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Citation	Organic geochemistry, 113, 229-238 https://doi.org/10.1016/j.orggeochem.2017.08.007
Issue Date	2017-11
Doc URL	https://hdl.handle.net/2115/76047
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Rights(URL)	https://creativecommons.org/licenses/by-nc-nd/4.0/
Type	journal article
File Information	organicgeochemistry113-229-238.pdf



Molecular distributions and isotopic compositions of organic aerosols over the western North Atlantic: Dicarboxylic acids, related compounds, sugars, and secondary organic aerosol tracers

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Published, Organic Geochemistry

Abstract

Marine aerosols were collected over the western North Atlantic off the coast of Boston to Bermuda in August 2012 using a high-volume air sampler. Aerosol samples were analyzed for organic and elemental carbon (OC/EC), low molecular weight dicarboxylic acids and related compounds, lipid class compounds (n-alkanes, fatty acids and fatty alcohols), sugars and various secondary organic aerosol (SOA) tracers. Homologous series (C₂-C₁₂) of dicarboxylic acids (31-335 ng/m³) were detected with a predominance of oxalic acid. Diacids were found to be the most abundant compound class followed by monoterpene-SOA tracers > isoprene-SOA tracers > sugars > oxoacids > fatty alcohols > fatty acids > α -dicarbonyls > aromatic acids > n-alkanes. The concentrations of these compounds were higher in the coastal site and decreased towards the open ocean. However, the abundance of diacids stayed relatively high even in the remote ocean. Interestingly, contributions of oxalic acid to total aerosol carbon increased from the coast (2.3%) to the open ocean (5.6%) near Bermuda.

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

Keywords: Marine aerosols; western North Atlantic; oxalic acid; photochemical aging; stable carbon isotopic composition

1. Introduction

Organic aerosols are comprised of complex mixture of various organic compounds ranging from water-soluble to water-insoluble species (Simoneit and Mazurek, 1982; Simoneit, 1986). Dicarboxylic acids such as oxalic, malonic and succinic acids are typical water-soluble organic compounds that can contribute up to 16% of aerosol total carbon in the remote marine atmosphere over the Pacific Ocean (Kawamura and Sakaguchi, 1999). Dicarboxylic acids, oxoacids and α -dicarbonyls such as glyoxal and methylglyoxal are abundant organic compound classes in continental aerosols from various locations (Ho et al., 2007; Agarwal et al., 2010; Ho et al., 2011). Atmospheric particles enriched with these water-soluble organic species can act as cloud condensation nuclei (CCN) in the atmosphere (Saxena et al., 1995; Saxena and Hildemann, 1996), whereas water-insoluble species such as lipid class compounds may depress the hygroscopic activity of aerosol particles. Carbonaceous aerosols affect radiative forcing positively by absorbing solar radiation and negatively by scattering the radiation via the interaction with water vapor in the atmosphere (Boreddy et al., 2014).

Dicarboxylic acids are primarily produced by fossil fuel combustion (Kawamura and Kaplan, 1987) and biomass burning (Legrand and de Angelis, 1996; Narukawa et al., 1999; Kawamura et al., 2013), but are also produced secondarily by photochemical oxidation of various organic precursors derived from both anthropogenic and biogenic sources (Kawamura et al., 1996). Natural sources such as direct emission of unsaturated fatty acids from the ocean surface followed by photochemical oxidation further produce dicarboxylic acids (Kawamura and Gagosian, 1987; Kawamura and Gagosian, 1990; Stephanou, 1992; Kawamura and Sakaguchi, 1999; Rinaldi et al., 2011). Isoprene, which is the most abundant non-methane hydrocarbon emitted from terrestrial plants, is an important source of secondary organic aerosols (SOA) (Lim et al., 2005; Carlton et al., 2006; Carlton et al., 2009). Isoprene-ozone reactions can produce small dicarboxylic acids such as malonic, malic and succinic acids (Nguen et al., 2010). Model calculations suggest that oxalic acid over the open ocean could be produced by the in-cloud-oxidation of isoprene emitted from biologically productive ocean waters (Myriokefalitakis et al., 2011). Unfortunately there have been very few measurements of the molecular composition of organic compounds over the Atlantic Ocean.

In this study, we analyzed marine aerosols collected along a transect from Boston to Bermuda in the western North Atlantic to better understand the sources and atmospheric processes of organic aerosols using multiple analytical methods for different organic compound classes. Here, we report molecular distributions of more than 140 compounds including homologous series of dicarboxylic acids, oxoacids, α -dicarbonyls, sugars, fatty acids, fatty alcohols, n-alkanes as well as isoprene- and monoterpene-SOA tracers. We also studied the stable carbon isotopic composition of bulk aerosol carbon and individual organic acids to investigate the photochemical aging of organic aerosols over the open ocean.

2. Samples and Methods

Aerosol samples (TSP) were collected using a high-volume air sampler and pre-combusted (500°C) quartz filter every two days from 20 to 27 August 2012 over the western North Atlantic during the Western Atlantic Climate Study (WACS) aboard the *R/V Ronald H. Brown* (see Figure 1). Before and after the sampling, each filter was stored in a clean glass jar, which was pre-combusted at 450°C for 3 hours, with a Teflon-lined screw cap. Five filter samples were collected during the cruise together with five blank filters; the blank filter was placed in the filter cartridge, exposed to air for few seconds and then returned to the glass jar. The filter samples were stored in a freezer at -20°C until analyses.

Aliquots of filter samples were extracted with organic-free pure water to isolate dicarboxylic acids, oxoacids and α -dicarbonyls. The water extracts were adjusted to pH=8.5-9.0 using a 0.1 M KOH solution and then concentrated using a rotary evaporator under vacuum. The extracts were then reacted with 14% BF₃ in n-butanol to derive carboxyl groups to dibutyl esters and aldehyde groups to dibutoxyacetals. The esters and acetals were washed with pure water and then dissolved in n-hexane and injected to a gas chromatograph (GC) to determine a series of diacids (C₂-C₁₂), oxoacids and α -dicarbonyls (Kawamura and Ikushima, 1993; Kawamura et al., 2012). The GC system (Agilent 6980) contained a split/splitless injector, HP-5 capillary column (0.2 mm x 25 m, film thickness 0.5 μ m) and flame ionization detector. Similar GC conditions were used for GC/mass spectrometry (GC/MS) analysis for peak identification of the compounds. The recoveries of authentic diacids spiked to quartz filter

were better than 80% for oxalic acid and 90% for malonic and succinic acids. Analytical uncertainties for major components were $\pm 15\%$. Blank filters were also analyzed. The results showed only minor peaks for oxalic and phthalic acids as well as glyoxylic acid. The blank levels are less than 5% of field samples. Concentrations of the compounds reported here were corrected for the procedural blanks.

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

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

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

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

^{222}Rn (half-life 3.82 days) was detected with a dual-flow loop two-filter detector (Whittlestone and Zahorowski, 1998). The photomultiplier counted the radon daughters produced in a 750L decay/counting tank with a lower limit of detection of 80 mBq m^{-3} for a 30 minute count (with 30% error). The radon detector was standardized using radon emitted from a dry radon source (RN-25, Pylon Electronics Corp., $2850 \text{ mBq min}^{-1}$) following procedures outlined by Whittlestone and Zahorowski (1998). The background counts were measured with the airflow set to zero.

3. Results

3.1 Meteorological context

Radon concentrations and Hysplit back-trajectory calculations (Stein et al., 2015) show that the first three samples collected were heavily impacted by continental emissions (Figures 1 and 2). On August 24 the ship entered into a very different air mass that had not been in contact with the continent for greater than 5 days. The last two samples (#7 and #9) are therefore considered here as “remote marine” (Figures 1 and 2). The two contrasting air masses provide an opportunity to compare continental and marine organic aerosol composition.

3.2 Molecular compositions of diacids and related compounds in the marine aerosols

Homologous series of dicarboxylic acids ($\text{C}_2\text{-C}_{12}$) were detected together with ω -oxocarboxylic acids ($\omega\text{C}_2\text{-}\omega\text{C}_9$), pyruvic acid and α -dicarbonyls (glyoxal and methylglyoxal) (Table 1). Concentration ranges of diacids, oxoacids and α -dicarbonyls were $31\text{-}335 \text{ ng/m}^3$ (av. 188 ng/m^3), $1.6\text{-}40.2 \text{ ng/m}^3$ (av. 20.7 ng/m^3) and $0.3\text{-}4.6 \text{ ng/m}^3$ (av. 2.2 ng/m^3), respectively. Diacid distributions showed the predominance of oxalic (C_2) acid followed by malonic (C_3) and succinic (C_4) acids (Figure 3). Concentrations of major diacids ($\text{C}_2\text{-C}_4$) were five times higher in the continental samples compared to the remote marine samples (Table 2). In the present study, C_2 represented $62\pm 12\%$ of total diacids.

Glyoxylic acid (ωC_2) is generally the most abundant oxoacid. However, in some samples, ωC_7 or ωC_8 was found to be more abundant than ωC_2 (Figure 3b,c). ωC_7 and ωC_8 oxoacids are produced via photo-oxidation of unsaturated fatty acids (Kawamura and Gagosian, 1987). Methylglyoxal was more abundant than glyoxal in all the samples (Figure 3).

Methylglyoxal can be produced by the gas phase oxidation of isoprene emitted from terrestrial higher plants (e.g., Guenter et al., 1993; Mochizuki et al., 2015) and phytoplankton in the ocean surface (e.g., Bikkina et al., 2014).

3.3. Distributions of sugars, SOA-tracers, fatty acids, fatty alcohols, and n-alkanes

Figure 4 presents a representative GC/MS trace (TIC chromatogram) of total extracts that were derivatized with BSTFA reagent. We detected various compound classes including sugar compounds, carboxylic acids, fatty alcohols, n-alkanes as well as secondary organic aerosol (SOA) tracers derived by the photochemical oxidation of isoprene and monoterpenes. Sugars including levoglucosan, arabitol, mannitol, inositol, glucose, fructose, sucrose, trehalose and erythritol were detected in the aerosols along the cruise track. The concentration of total sugars ranged from 0.2 to 55 ng/m³ (av. 16.7 ng/m³). Concentrations in the continental samples were 47 times higher than the marine samples, consistent with a terrestrial/continental origin (Figure 4). Sugars are released from soil particles, plants, animals and fungal spores (Lewis and Smith, 1967; Simoneit et al., 2004; Bauer et al., 2008).

Concentrations of erythritol and inositol ranged from 0.0 to 0.5 ng/m³ (av. 0.2 ng/m³) and 0.0 to 0.2 ng/m³ (av. 0.1 ng/m³), respectively. They were recently reported as very minor components of marine aerosols with a source similar to arabitol and mannitol (Chen et al., 2013; Zhu et al., 2015). Concentrations of sucrose, glucose and fructose ranged from 0.01 to 8.7 ng/m³ (av. 1.9 ng/m³), 0.06 to 13.2 ng/m³ (av. 4.2 ng/m³), and 0.04 to 5.0 ng/m³ (av. 1.9 ng/m³), respectively.

We also detected isoprene-SOA tracers including 2-methylglyceric acid, 2-methylthreitol, 2-methylerythritol, three C₅-alkene triols (cis-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene and trans-2-methyl-1,3,4-trihydroxy-1-butene) as well as monoterpenes-SOA tracers including pinonic acid, pinic acid and 3-hydroxyglutaric acid. These SOA-tracers have been reported in ambient aerosols from various sites in the continents and oceans (e.g., Claeys et al., 2007; Fu et al., 2013; Fu et al., 2014). Concentrations of isoprene- and monoterpenes-SOA tracers are given in Table 2. Their concentrations (isoprene-SOA tracers: 0.1-43.2 ng/m³, monoterpenes-SOA tracers: 0.1-38.0 ng/m³) are much lower than those of diacids but equivalent to those of ω -oxoacids and sugar compounds (Table

2).

Aromatic acids (benzoic acid and o-, m- and p-phthalic acids) were detected in the marine aerosols. Their concentrations are higher near the continents but very low in the remote marine aerosols (Table 2). Polyacids such as DL-tartaric and citric acids were also detected as well as phthalate esters including di-(2-ethylhexyl) and di-n-butyl phthalates. Their concentrations are relatively low although they significantly decrease in the remote marine aerosols (Table 2).

A series of long chain n-fatty acids (C_{12} - C_{32} , 0.0-12 ng/m³, av. 6 ng/m³) were detected in the samples studied, with the predominance of palmitic acid (C_{16}), followed by montanic acid (C_{28}) and behenic acid (C_{22}). Fatty acids are derived from variety of sources; strong even-to-odd carbon preference is an indication for their biogenic sources including bacteria, algae, fungi and epicuticular waxes of vascular plants (Simoneit, 1989; Rogge et al., 1993).

Normal chain fatty alcohols (C_{12} - C_{32} , 0.0-12 ng/m³) were also detected in the aerosols along the cruise track. Among the detected fatty alcohols, C_{26} was the dominant species. It is of interest to note that only fatty alcohols having even carbon numbers were detected in the current study. Fatty alcohols with carbon number $<C_{20}$ are released from soil microbes and marine biota, while fatty alcohols $>C_{24}$ are released from terrestrial higher plants (Fu et al., 2013).

Homologous series of normal alkanes (C_{22} - C_{33}) were detected during the study. Concentrations of n-alkanes ranged from 0.15 to 3.4 ng/m³ (av. 1.6 ng/m³). The predominance of odd carbon number n-alkanes (C_{27} , C_{29} and C_{31}) has frequently been used as indicators for the terrestrial origin (Bray and Evans, 1961; Eglinton et al., 1962; Eglinton and Hamilton, 1963, Caldicott and Eglinton, 1973). In the samples reported here, C_{29} was the most abundant n-alkane. The molecular distribution suggests that n-alkanes are derived from terrestrial higher plant waxes. The carbon preference index (CPI, a measure of the odd carbon dominance) for higher molecular weight (HMW) n-alkanes (C_{22} - C_{33}) ranged from 1.0 to 4.6 (av. 2.8). These values are slightly lower than those reported from Chichijima island (av. 4.5) in the western North Pacific (Fu et al., 1997), but higher than those reported for urban aerosols from Chinese cities (av. 1.3) (Fu et al., 1997) and Tokyo aerosols (av. 1.5) (Kawamura, 1995). The CPI

values confirm that these HMW n-alkanes are dominantly derived from terrestrial higher plant waxes (Bendle et al., 2007) and not from fossil fuel combustion.

Among the twelve organic compound classes, diacids were the most abundant class followed by isoprene- and/or monoterpene-SOA tracers or sugar compounds (Table 2). Polynuclear aromatic hydrocarbons (PAHs) and hopanes, which are tracers of fossil fuel combustion (Fu et al., 2014), were not detected in the aerosol samples, whereas phthalate esters that are used as plasticizers were present as stated above. Biogenic VOCs are emitted in the summer from terrestrial vegetation and are photochemically oxidized to form SOA in the continental atmosphere and during long-range atmospheric transport to the open ocean. Although atmospheric concentrations of all the aerosol components were higher in the coastal samples than the remote marine samples, the ratio of coastal to remote marine concentrations varied by compound classes (Table 2).

3.4 Stable carbon isotopic composition of diacids and total carbon in marine aerosols

Table 3 presents isotopic compositions of major diacids in the marine aerosols from the western North Atlantic. Oxalic acid showed the largest value (av. -16.0‰) followed by glutaric (-19.3‰), malonic (-21.6‰) and succinic acid (-26.3 ‰). The larger $\delta^{13}\text{C}$ value of oxalic acid than malonic and succinic acids have been reported for the remote marine aerosols from the Pacific Ocean (Wang and Kawamura, 2006), suburban aerosols from Sapporo, Japan (Aggarwal and Kawamura, 2008) and urban aerosols from India (Pavuluri et al., 2011).

Concentrations of total carbon (TC) for the remote aerosol samples ranged from 0.3 to $2.2 \mu\text{g m}^{-3}$ (av. $1.2 \mu\text{g m}^{-3}$) with the highest value off the coast of Boston (sample # 1, Table 3). The average TC concentrations in the marine aerosols are higher than the levels reported for the marine aerosols collected from the North and South Pacific (av. $0.6 \mu\text{g m}^{-3}$) (Hoque et al., 2016), and winter (av. $0.6 \mu\text{g m}^{-3}$) and summer (av. $0.32 \mu\text{g m}^{-3}$) aerosols collected at Alert in the high Arctic (Narukawa et al., 2008). Spatial distributions of TC showed decreasing trends from the coast towards the open ocean (Table 3), supporting a significant atmospheric transport of continentally derived organics over the remote marine atmosphere (Hoque et al., 2015). The $\delta^{13}\text{C}$ values of TC increased from the coastal to remote marine aerosols (Table 3).

4. Discussion

4.1 Dicarboxylic acids and related compounds

Oxalic acid (C_2) is an end product of oxidative degradation of various organics including longer chain diacids, oxoacids and α -dicarbonyls before the production of CO_2 (e.g., Sempéré and Kawamura, 2003; Bikkina et al., 2014; Hoque et al., 2016). The predominance of C_2 in all the marine aerosol samples studied suggests that organic aerosols in the Atlantic Ocean are photochemically processed. This inference is supported by higher abundances of C_3 over C_4 . C_3/C_4 ratio has been used to discuss photochemical aging of organic aerosols (e.g., Kawamura and Ikushima, 1993; Kawamura and Bikkina, 2016). Interestingly, C_3/C_4 ratios increased from coastal sample (1.7 for sample #1) to remote marine samples collected near Bermuda (e.g., 4.5 for sample #9) (see Table 1), although the mass concentrations of diacids decreased along the cruise track. These results suggest that organic aerosols are photochemically more aged in the remote marine atmosphere during long-range atmospheric transport.

4.2 Sugar compounds

Sucrose is a significant component of pollen grain and flowering vegetation (Yttri et al., 2007; Zhu et al., 2015). Glucose and fructose are emitted from terrestrial plant materials such as pollen, fruits and their fragments including plant debris (Speranza et al., 1997; Baker et al., 1998; Pacini, 2000; Medeiros et al., 2006; Zhu et al., 2015) and occasionally from microorganisms and soil dust (Simoneit et al., 2004; Rogge et al., 2007). It is important to note, however, sugars and proteins together with other organics may be emitted from seawater to the marine boundary layer (MBL) through bubble bursting processes (Facchini et al., 2008; Sempéré et al., 2008; Hoque et al., 2016). The longitudinal distributions of sucrose demonstrate that land-derived sugars are dispersed in the MBL or scavenged by dry and/or wet deposition during long-range transport in the marine atmosphere (Figure 5).

Among the sugar alcohols, arabitol and mannitol are major species in fungi (Velez et al., 2007; Di Filippo et al., 2013). As proposed by Bauer et al. (2008) and Zhang et al. (2010), arabitol and mannitol can be used as tracers for airborne fungal spores. Arabitol and mannitol were strongly correlated ($r^2=0.99$) along the cruise track, suggesting a similar source, that is,

terrestrial airborne fungal spores. Trehalose is a primary saccharide that can be emitted as a fungal metabolite. Trehalose was strongly correlated with arabitol ($r^2=0.99$) and mannitol ($r^2=0.98$) along the cruise track, being consistent with a fungal source. Levoglucosan is produced during the pyrolysis of cellulose and is a key tracer for biomass burning (Simoneit et al., 2002). In the present study, concentrations of levoglucosan ranged from 0.0 to 3.4 ng/m³ (av. 1.7 ng/m³) with higher levels in the coastal marine aerosols. Based on laboratory experiments, Hennigan et al. (2010) observed the degradation of levoglucosan by hydroxyl (OH) radicals with lifetime of 0.7–2.2 days when biomass-burning particles are exposed to 1×10^6 molecules cm⁻³ of OH in summer.

4.3 Fatty acids, fatty alcohols, and n-alkanes

High molecular weight (HMW) fatty acids having carbon numbers ≥ 24 are primarily derived from terrestrial higher plant waxes, whereas fatty acids having carbon number ≤ 23 may be derived from various sources including vascular plants, microbes and marine phytoplankton (Simoneit and Mazurek, 1982; Rogge et al., 1993; Kawamura et al., 2003). The atmospheric abundances of even-carbon numbered fatty acids showed higher concentrations in the continental samples than the marine samples. Concentrations of total fatty acids generally decrease from the coast to remote marine aerosols (Figure 6), although low molecular weight fatty acids such as palmitic acid (C_{16:0}) is relatively abundant in Sample #9 (not shown as a figure).

Large quantities of fatty alcohols and fatty acids are emitted to the atmosphere from biomass burning (Simoneit, 2002). Concentrations of fatty acids and n-alcohols are appreciably higher in the continental samples than marine samples (Figure 6). The high abundances of fatty acids and n-alcohols near the coast are most likely associated with biomass burning that occurred in North America.

4.4 Variation of organics in the western North Atlantic aerosols

Isoprene-SOA tracers such as 2-methylglyceric acid, cis-2-methyl-1, 3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene, and 2-methylthreitol were detected in the aerosol samples studied. Concentrations of total isoprene-SOA tracers ranged from 0.1 to 43 ng/m³ (av. 17.7 ng/m³). The concentration ratio of coastal to

remote marine isoprene-SOA tracers was nearly 300 (Table 2), suggesting a contribution of isoprene from terrestrial higher plants to the formation of secondary organic aerosols via gas-to-particle conversion over the ocean.

Glyoxylic acid (ωC_2), glyoxal (Gly) and methylglyoxal (MeGly) are produced by the photochemical oxidation of isoprene and other VOCs in the atmosphere (Carlton et al., 2006, 2009). Similar to the isoprene-SOA tracers, concentrations of these products (ωC_2 , Gly and MeGly) are higher in the coastal samples than remote marine samples by a factor of 2.6, 18.8 and 7.6, respectively. This result suggests that isoprene and other VOCs are oxidized and dispersed in the marine atmosphere during long-range transport.

In contrast to isoprene-SOA tracers, ωC_2 , Gly and MeGly, the concentration ratio of diacids in the coastal to remote marine samples is relatively low. Along the cruise track, diacids contributed to 4.5-8.9% (av. 6.2%) of aerosol total carbon (TC), where most common diacids such as oxalic (62% of total diacids), malonic and succinic acids account for 2.3 to 5.6% (av. 3.3%). The contribution of diacids to TC increased from the coastal aerosol to the remote marine aerosol samples (Figure 7a), suggesting photochemical production of diacids in the marine atmosphere during the transport from the continent or additional marine sources.

4.5 Stable carbon isotopic composition of diacids and aerosol total carbon

The $\delta^{13}\text{C}$ of oxalic acid was higher in the remote marine aerosols than those of coastal samples (Figure 7b). This is a result of the isotopic fractionation that occurs during atmospheric transport. Oxalic acid is photolyzed with a preferential breakdown of its ^{12}C - ^{12}C over ^{13}C - ^{12}C bond in the presence of iron and other transition metals (Pavuluri and Kawamura, 2012; Kawamura et al., 2014). Photochemical decomposition of oxalic acid causes an enrichment of ^{13}C in the remaining oxalic acid in aerosols. The $\delta^{13}\text{C}$ of aerosol TC also was higher in the coastal than the remote marine samples (Figure 7c). This finding is consistent with an increase in $\delta^{13}\text{C}$ of oxalic acid in the marine aerosols, suggesting that isotopic enrichment of ^{13}C of oxalic acid may control the bulk $\delta^{13}\text{C}$ values of aerosol TC.

The $\delta^{13}\text{C}$ of malonic acid (C_3) was isotopically lighter than oxalic acid by 4-8‰ (Table 3), except for sample #7 and 9 that are characterized as remote marine aerosols by radon and air mass trajectory analyses (Table 2). The $\delta^{13}\text{C}$ of succinic acid (C_4) was significantly

lower than oxalic acid (C_2) and slightly lower than malonic acid. This feature is consistent with the isotopic composition of small diacids reported in the atmospheric aerosols from continental sites in East Asia (Aggarwal et al., 2008; Wang et al., 2012). However, the $\delta^{13}C$ of glutaric acid (C_5) was greater than those of C_3 and C_4 . This is contrary to previous measurements (e.g., Aggarwal et al., 2008), although there were only two data points in this study (Table 3). There is a possibility that major portion of glutaric acid is produced by the photochemical oxidation of marine organic matter such as unsaturated fatty acids, whose $\delta^{13}C$ values are greater than those of terrestrial organic matter (Fang et al., 2002). More studies of the stable carbon isotopic composition of marine organic aerosols are needed to resolve these differences.

4. Summary and Conclusions

Marine aerosols collected from the western North Atlantic during the Western Atlantic Climate Study (WACS) were analyzed for low molecular weight diacids and related compounds, lipid class compounds (n-alkanes, fatty acids and fatty alcohols), sugars and various secondary organic aerosol (SOA) tracers. Diacids were the most abundant compound class followed by monoterpene-SOA tracers > isoprene-SOA tracers > sugars > oxoacids > fatty alcohols > fatty acids > α -dicarbonyls > aromatic acids > n-alkanes. Their spatial distributions showed higher concentrations in the continentally influenced samples than the remote marine samples. However, the concentrations of diacids were relatively high even in the remote ocean, suggesting photochemical production of diacids from continental precursors or a marine source. Molecular distributions of water-soluble diacids showed a predominance of oxalic (C_2) acid (62% of total diacids detected), which accounted for up to 5.6% of aerosol total carbon. These results show that C_2 is a major component of the water-soluble fraction of organic aerosols over the ocean.

We found that arabitol and mannitol are strongly correlated ($r^2=0.99$) along the cruise track, suggesting their similar source, that is, terrestrial airborne fungal spores. Moreover, trehalose, which is a fungal metabolite, showed strong correlations with arabitol ($r^2=0.99$) and mannitol ($r^2=0.98$) throughout the cruise, confirming that they are associated with fungal sources. Concentrations of fatty acids and n-alcohols were significantly higher in the coastal

than remote marine samples. The high abundances of fatty acids and n-alcohols near the coast are most likely linked with biomass burning in the North American continent. However, the concentration ratio of coastal to remote marine isoprene-SOA tracers was nearly 300, suggesting an important contribution of isoprene emitted from terrestrial higher plants to the formation of secondary organic aerosols via gas-to-particle conversion over the continent followed by atmospheric transport to the open ocean and/or the formation over the coastal ocean.

Acknowledgements

The authors acknowledge the financial support from the Japan Society for the Promotion of Science (JSPS) through Grant-in-Aid No. 24221001. Eri Tachibana and Kaori Ono are acknowledged for their helps of analyzing samples. We also thank the cruise members of the *R/V Ronald H. Brown*.

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610 Figure Captions

611 Figure 1. Cruise track of the *R/V Ronald H. Brown* in 2012 with WACS aerosol sample ID and
612 the location of Bermuda.

613 Figure 2. Every 3 hours backward air mass trajectories at 500 m above the ground for the
614 cruise track *R/V Ronald H. Brown* from the NOAA HYSPLIT model. For details about the
615 sample location, please see Figure 1.

616 Figure 3. Molecular distributions of low molecular weight dicarboxylic acids (C₂-C₁₂), ω-
617 oxoacids, pyruvic acid and α-dicarbonyls in the aerosols along the cruise track. For the
618 abbreviations of the compounds, see Table 1.

619 Figure 4. GC/MS trace (TIC chromatogram) for total extracts from WACS#1 sample, which
620 were derivatized with BSTFA reagent (see the experimental section for the details). 3-HGA
621 means 3-hydroxyglutaric acid. C_{16:0} means palmitic acid; fatty acid with 16 carbon
622 numbers and no double bond.

623 Figure 5. Distributions of sugars in the marine aerosols collected along the cruise track.

624 Figure 6. Distributions of total fatty acids, n-alcohols and levoglucosan in the marine aerosols
625 along the cruise track.

626 Figure 7. Distributions of (a) the contribution of total diacids to aerosol total carbon (TC), (b)
627 δ¹³C of oxalic acid (C₂), and (c) δ¹³C of aerosol TC in the aerosols along the cruise track.

628

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

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

630 ^aBDL= Bellow detection limit (ca. 0.01 ng/m³)

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632

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

Compound classes, ng/m ³	Boston			Bermuda		
	WACS Sample ID Number					
	continental #1	continental #3	continental #5	marine #7	marine #9	Ratio of continental to marine
Dicarboxylic acids	335	335	172	31	72	5.4
ω-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
α-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

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

Parameters	WACS Sample ID No.				
	#1	#3	#5	#7	#9
$\delta^{13}\text{C}$ of C_2	-17.5	-17.5	-16.6	-16.2	-12.4
$\delta^{13}\text{C}$ of C_3	-21.8	-24.6	-25.0	-17.3	-19.4
$\delta^{13}\text{C}$ of C_4	-24.2	-24.8	-29.8	ND ^a	ND ^a
$\delta^{13}\text{C}$ of C_5	-19.5	-19.2	ND ^a	ND ^a	ND ^a
TC ($\mu\text{g}/\text{m}^3$)	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

639 ^aND=Not detected

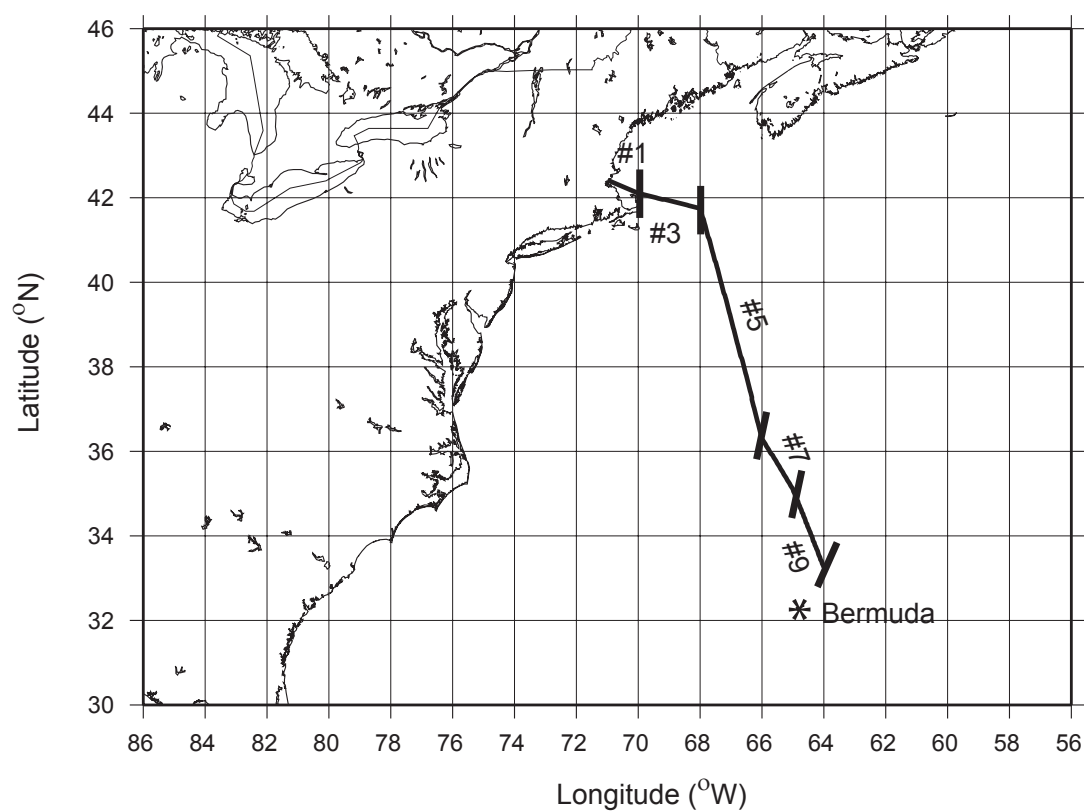
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644 Figure 1



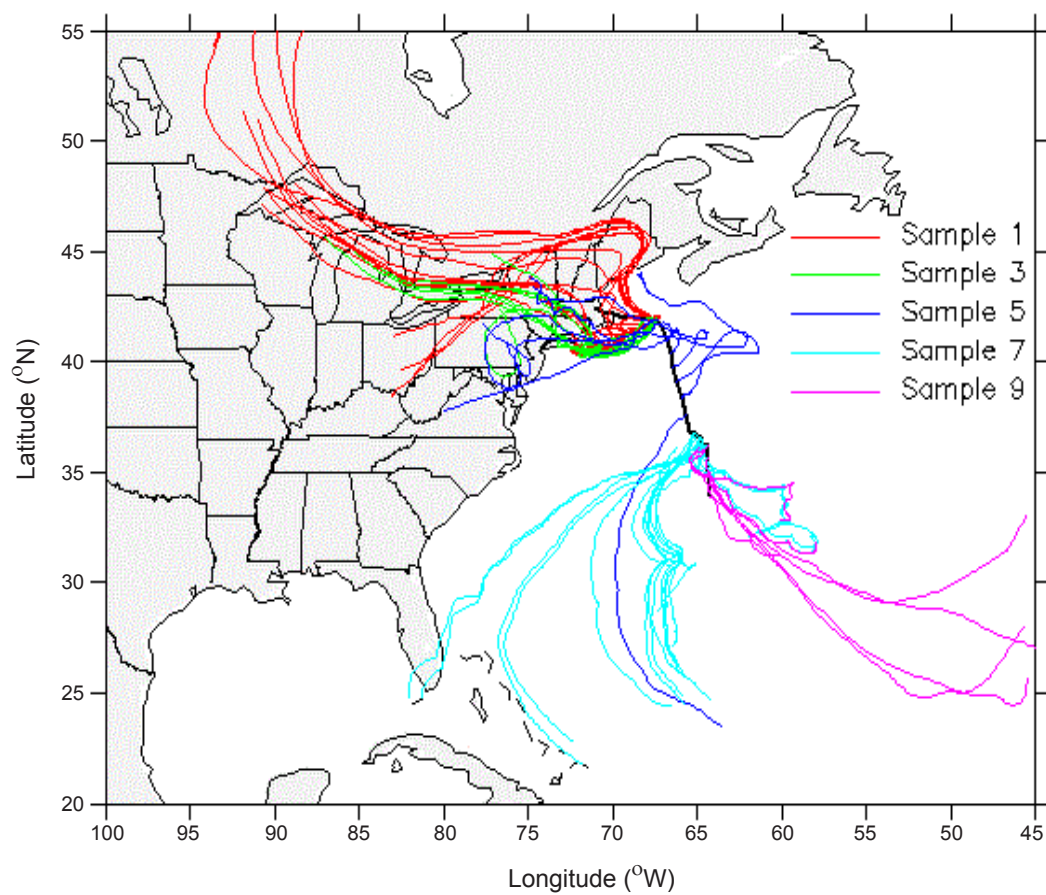
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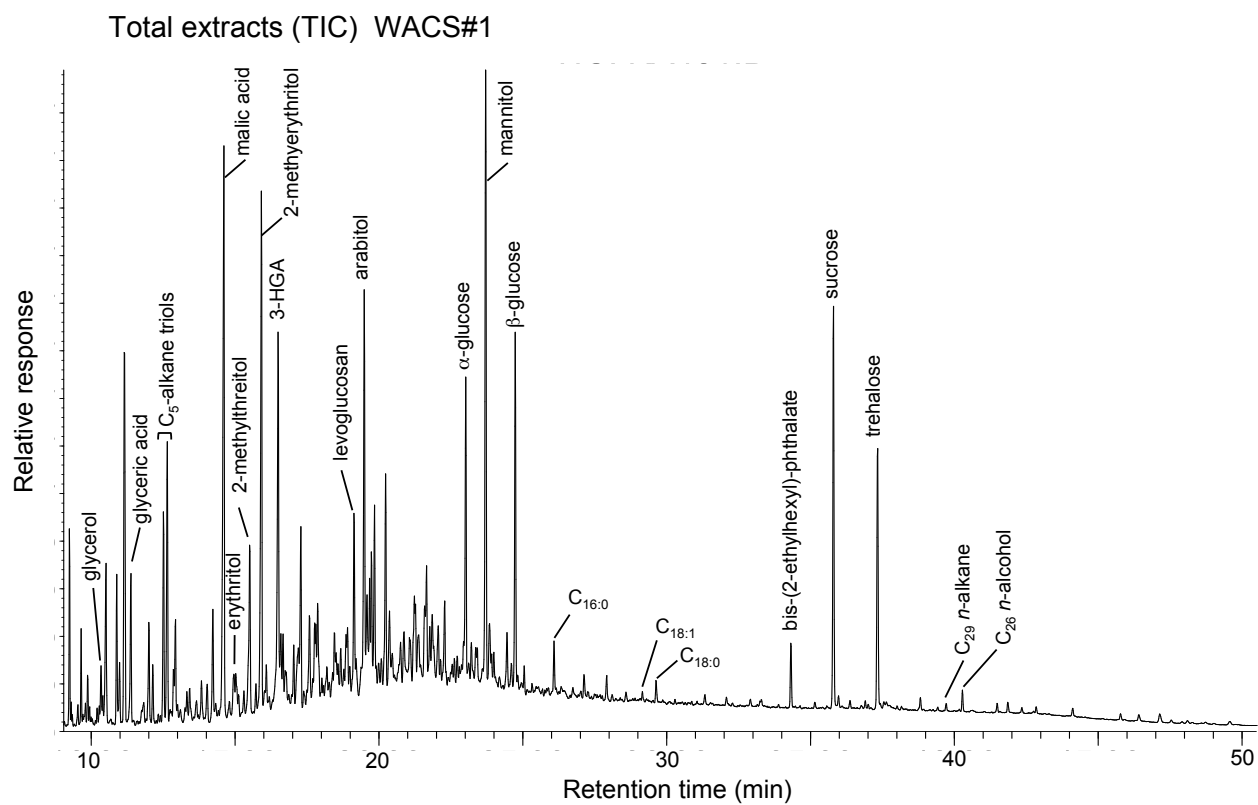
Figure 2





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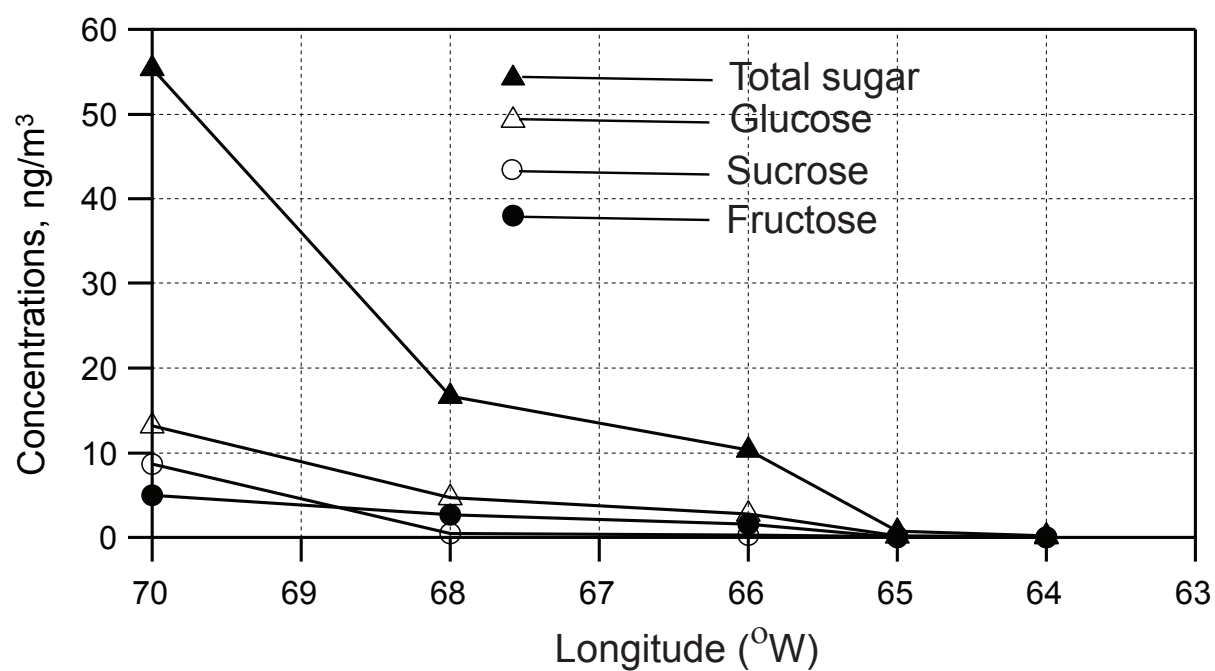
661 Figure 4



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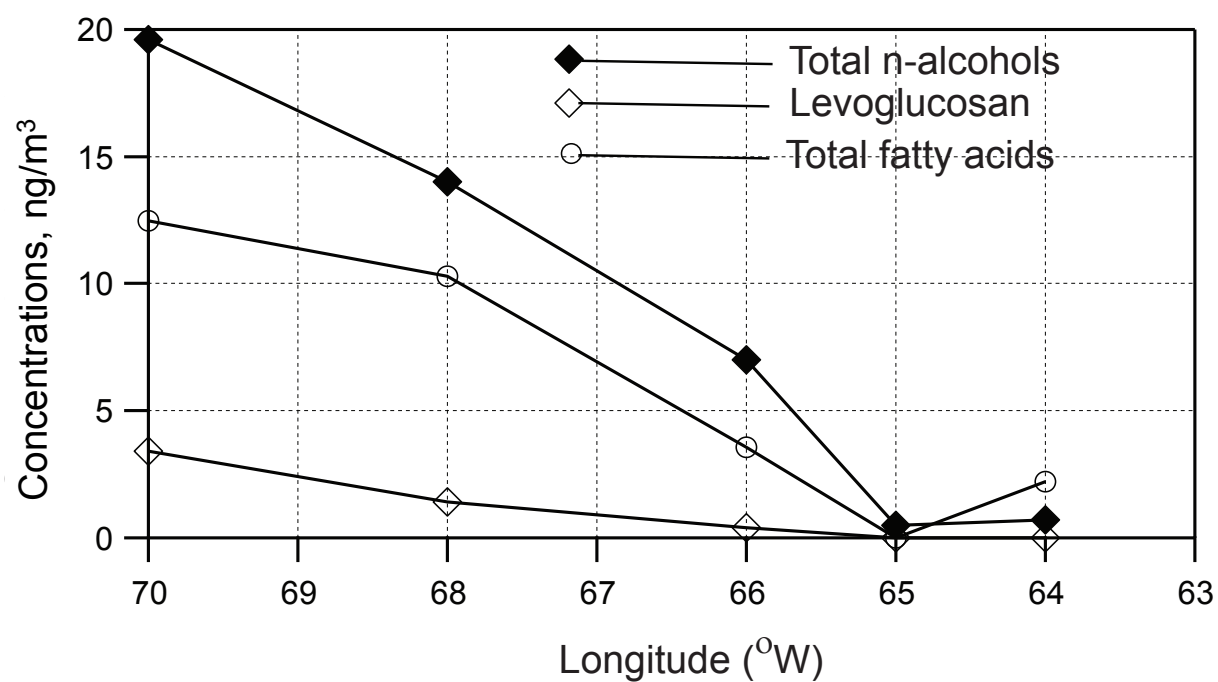
664 Figure 5



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667 Figure 6



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669 Figure 7

