic acid, photochemical aging, stable  
44 carbon isotopic composition

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## 47 **Introduction**

48           Organic aerosols are comprised of complex mixture of various organic compounds  
49 ranging from water-soluble to water-insoluble species (Simoneit, 1986; Simoneit and Mazurek,  
50 1982). Dicarboxylic acids such as oxalic, malonic and succinic acids are typical water-soluble  
51 organic compounds that can contribute up to 16% of aerosol total carbon in the remote marine  
52 atmosphere over the Pacific Ocean (Kawamura and Sakaguchi, 1999). Dicarboxylic acids,  
53 oxoacids and  $\alpha$ -dicarbonyls such as glyoxal and methylglyoxal are abundant organic  
54 compound classes in continental aerosols from various locations (Agarwal et al., 2010; Ho et  
55 al., 2007; Ho et al., 2011). These water-soluble organic species can act as cloud condensation  
56 nuclei (CCN) in the atmosphere (Saxena and Hildemann, 1996; Saxena et al., 1995), whereas  
57 water-insoluble species such as lipid class compounds may depress the hygroscopic activity of  
58 aerosol particles. Organic aerosols affect radiative forcing positively or negatively via the  
59 interaction with water vapor in the atmosphere (Boreddy et al., 2014).

60           Dicarboxylic acids are primarily produced by fossil fuel combustion [Kawamura and  
61 Kaplan, 1987] and biomass burning (Kawamura et al., 2013; Legrand and de Angelis, 1996;  
62 Narukawa et al., 1999), but are also produced secondarily by photochemical oxidation of  
63 various organic precursors derived from both anthropogenic and biogenic sources (Kawamura  
64 et al., 1996). Isoprene, which is the most abundant non-methane hydrocarbon emitted from  
65 terrestrial plants, is an important source of secondary organic aerosols (SOA) (Carlton et al.,  
66 2006; Carlton et al., 2009; Lim et al., 2005). Isoprene-ozone reactions can produce small  
67 dicarboxylic acids such as malonic, malic and succinic acids (Nguen et al., 2010). Model  
68 calculations suggest that oxalic acid over the open ocean could be produced by the in-cloud-  
69 oxidation of isoprene emitted from biologically productive ocean waters (Myriokefalitakis et  
70 al., 2011). Unfortunately there have been very few measurements of the molecular composition  
71 of organic compounds over the oceans, especially the Atlantic Ocean.

72           In this study, we analyzed marine aerosols collected along a transect from Boston to  
73 Bermuda in the western North Atlantic to better understand the sources and atmospheric  
74 processes of organic aerosols using multiple analytical methods for different organic  
75 compound classes. Here, we report molecular distributions of more than 140 compounds

76 including homologous series of dicarboxylic acids, oxoacids,  $\alpha$ -dicarbonyls, sugars, fatty acids,  
77 fatty alcohols, n-alkanes as well as isoprene- and monoterpene-SOA tracers. We also studied  
78 the stable carbon isotopic composition of bulk aerosol carbon and individual organic acids to  
79 investigate the photochemical aging of organic aerosols over the open ocean.

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## 81 **2. Samples and Methods**

82 Aerosol samples (TSP) were collected using a high-volume air sampler and pre-  
83 combusted quartz filter every two days from 20-27 August 2012 over the western North  
84 Atlantic during the Western Atlantic Climate Study (WACS) aboard the *R/V Ronald H. Brown*  
85 (see Figure 1). Before and after the sampling, each filter was stored in a clean glass jar with a  
86 Teflon-lined screw cap. Five filter samples were collected during the cruise together with five  
87 blank filters; the blank filter was placed in the filter cartridge, exposed to air for few seconds  
88 and then returned to the glass jar. The filter samples were stored in a freezer at  $-20^{\circ}\text{C}$  until  
89 analyses.

90 Aliquots of filter samples were extracted with organic-free pure water to isolate  
91 dicarboxylic acids, oxoacids and  $\alpha$ -dicarbonyls. The water extracts were adjusted to pH=8.5-  
92 9.0 using a 0.1 M KOH solution and then concentrated using a rotary evaporator under vacuum.  
93 The extracts were then reacted with 14%  $\text{BF}_3$  in n-butanol to derive carboxyl groups to dibutyl  
94 esters and aldehyde groups to dibutoxyacetals. The esters and acetals were washed with pure  
95 water and then dissolved in n-hexane and injected to a gas chromatograph (GC) to determine a  
96 series of diacids ( $\text{C}_2\text{-C}_{12}$ ), oxoacids and  $\alpha$ -dicarbonyls (Kawamura and Ikushima, 1993;  
97 Kawamura et al., 2012). The GC system (Agilent 6980) contained a split/splitless injector, HP-  
98 5 capillary column (0.2 mm x 25 m, film thickness 0.5  $\mu\text{m}$ ) and flame ionization detector.  
99 Similar GC conditions were used for GC/mass spectrometry (GC/MS) analysis for peak  
100 identification of the compounds. The recoveries of authentic diacids spiked to quartz filter  
101 were better than 80% for oxalic acid and 90% for malonic and succinic acids. Analytical  
102 uncertainties for major components were  $\pm 15\%$ . Blank filters were also analyzed. The results  
103 showed only minor peaks for oxalic and phthalic acids as well as glyoxylic acid. The blank  
104 levels are less than 5% of field samples. Concentrations of the compounds reported here were

105 corrected for the procedural blanks.

106 Another aliquot of the filter samples was extracted with a methanol/dichloromethane  
107 (1:2) mixture. The total extract containing solvent extractable lipid class compounds and polar  
108 organics was reacted with 50  $\mu$ l of N,O-bis-(trimethylsilyl) trifluoroacetamide containing 1%  
109 trimethylsilyl chloride and 10  $\mu$ l of pyridine for 3 h at 70 °C to convert OH functional groups  
110 to trimethylsilyl (TMS) ethers and COOH groups to TMS esters (Simoneit et al., 2004) and  
111 analyzed by GC/MS (Agilent 7890A GC coupled to Agilent 5975C mass-selective detector) to  
112 measure various tracer compounds including fatty acids, n-alkanes, fatty alcohols, sterols,  
113 sugars, and isoprene- and monoterpene-SOA tracers (Fu et al., 2013).

114 Organic carbon (OC) and elemental carbon (EC) were determined using a Sunset  
115 Laboratory carbon analyzer following the thermal/optical evolution protocol (Wang et al.,  
116 2005).

117 The stable carbon isotopic composition of dicarboxylic and oxocarboxylic acids were  
118 determined using a GC/combustion/isotope ratio mass spectrometer (Finnigan MAT Delta  
119 plus). Details of the analytical methodology are described elsewhere (Kawamura and  
120 Watanabe, 2004). The isotopic composition of glyoxal and methylglyoxal were below the  
121 instrument detection limit.

122 Total carbon (TC) concentrations and the stable carbon isotopic composition ( $\delta^{13}\text{C}$ ) of  
123 TC were determined using an elemental analyzer (EA; model Carlo Erba NA 1500) and an  
124 EA/isotope ratio mass spectrometer (IRMS) (Finnigan MAT Delta Plus), respectively  
125 (Kawamura et al., 2004; Narukawa et al., 2008). Acetanilide was used as an external standard.  
126 The reproducibility of the TC analysis is within 2% whereas the analytical errors for  $\delta^{13}\text{C}$  are  
127 within 0.2‰ (Kawamura et al., 2004). TC contents reported here were corrected for the field  
128 blank.  $\delta^{13}\text{C}$  values were also corrected to the field blank using an isotopic mass balance  
129 equation.

130  $^{222}\text{Rn}$  (half-life 3.82 days) was detected with a dual-flow loop two-filter detector  
131 (Whittlestone and Zahorowski, 1998). The photomultiplier counted the radon daughters  
132 produced in a 750L decay/counting tank with a lower limit of detection of 80 mBq  $\text{m}^{-3}$  for a 30  
133 minute count (with 30% error). The radon detector was standardized using radon emitted from

134 a dry radon source (RN-25, Pylon Electronics Corp., 2850 mBq min<sup>-1</sup>) following procedures  
135 outlined by Whittlestone and Zahorowski (1998). The background counts were measured with  
136 the airflow set to zero.

137

### 138 **3. Results and Discussion**

#### 139 **3.1 Meteorological context**

140 Radon concentrations and Hysplit back-trajectory calculations (Stein et al., 2015) show  
141 that the first three samples collected were heavily impacted by continental emissions (Figures  
142 2a and 1). On August 24 the ship entered into a very different air mass that had not been in  
143 contact with the continent for greater than 5 days. The last two samples are therefore  
144 considered here as “remote marine” (Figure 2b and 1). The two contrasting airmasses provide  
145 an opportunity to compare continental and marine organic aerosol composition.

#### 146 **3.2 Molecular distributions of diacids and related compounds in the marine aerosols**

147 Homologous series of dicarboxylic acids (C<sub>2</sub>-C<sub>12</sub>) were detected together with ω-  
148 oxocarboxylic acids (ωC<sub>2</sub>-ωC<sub>9</sub>), pyruvic acid and α-dicarbonyls (glyoxal and methylglyoxal)  
149 (Table 1). Concentration ranges of diacids, oxoacids and α-dicarbonyls were 31-335 ng m<sup>-3</sup> (av.  
150 188 ng m<sup>-3</sup>), 1.6-40.2 ng m<sup>-3</sup> (av. 20.7 ng m<sup>-3</sup>) and 0.3-4.6 ng m<sup>-3</sup> (av. 2.2 ng m<sup>-3</sup>), respectively.  
151 Diacid distributions showed the predominance of oxalic (C<sub>2</sub>) acid followed by malonic (C<sub>3</sub>)  
152 and succinic (C<sub>4</sub>) acids (Figure 3). Concentrations of major diacids (C<sub>2</sub>-C<sub>4</sub>) were five times  
153 higher in the continental samples compared to the remote marine samples (Table 2). C<sub>2</sub> is an  
154 end product of oxidative degradation of various organics including diacids, oxoacids and α-  
155 dicarbonyls (Sempéré and Kawamura, 2003; Bikina et al., 2014; Hoque et al., 2016). In the  
156 present study, C<sub>2</sub> represented 62% of total diacids.

157 Glyoxylic acid (ωC<sub>2</sub>) is generally the most abundant oxoacid. However, in some  
158 samples, ωC<sub>7</sub> or ωC<sub>8</sub> was found to be more abundant than ωC<sub>2</sub> (Figure 3b,c). ωC<sub>7</sub> and ωC<sub>8</sub>  
159 oxoacids are produced via photo-oxidation of unsaturated fatty acids (Kawamura and Gagosian,  
160 1987). Methylglyoxal was more abundant than glyoxal in all the samples (Figure 3).  
161 Methylglyoxal can be produced by the gas phase oxidation of isoprene emitted from terrestrial  
162 higher plants (e.g., Guenter et al., 1993; Mochizuki et al., 2015) and phytoplankton in the

163 ocean surface (e.g., Bikkina et al., 2014).

### 164 **3. 3 Sugar compounds**

165 Sugars including levoglucosan, arabitol, mannitol, inositol, glucose, fructose,  
166 sucrose, trehalose and erythritol were detected in the aerosols along the cruise track. The  
167 concentration of total sugars ranged from 0.2 to 55 ng m<sup>-3</sup> (av. 16.7 ng m<sup>-3</sup>). Concentrations in  
168 the continental samples were 47 times higher than the marine samples, consistent with a  
169 terrestrial/continental origin (Figure 4). Sugars are released from soil particles, plants, animals  
170 and fungal spores (Lewis and Smith, 1967; Simoneit et al., 2004; Bauer et al., 2008).

171 Among the sugar alcohols, arabitol and mannitol are major species in fungi (Velez et  
172 al., 2007; Di Filippo et al., 2013). As proposed by Bauer et al. (2008) and Zhang et al. (2010),  
173 arabitol and mannitol can be used as tracers for airborne fungal spores. Arabitol and mannitol  
174 were strongly correlated ( $r^2=0.99$ ) along the cruise track, suggesting a similar source, that is,  
175 terrestrial airborne fungal spores. Trehalose is a primary saccharide that can be emitted as a  
176 fungal metabolite. Trehalose was strongly correlated with arabitol ( $r^2=0.99$ ) and mannitol  
177 ( $r^2=0.98$ ) along the cruise track, being consistent with a fungal source.

178 Concentrations of erythritol and inositol ranged from 0.0 to 0.5 ng m<sup>-3</sup> (av. 0.2 ng m<sup>-3</sup>)  
179 and 0.0 to 0.2 ng m<sup>-3</sup> (av. 0.1 ng m<sup>-3</sup>), respectively. They were recently reported as very  
180 minor components of marine aerosols with a source similar to arabitol and mannitol (Chen et  
181 al., 2013; Zhu et al., 2015).

182 Concentrations of sucrose, glucose and fructose ranged from 0.01 to 8.7 ng m<sup>-3</sup> (av.  
183 1.9 ng m<sup>-3</sup>), 0.06 to 13.2 ng m<sup>-3</sup> (av. 4.2 ng m<sup>-3</sup>), and 0.04 to 5.0 ng m<sup>-3</sup> (av. 1.9 ng m<sup>-3</sup>),  
184 respectively. Sucrose is a significant component of pollen grain and flowering vegetation (Yttri  
185 et al., 2007; Zhu et al., 2015). Glucose and fructose are emitted from terrestrial plant materials  
186 such as pollen, fruits and their fragments including plant debris (Speranza et al., 1997; Baker et  
187 al., 1998; Pacini, 2000; Medeiros et al., 2006; Zhu et al., 2015) and occasionally from  
188 microorganisms and soil dust (Simoneit et al., 2004; Rogge et al., 2007). It is important to note,  
189 however, sugars and proteins together with other organics may be emitted from seawater to the  
190 marine boundary layer (MBL) through bubble bursting processes (Hoque et al., 2016; Facchini  
191 et al., 2008; Sempéré et al., 2008).

### 192 **3.5 Fatty acids, fatty alcohols, levoglucosan and n-alkanes**

193 A series of long chain n-fatty acids ( $C_{12}$ - $C_{32}$ , 0.0-12 ng m<sup>-3</sup>, av. 6 ng m<sup>-3</sup>) were  
194 detected in the samples studied, with the predominance of palmitic acid ( $C_{16}$ ), followed by  
195 montanic acid ( $C_{28}$ ) and behenic acid ( $C_{22}$ ). Fatty acids are derived from variety of sources;  
196 strong even-to-odd carbon preference is an indication for their biogenic sources including  
197 bacteria, algae, fungi and epicuticular waxes of vascular plants (Simoneit, 1989; Rogge et al.,  
198 1993). High molecular weight (HMW) fatty acids having carbon numbers  $\geq 24$  are primarily  
199 derived from terrestrial higher plant waxes, whereas fatty acids having carbon number  $\leq 23$   
200 may be derived from various sources including vascular plants, microbes and marine  
201 phytoplankton (Simoneit and Mazurek, 1982; Rogge et al., 1993; Kawamura et al., 2003). The  
202 atmospheric abundances of even-carbon numbered fatty acids showed higher concentrations in  
203 the continental samples than the marine samples.

204 A series of normal chain fatty alcohols ( $C_{12}$ - $C_{32}$ , 0.0-12 ng m<sup>-3</sup>) were also detected in  
205 the aerosols along the cruise track. Among the detected fatty alcohols,  $C_{26}$  was the dominant  
206 species. It is of interest to note that in the current study, only fatty alcohols having even carbon  
207 numbers were detected. Fatty alcohols with carbon number  $< C_{20}$  are released from soil  
208 microbes and marine biota, while fatty alcohols  $> C_{24}$  are released from terrestrial higher plants  
209 [Fu et al., 2013]. Large quantities of fatty alcohols and fatty acids are emitted to the  
210 atmosphere from biomass burning (Simoneit, 2002). Levoglucosan is produced during the  
211 pyrolysis of cellulose and is a key tracer for biomass burning (Simoneit et al., 2002). In the  
212 present study, concentrations of levoglucosan ranged from 0.0 to 3.4 ng m<sup>-3</sup> (av. 1.7 ng m<sup>-3</sup>).  
213 Fatty acids, n-alcohols and levoglucosan concentrations were appreciably higher in the  
214 continental samples than the marine samples (Figure 5). The high abundances of fatty acids, n-  
215 alcohols and levoglucosan near the coast are most likely associated with biomass burning.

216 Homologous series of normal alkanes ( $C_{22}$ - $C_{33}$ ) were detected during the study.  
217 Concentrations of n-alkanes ranged from 0.15 to 3.4 ng m<sup>-3</sup> (av. 1.6 ng m<sup>-3</sup>). The predominance  
218 of odd carbon number n-alkanes ( $C_{27}$ ,  $C_{29}$  and  $C_{31}$ ) has frequently been used as indicators for  
219 the terrestrial origin (Bray and Evans, 1961; Eglinton et al., 1962; Eglinton and Hamilton, 1963,  
220 Caldicott and Eglinton, 1973). In the samples reported here,  $C_{29}$  was the most abundant n-



221 alkane. The molecular distribution suggests that the n-alkanes are derived from terrestrial  
222 higher plant waxes. The carbon preference index (CPI, a measure of the odd carbon  
223 dominance) for higher molecular weight (HMW) n-alkanes (C<sub>22</sub>-C<sub>33</sub>) ranged from 1.0 to 4.6  
224 (av. 2.8). These values are slightly lower than those reported from Chichijima island (av. 4.5)  
225 in the western North Pacific (Fu et al., 1997), but higher than those reported for urban aerosols  
226 from Chinese cities (av. 1.3) (Fu et al., 1997) and Tokyo aerosols (av. 1.5) (Kawamura, 1995).  
227 The CPI values confirm that these HMW n-alkanes are dominantly derived from terrestrial  
228 higher plant waxes (Bendle et al., 2007) and not from fossil fuel combustion.

### 229 **3.6 Variation of organics in the western North Atlantic aerosols**

230           Among the twelve organic compound classes, diacids were the most abundant class  
231 followed by monoterpene-SOA tracers (Table 1). Polynuclear aromatic hydrocarbons (PAHs)  
232 were not detected in the aerosol samples, whereas phthalate esters that are used as plasticizers  
233 were present. Biogenic VOCs are emitted in the summer from terrestrial vegetation and are  
234 photochemically oxidized to form SOA in the continental atmosphere and during long-range  
235 atmospheric transport to the open ocean. During the cruise, atmospheric concentrations of all  
236 the aerosol components were higher in the coastal samples than the remote marine samples  
237 (Table 2). However, the ratio of coastal to remote marine concentrations varied by compound  
238 classes.

239           Isoprene-SOA tracers such as 2-methylglyceric acid, cis-2-methyl-1, 3,4-trihydroxy-  
240 1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene, and  
241 2-methylthreitol were detected in the aerosol samples studied. Concentrations of total isoprene-  
242 SOA tracers ranged from 0.1 to 43 ng m<sup>-3</sup> (av. 17.7 ng m<sup>-3</sup>). The concentration ratio of coastal  
243 to remote marine isoprene-SOA tracers was nearly 300 (Table 2), suggesting a contribution of  
244 isoprene from terrestrial higher plants to the formation of secondary organic aerosols via gas-  
245 to-particle conversion over the ocean.

246           Glyoxylic acid ( $\omega$ C<sub>2</sub>), glyoxal (Gly) and methylglyoxal (MeGly) are produced by the  
247 photochemical oxidation of isoprene and other VOCs in the atmosphere (Carlton et al., 2006,  
248 2009). Similar to the isoprene-SOA tracers, the concentrations of these products are higher in  
249 the coastal samples than remote marine samples by a factor of 2.6, 18.8 and 7.6, respectively.

250 This result suggests that isoprene and other VOCs are oxidized and dispersed in the marine  
251 atmosphere.

252 In contrast to isoprene-SOA tracers,  $\omega$ C<sub>2</sub>, Gly and MeGly, the concentration ratio of  
253 diacids in the coastal to remote marine samples is relatively low. Along the cruise track diacids  
254 contributed to 4.5-8.9% (av. 6.2%) of TC, where most common diacids such as oxalic (62% of  
255 total diacids), malonic and succinic acids account for 2.3 to 5.6% (av. 3.3%). The contribution  
256 of diacids to aerosol total carbon (TC) increased from the coastal aerosol to the remote marine  
257 aerosol (Figure 6a), suggesting photochemical production of diacids in the marine atmosphere  
258 during transport from the continent or additional marine sources.

259 The  $\delta^{13}\text{C}$  of oxalic acid was higher in the coastal than the remote marine samples  
260 (Figure 6b). This is a result of the isotopic fractionation that occurs during atmospheric  
261 transport. Oxalic acid is photolyzed with a preferential breakdown of its  $^{12}\text{C}$ - $^{12}\text{C}$  over  $^{13}\text{C}$ - $^{12}\text{C}$   
262 bond in the presence of iron and other transition metals (Pavuluri and Kawamura, 2012;  
263 Kawamura et al., 2014). Photochemical decomposition of oxalic acid causes an enrichment of  
264  $^{13}\text{C}$  in the remaining oxalic acid in aerosols. The  $\delta^{13}\text{C}$  of aerosol TC also was higher in the  
265 coastal than the remote marine samples (Figure 6c). This finding is consistent with an increase  
266 in  $\delta^{13}\text{C}$  of oxalic acid in the marine aerosols suggesting that isotopic enrichment of  $^{13}\text{C}$  of  
267 oxalic acid may control the  $\delta^{13}\text{C}$  values of aerosol TC.

268 The  $\delta^{13}\text{C}$  of malonic acid (C<sub>3</sub>) was isotopically lighter by 4-8‰ than oxalic acid  
269 (Table 3), except for sample #7 and 9 that are characterized as remote marine aerosols by radon  
270 and air mass trajectory analyses (Table 2). The  $\delta^{13}\text{C}$  of succinic acid (C<sub>4</sub>) was significantly  
271 lighter than oxalic acid (C<sub>2</sub>) and slightly lighter than malonic acid. This feature is consistent  
272 with the isotopic composition of small diacids reported in the atmospheric aerosols from  
273 continental sites in East Asia (Aggarwal et al., 2008; Wang et al., 2012). However, the  $\delta^{13}\text{C}$  of  
274 glutaric acid (C<sub>5</sub>) was heavier than those of C<sub>3</sub> and C<sub>4</sub>. This is contrary to previous  
275 measurements (e.g., Aggarwal et al., 2008), although there were only two data points in this  
276 study (Table 3). More studies of the stable carbon isotopic composition of marine organic  
277 aerosols are needed to resolve these differences.

278

#### 279 **4. Conclusions**

280 Marine aerosols collected from the western North Atlantic during the Western  
281 Atlantic Climate Study (WACS) were analyzed for low molecular weight diacids and related  
282 compounds, lipid class compounds (n-alkanes, fatty acids and fatty alcohols), sugars and  
283 various secondary organic aerosol (SOA) tracers. Diacids were the most abundant compound  
284 class followed by monoterpene-SOA tracers > isoprene-SOA tracers > sugars > oxoacids >  
285 fatty alcohols > fatty acids >  $\alpha$ -dicarbonyls > aromatic acids > n-alkanes. Their spatial  
286 distributions showed higher concentrations in the continentally influenced samples than the  
287 remote marine samples. However, the concentrations of diacids were relatively high even in  
288 the remote ocean, suggesting photochemical production of diacids from continental precursors  
289 or a marine source. Molecular distributions of water-soluble diacids showed a predominance of  
290 oxalic (C<sub>2</sub>) acid (62% of total diacids detected), which accounted for up to 5.6% of aerosol  
291 total carbon. These results show that C<sub>2</sub> is a major component of the water-soluble fraction of  
292 organic aerosols over the ocean.

293

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299

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**502 Figure Captions**

503 Figure 1. Cruise track of the *R/V Ronald H. Brown* in 2012. The numbers, thick black marks  
504 and the WACS sample numbers, sample locations, and the location of Bermuda,  
505 respectively.

506 Figure 2. Seven-day backward air mass trajectories at 500 m above the ground for the marine  
507 (WACS#1) and continental (WACS#9) aerosol samples, from the NOAA HYSPLIT model.  
508 For details about the sample location, please see Figure 1.

509 Figure 3. Molecular distributions of low molecular weight dicarboxylic acids ( $C_2$ - $C_{12}$ ),  $\omega$ -  
510 oxoacids, pyruvic acid and  $\alpha$ -dicarbonyls in the aerosols along the cruise track. For the  
511 abbreviations of the compounds, see Table 1.

512 Figure 4. Distributions of sugars in the marine aerosols collected along the cruise track.

513 Figure 5. Distributions of total fatty acids, n-alcohols and levoglucosan in the marine aerosols  
514 along the cruise track.

515 Figure 6. Distributions of (a) the contribution of total diacids to aerosol total carbon (TC), (b)  
516  $\delta^{13}C$  of oxalic acid ( $C_2$ ), and (c)  $\delta^{13}C$  of aerosol TC in the aerosols along the cruise track.

517

518 **Table 1. Concentrations of individual organic compounds along the cruise track.**

| Compounds<br>(ng m <sup>-3</sup> ) | WACS Sample ID, Date/Time (2012)            |                                             |                                             |                                             |                                            |
|------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|--------------------------------------------|
|                                    | #1, Aug. 20-22<br>Start 13:15<br>Stop 13:05 | #3, Aug. 22-23<br>Start 13:28<br>Stop 12:36 | #5, Aug. 23-24<br>Start 13:00<br>Stop 11:29 | #7, Aug. 24-26<br>Start 12:03<br>Stop 13:11 | #9, Aug.26-27<br>Start 13:33<br>Stop 16:00 |
| <b>Diacids</b>                     |                                             |                                             |                                             |                                             |                                            |
| Oxalic, C <sub>2</sub>             | 190                                         | 169                                         | 105                                         | 24.4                                        | 52.5                                       |
| Malonic, C <sub>3</sub>            | 60.0                                        | 58.0                                        | 29.0                                        | 3.45                                        | 12.5                                       |
| Succinic, C <sub>4</sub>           | 35.0                                        | 50.0                                        | 18.0                                        | 1.35                                        | 2.80                                       |
| Glutaric, C <sub>5</sub>           | 10.0                                        | 15.5                                        | 4.00                                        | 0.15                                        | 0.50                                       |
| Adipic, C <sub>6</sub>             | 3.80                                        | 4.50                                        | 1.43                                        | 0.15                                        | 0.35                                       |
| Palmatic, C <sub>7</sub>           | 2.40                                        | 2.00                                        | 0.07                                        | 0.04                                        | 0.07                                       |
| Suberic, C <sub>8</sub>            | 2.70                                        | 0.46                                        | 0.77                                        | 0.13                                        | 0.18                                       |
| Azelaic, C <sub>9</sub>            | 4.00                                        | 1.10                                        | 1.50                                        | 0.23                                        | 0.40                                       |
| Sebaric, C <sub>10</sub>           | 0.60                                        | 1.30                                        | 0.32                                        | BDL <sup>a</sup>                            | 0.04                                       |
| Undecanoic, C <sub>11</sub>        | 0.40                                        | 0.35                                        | 0.23                                        | 0.17                                        | 0.20                                       |
| Dodecandioic, C <sub>12</sub>      | 0.30                                        | 0.20                                        | BDL <sup>a</sup>                            | 0.20                                        | 0.50                                       |
| Methylmalonic, iC <sub>4</sub>     | 1.60                                        | 2.00                                        | 0.80                                        | BDL <sup>a</sup>                            | 0.40                                       |
| Methylsuccinic, iC <sub>5</sub>    | 2.50                                        | 3.40                                        | 0.80                                        | BDL <sup>a</sup>                            | 0.6                                        |
| 2-Methylglutaric, iC <sub>6</sub>  | 0.60                                        | 0.50                                        | 0.20                                        | BDL <sup>a</sup>                            | BDL <sup>a</sup>                           |
| Maleic, M                          | 0.90                                        | 0.55                                        | 0.40                                        | 0.07                                        | 0.07                                       |
| Fumaric, F                         | 1.30                                        | 1.10                                        | 0.20                                        | BDL <sup>a</sup>                            | BDL <sup>a</sup>                           |
| Methylmaleic, mM                   | 1.00                                        | 0.60                                        | 0.02                                        | BDL <sup>a</sup>                            | BDL <sup>a</sup>                           |
| Phthalic, Ph                       | 3.60                                        | 4.30                                        | 1.50                                        | 0.30                                        | 0.70                                       |
| Isophthalic, iPh                   | 0.12                                        | 0.15                                        | BDL <sup>a</sup>                            | BDL <sup>a</sup>                            | 0.08                                       |
| Terephthalic, tPh                  | 3.40                                        | 1.70                                        | 0.80                                        | 0.04                                        | 0.60                                       |
| Hydroxysuccinic, hC <sub>4</sub>   | 1.40                                        | 0.80                                        | 0.40                                        | 0.05                                        | 0.05                                       |
| Oxomalonic, kC <sub>3</sub>        | 2.20                                        | 3.00                                        | 1.30                                        | 0.06                                        | 0.50                                       |
| 4-Oxopimelic, kC <sub>7</sub>      | 7.70                                        | 15.70                                       | 5.70                                        | 0.10                                        | 0.20                                       |
| Total diacids                      | <b>335</b>                                  | <b>335</b>                                  | <b>172</b>                                  | <b>31</b>                                   | <b>72</b>                                  |
| <b>Oxoacids</b>                    |                                             |                                             |                                             |                                             |                                            |
| Pyruvic, Pyr                       | 6.20                                        | 5.60                                        | 3.00                                        | 0.40                                        | 0.50                                       |
| Glyoxylic, ωC <sub>2</sub>         | 11.6                                        | 9.00                                        | 5.00                                        | 8.50                                        | 1.30                                       |
| 3-oxopropanoic, ωC <sub>3</sub>    | 3.50                                        | 2.00                                        | 0.80                                        | 0.06                                        | 0.14                                       |
| 4-oxobutanoic, ωC <sub>4</sub>     | 4.20                                        | 5.00                                        | 2.00                                        | 0.13                                        | 0.40                                       |
| 5-Oxopentanoic, ωC <sub>5</sub>    | 1.40                                        | 1.30                                        | 0.60                                        | 0.06                                        | 0.10                                       |
| 7-Oxoheptanoic, ωC <sub>7</sub>    | 6.40                                        | 6.00                                        | 7.40                                        | 0.30                                        | 1.60                                       |
| 8-Oxoocetanoic, ωC <sub>8</sub>    | 9.30                                        | 10.30                                       | 6.40                                        | 0.20                                        | 1.00                                       |
| 9-Oxononanoic, ωC <sub>9</sub>     | 3.70                                        | 1.10                                        | BDL <sup>a</sup>                            | 0.02                                        | 0.20                                       |
| Total oxoacids                     | <b>40.2</b>                                 | <b>34.8</b>                                 | <b>22.2</b>                                 | <b>1.6</b>                                  | <b>4.8</b>                                 |
| <b>α-Dicarbonyls</b>               |                                             |                                             |                                             |                                             |                                            |
| Glyoxal, Gly                       | 1.90                                        | 1.20                                        | 0.66                                        | 0.10                                        | 0.10                                       |
| Methylglyoxal, MeGly               | 2.60                                        | 2.30                                        | 1.20                                        | 0.60                                        | 0.20                                       |
| Total α-dicarbonyls                | <b>4.6</b>                                  | <b>3.5</b>                                  | <b>2.0</b>                                  | <b>0.7</b>                                  | <b>0.3</b>                                 |


519 <sup>a</sup>BDL= Bellow detection limit (ca. 0.01 ng m<sup>-3</sup>)

520

521

522 **Table 2. Concentrations of organic compound classes along the cruise track.**

523

| Compound classes,<br>ng m <sup>-3</sup> | Boston                |                   |  |              |              | Bermuda |                                      |
|-----------------------------------------|-----------------------|-------------------|-----------------------------------------------------------------------------------|--------------|--------------|---------|--------------------------------------|
|                                         | WACS Sample ID Number |                   |                                                                                   |              |              |         | Ratio of<br>continental<br>to marine |
|                                         | continental<br>#1     | continental<br>#3 | continental<br>#5                                                                 | marine<br>#7 | marine<br>#9 |         |                                      |
| Dicarboxylic acids                      | 335                   | 335               | 172                                                                               | 31           | 72           | 5.4     |                                      |
| $\omega$ -Oxoacids                      | 40.2                  | 34.8              | 22.2                                                                              | 1.6          | 4.8          | 10      |                                      |
| Pyruvic acid                            | 6.20                  | 5.60              | 3.00                                                                              | 0.40         | 0.50         | 7.3     |                                      |
| $\alpha$ -Dicarbonyls                   | 4.6                   | 3.5               | 2.0                                                                               | 0.7          | 0.3          | 6.7     |                                      |
| Sugar compounds                         | 56.0                  | 18.6              | 10.5                                                                              | 0.8          | 0.4          | 47      |                                      |
| Isoprene-SOA tracers                    | 43.2                  | 32.4              | 12.9                                                                              | 0.1          | 0.1          | 295     |                                      |
| Monoterpene-SOA tracers                 | 38.0                  | 47.1              | 13.7                                                                              | 0.1          | 0.1          | 329     |                                      |
| Aromatic acids                          | 4.2                   | 2.9               | 1.2                                                                               | 0.1          | 0.1          | 28      |                                      |
| Polyacids                               | 6.3                   | 9.5               | 1.8                                                                               | 0.0          | 0.1          | 117     |                                      |
| Phthalate esters                        | 5.7                   | 4.8               | 4.2                                                                               | 2.7          | 1.6          | 2.3     |                                      |
| Fatty acids                             | 12.5                  | 10.3              | 3.5                                                                               | 0.0          | 2.2          | 8.0     |                                      |
| Fatty alcohols                          | 19.6                  | 14.0              | 7.0                                                                               | 0.5          | 0.7          | 22      |                                      |
| n-Alkanes                               | 3.4                   | 2.0               | 1.3                                                                               | 0.1          | 1.0          | 4.1     |                                      |

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526 **Table 3. The  $\delta^{13}\text{C}$  (‰) of diacids and aerosol total carbon (TC), and concentrations of TC**  
 527 **along the cruise track.**

| Parameters                            | WACS Sample ID No. |       |                 |                 |                 |
|---------------------------------------|--------------------|-------|-----------------|-----------------|-----------------|
|                                       | #1                 | #3    | #5              | #7              | #9              |
| $\delta^{13}\text{C}$ of $\text{C}_2$ | -17.5              | -17.5 | -16.6           | -16.2           | -12.4           |
| $\delta^{13}\text{C}$ of $\text{C}_3$ | -21.8              | -24.6 | -25.0           | -17.3           | -19.4           |
| $\delta^{13}\text{C}$ of $\text{C}_4$ | -24.2              | -24.8 | -29.8           | ND <sup>a</sup> | ND <sup>a</sup> |
| $\delta^{13}\text{C}$ of $\text{C}_5$ | -19.5              | -19.2 | ND <sup>a</sup> | ND <sup>a</sup> | ND <sup>a</sup> |
| TC ( $\mu\text{g m}^{-3}$ )           | 2.22               | 1.7   | 1.4             | 0.3             | 0.3             |
| $\delta^{13}\text{C}$ of TC           | -24.3              | -23.8 | -22.7           | -22.4           | -18.1           |

528 <sup>a</sup>ND=Not detected

529

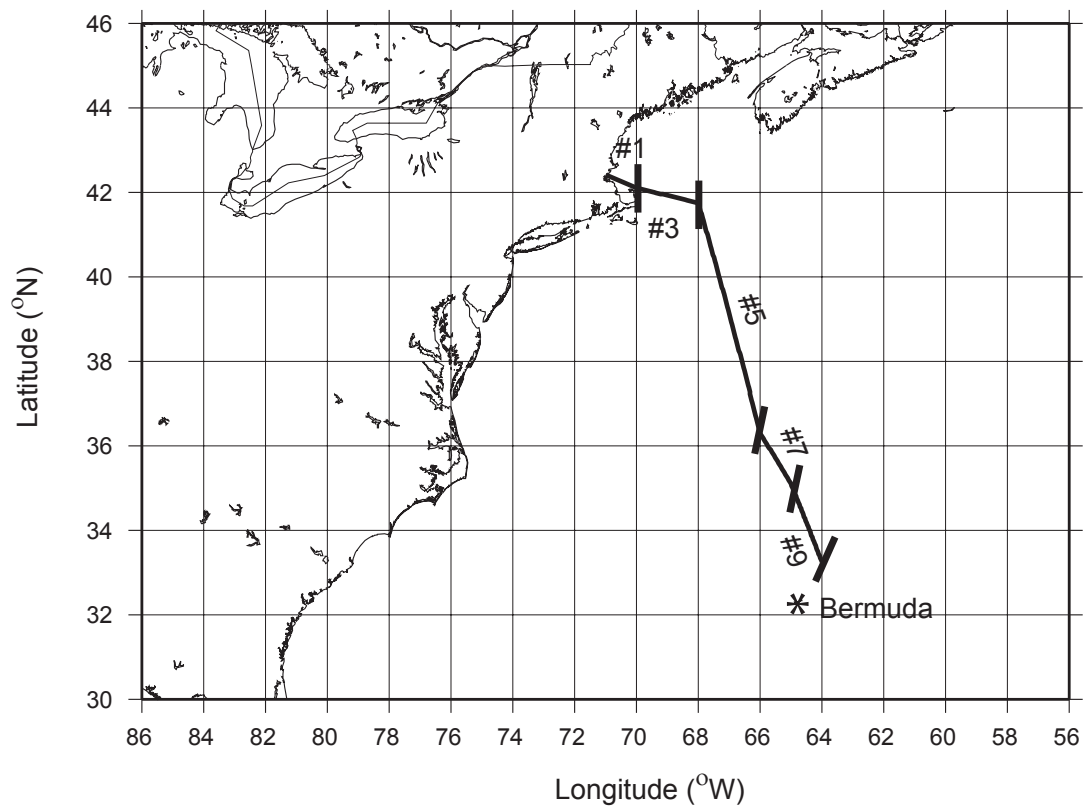
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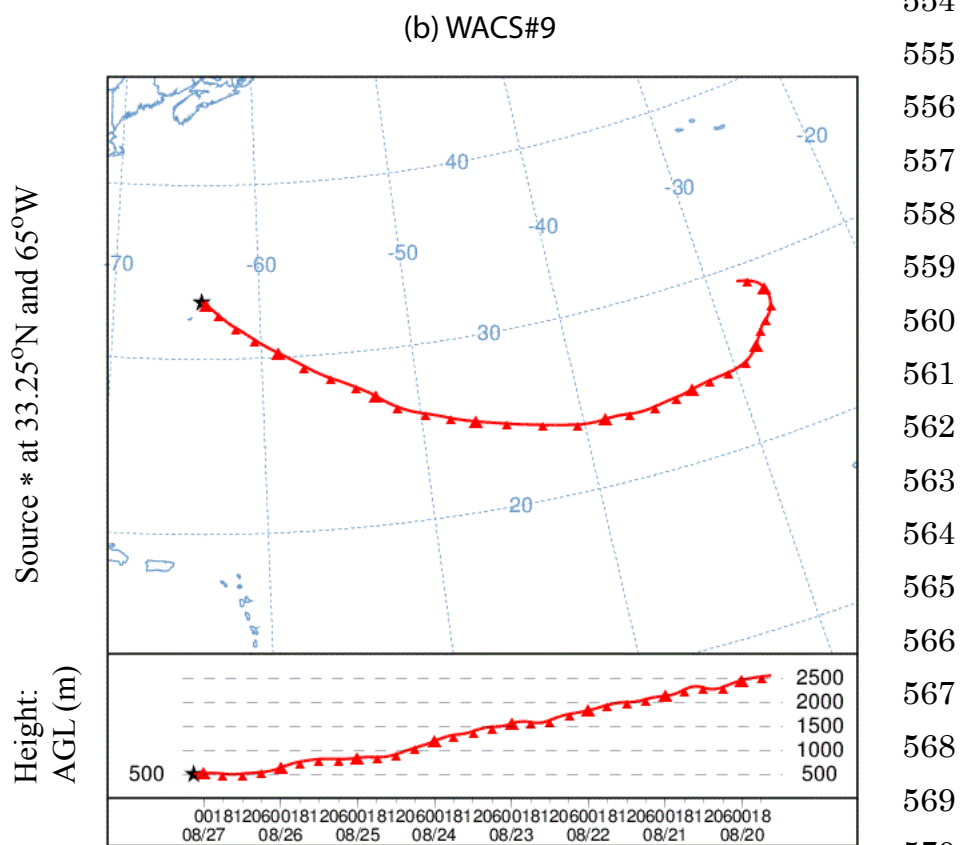
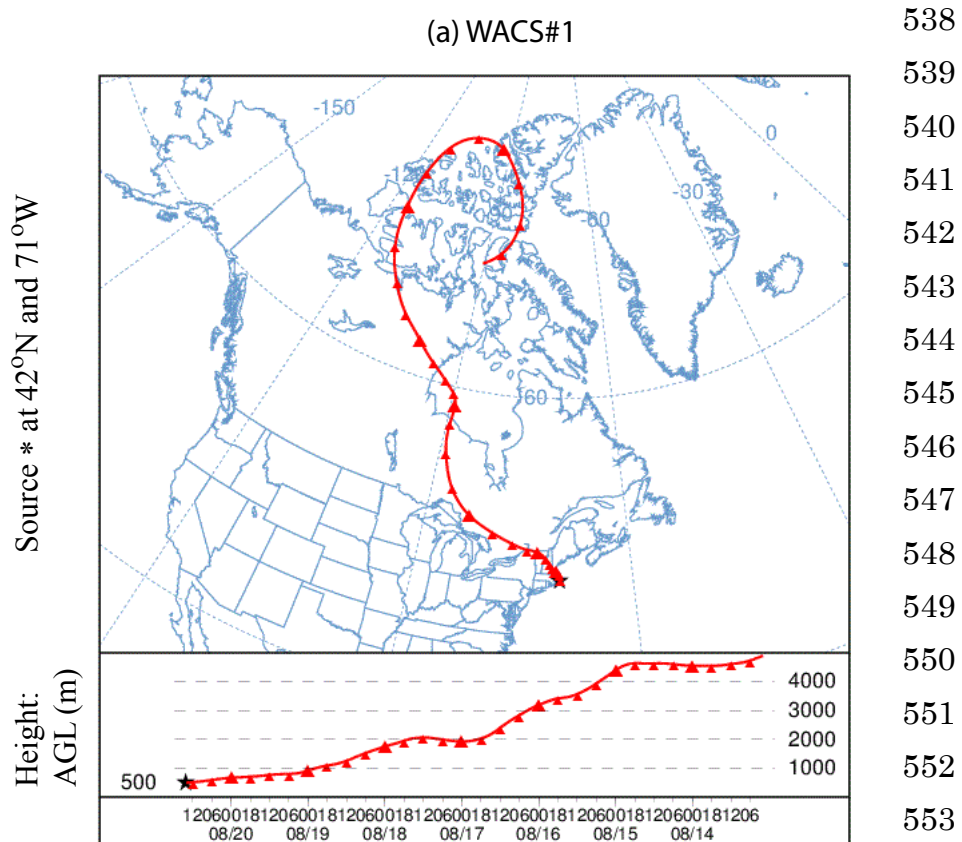
534 Figure 1



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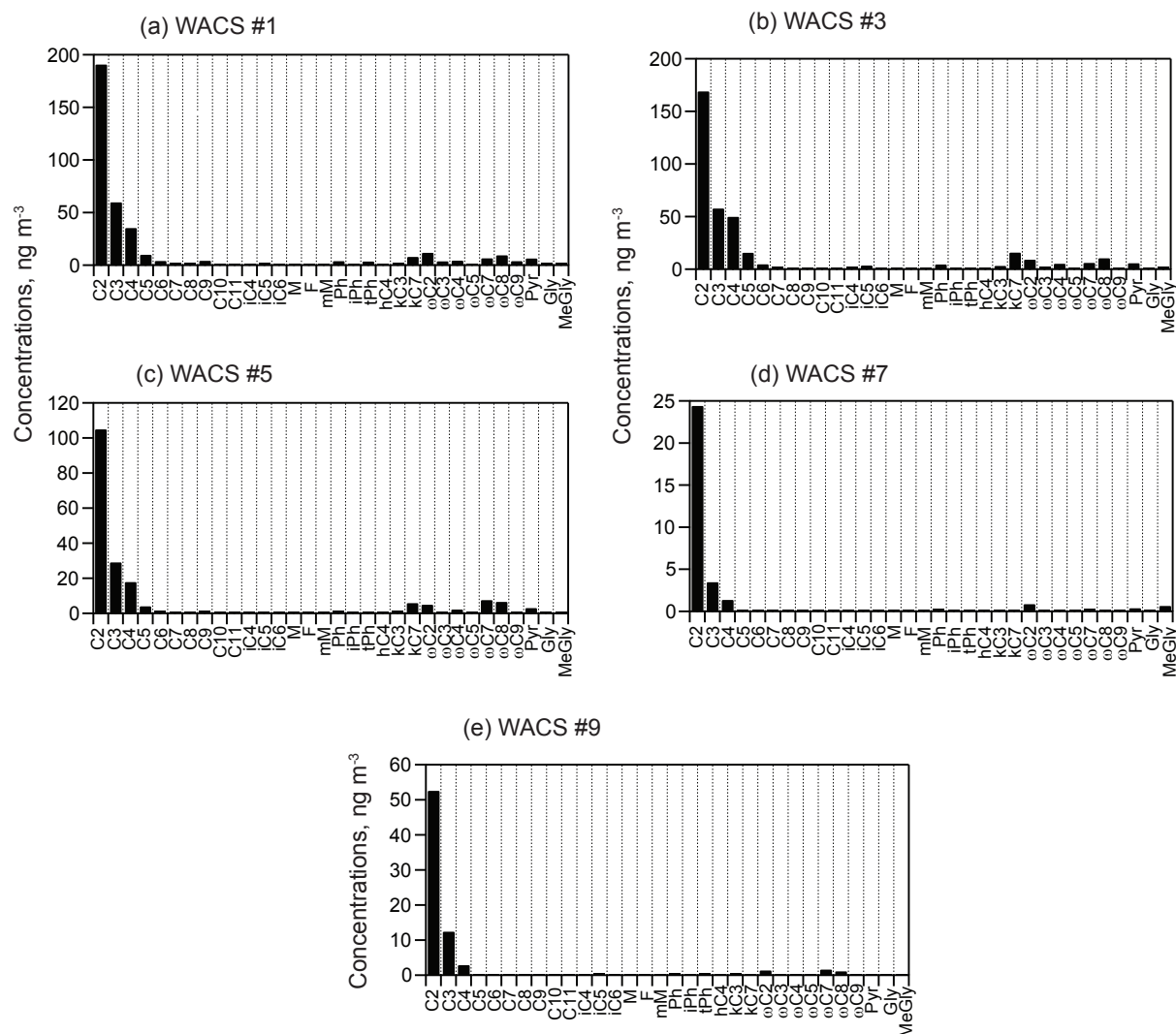
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537 Figure 2



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572 Figure 3



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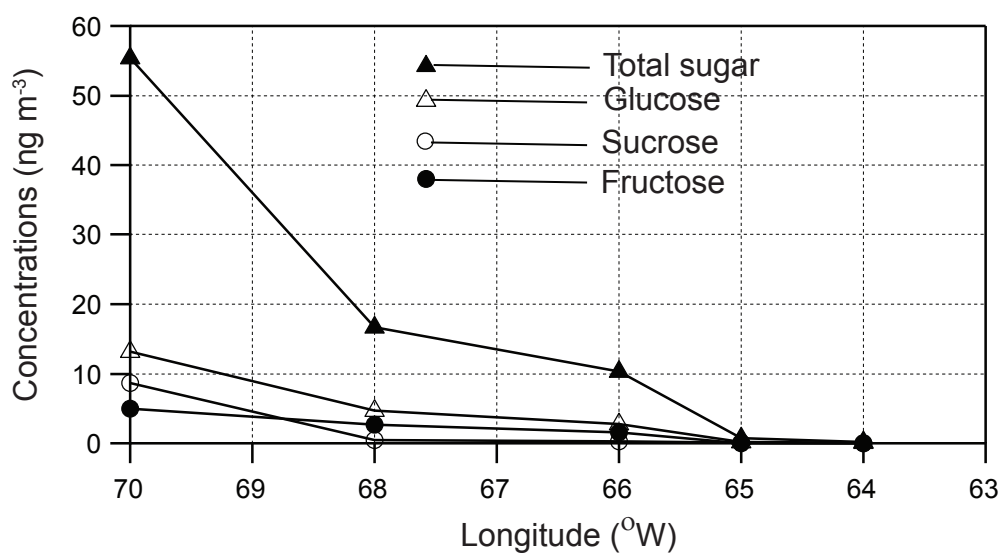
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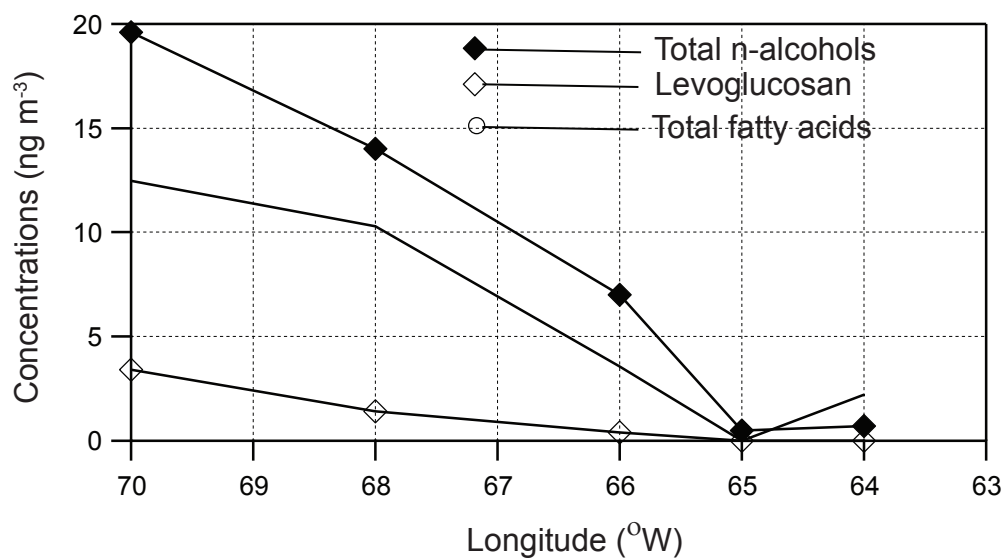
580 Figure 4



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583 Figure 5



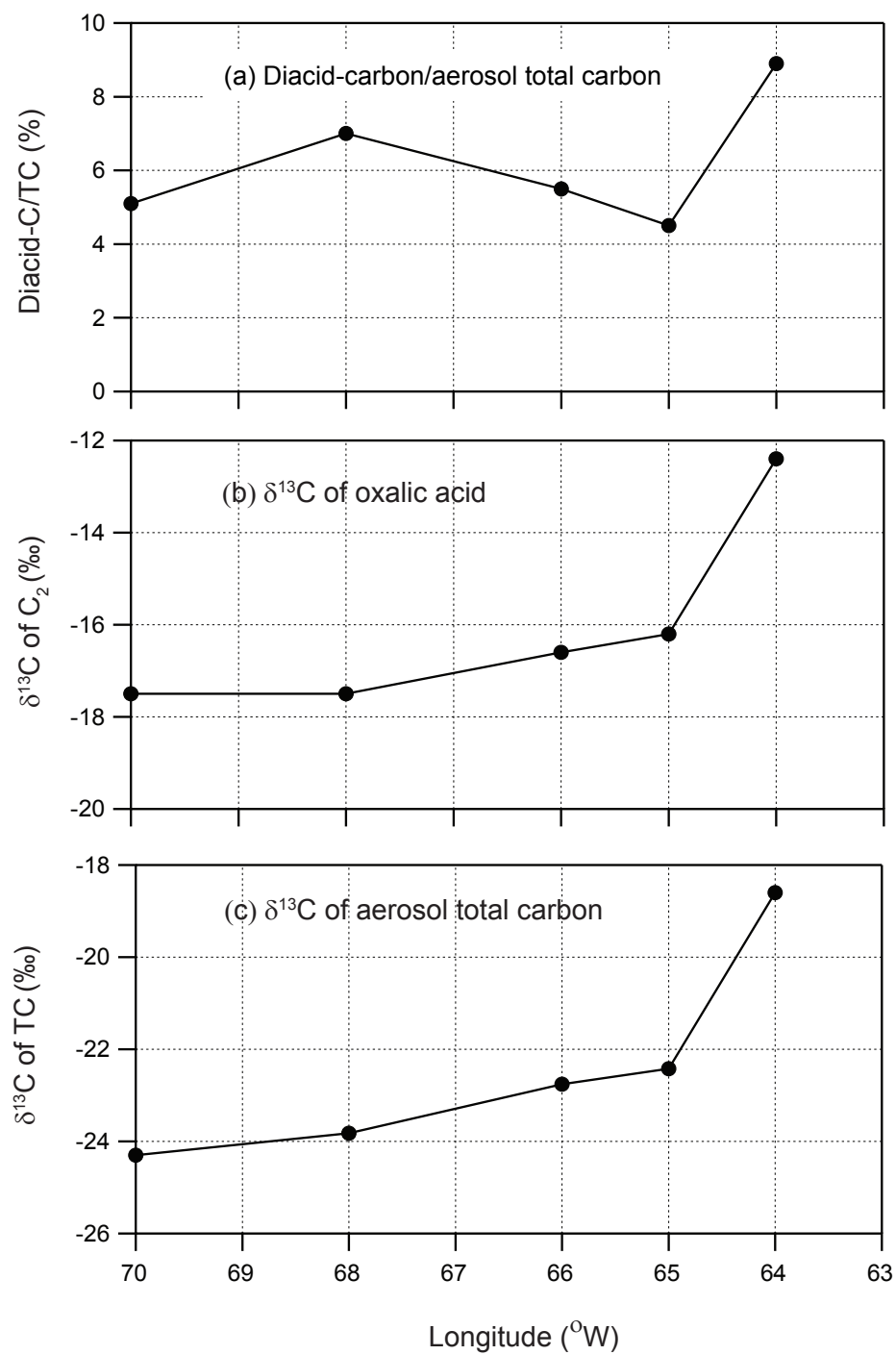
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588 Figure 6



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