

1 **Distinguishing molecular characteristics of aerosol water soluble organic matter from the 2011**  
2 **trans-North Atlantic US GEOTRACES cruise**

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7  
8 **Abstract**

9 The molecular characteristics of aerosol organic matter (OM) determines to a large extent its impacts on the atmospheric radiative  
10 budget and ecosystem function in in terrestrial and aquatic environments, yet the OM molecular details of aerosols from different  
11 sources are not well established. Aerosol particulate samples having North American-influenced, North African-influenced, and  
12 marine (minimal recent continental influence) air mass back trajectories were collected as part of the 2011 trans-North Atlantic US  
13 GEOTRACES cruise and analyzed for their water soluble OM (WSOM) molecular characteristics using electrospray ionization  
14 Fourier transform ion cyclotron resonance mass spectrometry. Principal component analysis (PCA) separated the samples into five  
15 groups defined by distinct molecular formula characteristics. An abundance of nitrogen containing compounds with molecular  
16 formulas consistent with amino acid derivatives defined the two samples comprising the Primary Marine group suggesting a primary  
17 marine biological source to their WSOM in spite of their North American-influenced air mass trajectories. A second group of samples  
18 (Aged Marine) having primarily marine air mass trajectories was characterized by an abundance of low O/C (0.15-0.45) sulfur

19 containing compounds consistent with organosulfate compounds formed via secondary aging reactions in the atmosphere. Several  
20 samples having North American-influenced air mass trajectories formed another group again characterized by organosulfate and  
21 nitrooxyorganosulfate type compounds with higher O/C ratios (0.5-1.0) than the Aged Marine samples reflecting the combustion  
22 influence from the North American continent. All the samples having North African-influenced air mass trajectories grouped together  
23 in the PCA and were characterized by a lack of heteroatom (N, S, P) containing molecular formulas covering a wide O/C range (0.15-  
24 0.90) reflecting the desert source of this WSOM. The two marine groups showed molecular formulas that, on average, had higher H/C  
25 ratios and lower O/C ratios and modified aromaticity indices than the two continentally-influenced groups suggesting these properties  
26 are characteristic of marine vs. continental aerosol WSOM. The final sample group, the Mixed Source samples, showed intermediate  
27 molecular characteristics suggesting no dominant continental or marine source. The source-specific OM details described here will aid  
28 efforts to link aerosol OM source with molecular characteristics and impacts in the environment.

29

## 30 **1 Introduction**

31 Natural and anthropogenic atmospheric aerosols play significant roles in important environmental processes impacting climate via  
32 direct and indirect effects on the Earth's radiative balance (e.g., Charlson et al., 1992; Ramanathan et al., 2001; Hansen et al., 2005;  
33 Booth et al. 2012), human health via reduction in air quality due to increased atmospheric loadings of particles and pollutant  
34 compounds (e.g., Davidson et al., 2005; Brook, 2008), and biogeochemical cycles and ecosystem function via the atmospheric  
35 delivery of nutrients (e.g., Duce and Tindale, 1991; Prospero et al., 1996; Duarte et al., 2006; Baker et al., 2010), organic matter (e.g.,  
36 Wozniak et al., 2011; 2013), and pollutants (e.g., Driscoll et al., 2001; Rhind, 2009). Aerosol organic matter (OM) is an important  
37 component within aerosols making up to 90% of the aerosol fine particle load in some areas (Kanakidou et al., 2005). In the

38 atmosphere, aerosol OM can absorb (or scatter) light contributing a warming (or cooling) effect to the atmospheric radiative budget  
39 via the direct effect (e.g., Ramanathan et al., 2001; Hansen et al., 2005) or act as condensation nuclei contributing to the growth of  
40 clouds impacting climate via the indirect effect (e.g., Ramanathan et al., 2001). Much of this OM is ultimately transported and  
41 deposited to terrestrial and aquatic systems where it has been implicated as an important OM source to riverine export (Likens et al.,  
42 1984; Velinsky et al., 1986; Wozniak et al., 2011) and as a complexing agent facilitating the delivery of soluble, bioavailable Fe to the  
43 ocean (Paris and Desboeufs, 2013; Wozniak et al., 2013).

44 The chemical characteristics of aerosol OM have a major role on its environmental effects. For example, aromatic and double  
45 bond functional groups impart a light absorbing property to OM (Andreae and Gelencser, 2006), water soluble OM components have  
46 hygroscopic properties that increase cloud condensation nuclei formation (Chan et al., 2005), and the presence of carboxylic  
47 functionalities has been suggested to allow combustion-derived aerosol OM to complex with Fe and facilitate its delivery to the ocean  
48 in bioavailable form (Wozniak et al., 2013). With the acknowledged roles in climate and ecosystem function and the disparate sources  
49 (e.g., natural terrestrial, anthropogenic biomass and fossil fuel combustion, primary marine biogenic, secondary formation) of aerosol  
50 OM, it is important to understand the defining physical and chemical characteristics of aerosol OM from the different sources so we  
51 can model and predict ecosystem and climate responses to changes in the relative and overall magnitudes of source-specific aerosol  
52 OM emissions. Yet, at present the source specific chemical characteristics of aerosol OM are not well defined. This problem is  
53 particularly challenging for primary sea spray sources due to difficulties collecting aerosol samples in remote marine environments,

54 analytical challenges related to the low OM atmospheric loadings of marine aerosols, and the fact that aerosols over ocean  
55 environments often contain OM from both continental and marine sources (Meskhidze et al., 2013).

56 While global aerosol OM budgets are uncertain, models suggest that marine-derived aerosol OM, emitted via sea spray as primary  
57 aerosols or formed by secondary processes from volatile organic precursors (O'Dowd and de Leeuw, 2007; Gantt and Meskhidze,  
58 2013), account for approximately 10 Tg (range: 2-100 Tg yr<sup>-1</sup>; Gantt and Meskhidze, 2013 and references therein) of the estimated  
59 150 Tg organic aerosols emitted each year globally (range: 60-240 Tg yr<sup>-1</sup>; Hallquist et al., 2009). Access to the marine environment  
60 for the purposes of aerosol sampling can be difficult, and as a result, much less is known about the chemical composition of aerosol  
61 OM from marine as compared to continental sources. Much of what is known about marine aerosol OM chemical composition results  
62 from studies of aerosols collected at coastal or remote island sites (e.g., Gagosian et al., 1981; Facchini et al., 2008; Claeys et al.,  
63 2010; Ovadnevaite et al., 2011), shipboard during research cruises (e.g., Hawkins et al., 2010; Schmitt-Koplin et al., 2012), aboard  
64 research flights (Hawkins and Russell, 2010; Russell et al., 2010), or via bubble bursting experiments that produce aerosols artificially  
65 from seawater (e.g., Kuznetsova et al., 2005; Facchini et al., 2008; Schmitt-Koplin et al., 2012). These studies have identified likely  
66 biological primary emissions of marine aerosol OM such as carbohydrate or polysaccharide-like and amino acid or protein-like  
67 compounds (Kuznetsova et al., 2005; Hawkins et al., 2010; Hawkins and Russell, 2010; Russell et al., 2010) as important constituents.  
68 Other studies have detected organosulfate compounds (Claeys et al., 2010; Hawkins et al., 2010; Ovadnevaite et al., 2011) and small  
69 organic ammonium compounds (Facchini et al., 2008) suggesting them to have marine secondary sources. Still other studies have

70 identified various carboxylic acid compounds (Decesari et al., 2011; Schmitt-Koplin et al., 2012) and aliphatic amines (Decesari et al.,  
71 2011).

72 While these studies have increased our understanding of aerosol OM composition that allow us to relate aerosol OM composition  
73 to environmental impact, much work still needs to be done to understand what governs the molecular composition of aerosol OM and  
74 its components (e.g., water insoluble OM (WIOM), water soluble OM (WSOM), particle size fractions) in various parts of the world's  
75 oceans, at different times of the year, subject to different influences (e.g., aerosol sources, oceanographic and meteorological  
76 conditions), and using all available analytical tools. In particular, studies that increase coverage of the ocean and that are able to  
77 distinguish between marine and continental sources are needed. Analyses of field collected marine aerosol OM seeking to  
78 unambiguously identify marine-derived components are complicated by the presence of continentally transported aerosol OM over the  
79 marine environment, but multivariate statistical approaches offer a way to distinguish defining differences among datasets. For  
80 example, Hawkins et al. (2010) used positive matrix factorization to separate aerosols collected over the southeast Pacific Ocean into a  
81 marine component containing organic hydroxyl functional groups indicative of carbohydrate-like compounds and a saturated aliphatic  
82 carboxylic acid combustion component.

83 The WSOM fraction of aerosols is thought to enhance cloud condensation nuclei formation (Chan et al., 2005), has been  
84 investigated as a possible ligand for bioavailable and soluble Fe (Wozniak et al 2013) for biological production in high nutrient low  
85 chlorophyll regions, and is the focus of this study. WSOM is analyzed here by Fourier transform ion cyclotron resonance mass

86 spectrometry (FTICR MS) coupled to electrospray ionization (ESI), an analytical tool that effectively characterizes natural OM and  
87 has begun to be used to study aerosol OM (e.g., Reemtsma et al., 2006; Wozniak et al., 2008; Lin et al., 2012) including marine  
88 aerosol OM (Schmitt-Koplin et al., 2012). This study examines the WSOM characteristics of 24 aerosol samples collected as part of  
89 the 2011 trans-North Atlantic US GEOTRACES cruise. Principal component analysis (PCA) is performed on data derived from the  
90 FTICR MS spectra obtained for the 24 samples to investigate the defining molecular characteristics of aerosols influenced to varying  
91 degrees by primary and secondary marine, continental combustion (North America), and continental dust (North Africa/Saharan dust)  
92 sources. In so doing, this study provides 1) increased spatial coverage of the molecular characteristics of aerosol WSOM over a vast  
93 portion of the North Atlantic Ocean for which aerosol WSOM has not been characterized and 2) important information on the source-  
94 specific molecular characteristics of aerosol WSOM produced in and transported to the marine environment.

## 95 **2 Methods**

### 96 ***2.1 Sample collection, handling, and storage.***

97 Aerosol total suspended particulate samples were collected aboard the R/V Knorr along a transatlantic transect between 7  
98 November and 9 December 2011 (n=24) (Figure 1) as part of the 2011 US GEOTRACES program cruise ([www.geotraces.org](http://www.geotraces.org)).  
99 Briefly, air was pulled through precombusted (480°C, 10 h) quartz microfiber (QMA) filters (20.3 cm x 25.4 cm, 406 cm<sup>2</sup> exposed  
100 area, 0.6 µm effective pore size) deployed in a high-volume aerosol sampler (model 5170-BL, Tisch Environmental) operating at  
101 approximately 1.2 m<sup>3</sup> air min<sup>-1</sup>. These high-volume aerosol samplers are similar to those used in many studies of marine aerosols

102 (Arimoto et al., 1995; Prospero, 1999; Baker et al., 2006). Material retained on the filters was operationally-defined as “total  
103 suspended particulates”. Sample face velocities were  $50 \text{ cm s}^{-1}$  and durations averaged 19.4 h (range = 5.9-29.6 h) with the volume of  
104 air filtered averaging  $1440 \text{ m}^3$  (range =  $400\text{-}2200 \text{ m}^3$ ). Sample details can be found in the supplementary information (Supplementary  
105 Table 1). Filters were visually inspected during sampling to estimate particulate loading, and where low particulate loads were  
106 observed the samplers were allowed to run for longer durations. All filters were stored frozen prior to processing, both on the ship and  
107 upon returning to the laboratory.

108         Samplers were deployed on the ship’s flying bridge (14 m above sea level) as high off the water as possible. Contamination  
109 from the ship’s stack exhaust was avoided by controlling aerosol sampling with respect to wind sector and wind speed using an  
110 anemometer interfaced with a Campbell Scientific CR800 datalogger. The samplers were allowed to run when the wind was  $\pm 60$   
111 degrees from the bow and  $> 0.5 \text{ m/s}$ . When the wind failed to meet these two criteria, the motors were shut off automatically and not  
112 allowed to restart until the wind met both the speed and direction criteria for 5 continuous minutes. The anemometer was deployed  
113 nearby on a separate pole in “free air” where turbulence from the wind crossing the bow did not cause the wind vane to wobble  
114 excessively.

## 115 **2.2 WSOM Isolation.**

116         The QMA filter samples were cut into subsamples using ceramic-bladed scissors, stored frozen in the dark to preserve the OM,  
117 and 1/4 of each sample was shipped on ice to Old Dominion University (ODU) and stored frozen prior to analysis. WSOM was

118 isolated following published procedures for desorbing aerosol WSOM from total suspended particulate material on filters (e.g., Siefert  
119 et al., 1994; Wozniak et al., 2008; 2012; 2013). Aerosol subsamples ( $\sim 29 \text{ cm}^2$ ) were placed in pre-combusted glass jars, and 25 mL of  
120 ultrahigh purity (MilliQ) water was added. The jars were wrapped in aluminum foil to keep out ambient light and placed on an orbital  
121 shaker table (VWR model 57018-754) for 2 hours, which is sufficient time to desorb  $>90\%$  of WSOM (Wozniak et al., 2012). The  
122 water was then filtered through a pre-combusted GF/F filter ( $0.7 \mu\text{m}$  pore size) using a pre-cleaned (10% HCl) syringe to isolate the  
123 WSOM. Ten mL of WSOM was saved for FTICR analyses, and the remaining 15 mL was frozen and saved for analyses not discussed  
124 here.

### 125 ***2.3 Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS).***

126 Aerosol WSOM (10 mL) was solid-phase extracted using a styrene divinyl benzene polymer (PPL, Varian) cartridges  
127 following published procedures (e.g., Dittmar et al., 2008; Mitra et al., 2013). The PPL cartridge was rinsed with two cartridge  
128 volumes of LC-MS grade methanol and acidified Milli-Q water before the pre-filtered and acidified aerosol WSOM was loaded onto  
129 the cartridge. The relatively hydrophobic dissolved OM (DOM) is retained on the PPL cartridge while highly hydrophilic WSOM and  
130 salts (which would otherwise compete with the aerosol WSOM for charge during ESI) pass through the cartridge. The cartridge was  
131 then rinsed with 0.01 M HCl to ensure complete removal of salts, dried under a stream of ultrapure nitrogen, and eluted with one  
132 cartridge volume ( $\sim 3 \text{ mL}$ ) of methanol. Previous work has estimated that  $\sim 60\%$  of dissolved OM is retained using this technique  
133 (Dittmar et al., 2008). Though previous studies have added ammonium hydroxide prior to ESI in order to increase ionization, tests



134 showed that higher quality spectra (more organic matter peaks) were obtained without the addition of base, and samples were infused  
135 to the ESI in methanol alone. Samples were continuously infused into an Apollo II ESI ion source of a Bruker Daltonics 12 T Apex  
136 Qe FTICR, housed at ODU's COSMIC facility. Samples were introduced by a syringe pump at  $120 \mu\text{L h}^{-1}$ . All samples were analyzed  
137 in negative ion mode; ions were accumulated in a hexapole for 0.5 s before being transferred to the ICR cell, where 300 transients  
138 were co-added. The summed free induction decay signal was zero-filled once and sinebell apodized prior to fast Fourier  
139 transformation and magnitude calculation using the Bruker Daltonics Data Analysis software.

140 All mass spectra were externally calibrated with a polyethylene glycol standard and internally calibrated with naturally  
141 occurring fatty acids and other homologous series present within the sample (Sleighter and Hatcher, 2008). A molecular formula  
142 calculator (Molecular Formula Calc v. 1.0 ©NHMFL, 1998) generated molecular formulas using carbon ( $^{12}\text{C}_{8-50}$ ), hydrogen ( $^1\text{H}_{8-100}$ ),  
143 oxygen ( $^{16}\text{O}_{1-30}$ ), nitrogen ( $^{14}\text{N}_{0-5}$ ), sulfur ( $^{32}\text{S}_{0-2}$ ), and phosphorous ( $^{31}\text{P}_{0-2}$ ). Peaks identified in process blanks (PPL extract of QMA  
144 filter blank WSOM) were subtracted from the sample peak list prior to formula assignment. Only m/z values in the range of 200-800  
145 with a signal to noise ratio above 3 were used for molecular formula assignments. The mean mass resolution for all samples over that  
146 mass range was 560,000.

147 Constraints corresponding to the standard range of atomic composition for natural organic matter were applied during formula  
148 assignment following previous work (Stubbins et al., 2010; Wozniak et al., 2008): 1)  $\text{O/C} \leq 1.2$ ; 2)  $0.3 \leq \text{H/C} \leq 2.25$ ; 3)  $\text{N/C} \leq 0.5$ ; 4)  
149  $\text{S/C} \leq 0.2$ ; 5)  $\text{P/C} \leq 0.2$ ; 6)  $\text{DBE} \geq 0$  and an integer value. The term DBE is the number of double bond equivalents, which is the

150 number of double bonds and rings in a formula (e.g., Hockaday et al., 2006). The measured m/z values and assigned formula  
151 calculated exact masses all agreed within the maximum allowed error of 1.0 ppm, and >90% of formulas were within 0.5 ppm. An  
152 unequivocal formula is found for m/z values below 450, but above this, multiple formulas may match the measured m/z value. In  
153 order to ensure a unique formula per peak, a formula extension approach similar to that described by Kujawinski et al. (2009) was  
154 used to identify appropriate formulas. Additional constraints are placed on the proportion of heteroatoms using the following criteria  
155 (Kujawinski et al., 2009): 1) each formula should have numbers of N and S atoms that are each fewer than the number of oxygen  
156 atoms, and 2) the sum of the N and S atoms should be the lowest possible.

157         The spectral magnitude for a given peak results from a combination of the concentrations of the isomeric compounds  
158 representing a given molecular formula in the actual WSOM, how ionizable those compounds are using ESI, and the FTICR MS  
159 analytical window. ESI FTICR MS is thus not a purely quantitative technique. Nonetheless, for comparisons of samples measured  
160 using the same instrumental conditions, the relative spectral magnitude contributed by elemental formulas and formula groups  
161 (magnitude weighted contributions) has been used as an instructive qualitative measure (e.g., Wozniak et al., 2008; Sleighter et al.,  
162 2009; Mazzoleni et al., 2010; O'Brien et al., 2012; Schmitt-Koplin et al., 2012). Magnitude weighted elemental formula group  
163 fractional contributions (e.g., %CHO, %CHON, %CHOS, etc.) were calculated as follows:

164

$$165 \quad \%X_w = 100 * \Sigma M_x \tag{1}$$

166

167 where % $X_w$  represents the magnitude weighted elemental formula fractional contribution, and  $\Sigma M_x$  denotes that the relative  
168 magnitudes are summed over the elemental formula combination (e.g., CHO, CHON, CHOS, CHONS, CHONP, CHOSP) of interest.  
169 Magnitude weighted O/C, H/C, and modified aromatic index ( $AI_{mod}$ ) values for a given sample were calculated as follows:

170

$$171 \quad Y_w = \Sigma Y_n * M_n, \quad (2)$$

172

173 where  $Y_w$  represents the magnitude-weighted parameter of interest (O/C, H/C,  $AI_{mod}$ ),  $n$  denotes that the summation includes all  
174 assigned formulas in a given sample, and  $M$  represents the relative spectral magnitude for the assigned elemental formula. The O/C  
175 and H/C ratios are calculated by dividing the number of O (or H) atoms by the number of C atoms in a given assigned formula.  $AI_{mod}$   
176 is a measure of the probable aromaticity for a given OM molecular formula assuming that half of the oxygen atoms are doubly bound  
177 and half are present as  $\sigma$  bonds (Koch and Dittmar, 2006):

178

$$179 \quad AI_{mod} = (1 + C - 0.5O - S - 0.5H)/(C - 0.5O - S - N - P), \quad (3)$$

180

181 where C, O, S, H, N, and P represent the number of carbon, oxygen, sulfur, nitrogen, and phosphorus atoms in a given molecular  
182 formula. The  $AI_{\text{mod}}$  scale ranges from 0 for a purely aliphatic compound to 1 with increasing values found for compounds showing  
183 higher numbers of double bonds and relative aromaticity.

## 184 185 **2.4 Data Analyses.**

186 **2.4.1 Principal Component Analysis (PCA)** was performed on FTICR-MS datasets using an in-house developed Matlab script.  
187 Before being utilized for PCA, the 500 most intense peaks that were assigned molecular formulas were identified for each sample.  
188 This amounted to a total of 3077 molecular formulas that represented the input variables for the PCA. The relative intensity (the  
189 intensity of a peak divided by the summed intensities for all peaks assigned formulas, a score of 0 was given to molecular formulas not  
190 present in a sample) of each of these peaks within all 24 samples was determined and used to generate the matrix for the PCA. The  
191 PCA was performed for this initial list of 3077 molecular formulas and with the 2408 molecular formulas that were present in at least  
192 3 samples (>12% of all samples). The OM compounds represented by this molecular formula list ( $n = 2408$ ) are responsible for the  
193 majority (52-92%) of the spectral magnitude in the samples indicating that the compounds are high in concentration and/or are  
194 efficiently ionized and detected by negative ion ESI FTICR MS. Using this reduced molecular formula list concentrated the analyses  
195 on the most abundant peaks and removed the influence of molecular formulas present in only a few samples.

196 PCA uses an orthogonal transformation to reduce multiple variables into fewer dimensions called principal components (PCs)  
197 that are generated by the PCA and defined by PC loadings ascribed to each variable (in this case, the 2408 or 3077 assigned molecular  
198 formulas). Each sample receives a score for each PC based on the magnitude of its input variables and the corresponding loadings for  
199 those variables to each PC. Samples with high PC1 scores (for example) can thus be expected to have high contributions from  
200 variables showing high loadings for PC1. The first PC explains the largest portion of the variance in the dataset, and each successive  
201 PC is orthogonal to the previous PC and explains the largest portion of the remaining variance in the dataset. PCs can then be plotted  
202 on 2-d and 3-d plots created from sample scores to evaluate the differences between samples.

203 **2.4.2 Air Mass Back Trajectory Simulations** were performed using the publicly available NOAA ARL HYSPLIT model (Rolph,  
204 2012; Draxler and Rolph, 2012). Back trajectories (120 hours) were calculated from the ship's position and collection time using the  
205 ensemble form of the model. The ensemble mode reveals the effects from small-scale meteorological variability on the trajectories  
206 (Draxler, 2003). In order to investigate the behavior and fate of aerosols in the marine boundary layer (MBL, typically 400-1200 m  
207 thickness), an arrival height of 250 m was chosen. This height is also the minimum height for optimal configuration of the ensemble.  
208 Given the uncertainty of the air mass behaviors within the MBL, this height was chosen to best characterize air mass trajectories at our  
209 sample collection height. Simulations were also conducted using higher (1500 m) arrival heights, which returned similar results (data  
210 not shown). Air masses were characterized operationally as North American or North African if more than half of the air mass  
211 trajectory simulations extended to these regions, as is shown in Figure 2. If less than half of 5 day air mass trajectory simulations

212 extended to continents, the sample was classified as ‘marine’. It is noted that air masses categorized as ‘marine’ may very well contain  
213 aerosol OM from distant (> 5 days) continental sources. Additionally, because all the samples were collected over the marine  
214 environment, they are all expected to be influenced by marine sources to some degree. Where possible, visual inspection of the QMA  
215 filters was used to corroborate air mass trajectory simulations for determination of aerosol source influence. Specifically, filters with  
216 an orange color to the particulate matter were determined to have a North African dust influence and were assigned as North African if  
217 air mass trajectories were ambiguous.

218

### 219 **3 Results and Discussion**

220 Air mass trajectory analyses showed the dataset to be comprised of 9 marine (Mar4-12), 7 North African-influenced (N Afr9-15), and  
221 8 North American-influenced (N Am1-8) aerosol samples (Figure 1). These classifications are operationally-defined and used as just  
222 one guideline to help delineate the provenance of aerosol WSOM in each sample. Visual inspection of the filters show each of the  
223 North-African-influenced samples to have a reddish-orange color demonstrating an influence from desert dust as has been found in  
224 previous studies (e.g., Baker et al., 2006) while the remaining samples all showed very little color at all.

225 **3.1 General FTICR MS Characteristics.** Formula assignments from the FTICR MS-derived m/z information for the 24 aerosol  
226 WSOM samples revealed 11,813 unique molecular formulas. CHON formulas were the most abundant of the elemental formula  
227 combinations (3,441, 29% of all formulas) followed by CHO (3,282, 28% of all formulas), CHOS (1,910, 16% of all formulas),

228 CHOP (1,355, 11% of all formulas), CHONS (971, 8% of all formulas), CHONP (686, 6% of all formulas), and CHOSP (168, 1% of  
229 all formulas) formulas (supplementary Table 2). In spite of this distribution among the total dataset, CHO (26-79%) formulas were the  
230 most abundant elemental formula type for 22 of the 24 individual samples and the second most abundant formula type in N Am 6 and  
231 N Am 7 which both showed high contributions from CHON formulas. CHON (2-44%), CHOS (5-38%), and CHOP (3-13%) formulas  
232 were the second most abundant elemental formula type within a sample for 6, 15, and 1 samples, respectively, (see supplementary  
233 Table for details) while CHONS (~0-11%), CHONP (~0-6%), and CHOSP (0-5%) formulas were less frequently observed.

234

235 As has been observed in previous studies of negative ion ESI FTICR MS data, using magnitude weighted abundances  
236 increases the importance of CHO and CHOS formulas relative to formulas containing N or P (Wozniak et al., 2008; Sleighter et al.,  
237 2009). CHO formulas accounted for the largest portion of the spectral magnitude in 19 of 24 samples, CHOS formulas were most  
238 abundant in 3 marine samples (Mar6, Mar7, Mar 12), and CHON formulas were most abundant in N Am 6 and N Am 7. The CHOS  
239 (12 of 24), CHON (6 of 24), CHO (5 of 24), and CHOP (1 sample) formula groups were all second in magnitude-weighted abundance  
240 for various samples (Supplementary Table 1).

241 Of the 11,813 molecular formulas, 614 and 248 formulas were present in at least 18 (75%) and 22 (92%) of the 24 samples,  
242 respectively (Figure 3). The majority of these formulas were CHO formulas with H/C ratios between 1.05 and 1.75 and O/C ratios  
243 between 0.2 and 0.7 or CHOS formulas with H/C ratios between 1.45 and 1.95 and O/C ratios between 0.25 and 0.7. All of these

244 formulas were also found in at least one of 18 aerosol WSOM samples isolated from aerosol particulates collected in Virginia and  
245 New York, USA (Wozniak et al., 2008; Wozniak, unpublished data) suggesting that these CHO and CHOS compounds are ubiquitous  
246 in continental and oceanic atmospheres and not particularly characteristic for WSOM from marine sources. CHO and CHOS formulas  
247 with these H/C and O/C ratios are ubiquitous in natural DOM of many types including continental rainwater, fog water, riverine,  
248 estuarine, and deep sea DOM (e.g., Sleighter et al., 2008; Mazzoleni et al., 2010; Mitra et al., 2013; Rossel et al., 2013) making  
249 assignment of the source of any of these formulas in a given natural OM sample difficult. Their ubiquity amongst marine and  
250 terrestrial samples and similar H/C and O/C ratios to those for laboratory generated SOA (Kourtchev et al., 2014) suggest that they  
251 may be SOA products of monoterpene volatile organic compounds.

252 **3.2 Principal Component Analysis.** An initial PCA (data not shown) performed using the relative spectral magnitude of the 500  
253 most intense formulas found in every sample showed two samples (N Am 6 and N Am 7) with molecular characteristics that are  
254 extremely different than the other 22 samples. These two samples were collected very close to Bermuda (< 150 km), the island nation  
255 near the western edge of the Sargasso Sea 1000 km from the North American mainland, one week after tropical storm Sean passed  
256 through the region and had air mass back trajectories characterized as North American-influenced. The unique molecular composition  
257 of these two samples may thus be due to the effects of tropical storm Sean creating a turbulent wave environment that emitted marine-  
258 derived sea spray aerosol OM into the atmosphere or to a strong North American source of OM. Examination of the molecular  
259 formulas in these two samples found 162 molecular formulas present in these two samples that were found in no other sample. The



260 majority (144) of these unique molecular formulas contain N (1-5 nitrogens) and have high H/C (1.6-2.0) and low O/C (0.2-0.4) ratios,  
261 characteristics of peptide-like compounds. These samples are discussed in more detail in the Primary Marine sample group section.

262 To remove the impact of infrequently occurring molecular formulas that drive the PCA scores (following Sleighter et al.,  
263 2010), molecular formulas occurring in fewer than 3 samples (< 12% of the 24 samples) were removed from the PCA loading matrix  
264 reducing the number of loading variables from 3,077 to 2,408. The relative distribution of elements in the formulas is quite different  
265 than the complete list of 11,813 assigned formulas better reflecting the relative spectral magnitude and the approximate distribution of  
266 the elemental formula groups within a given sample. These 2,408 formulas are made up of 1,172 (49%) CHO, 592 (25%) CHOS, 364  
267 (15%) CHON, 112 (4.7%) CHOP, 90 (3.7%) CHONS, 70 (2.9%) CHONP, and 8 (0.3%) CHOSP formulas (Figure 4). The first 3 PCs  
268 generated by this PCA account for 51% of the variance in the dataset and separate the 24 samples into 5 distinct groups (Figure 5a).  
269 The sample groups are categorized based on their distinct characteristics as defined by the PCA loadings (the molecular formulas;  
270 Figure 5b) that correspond to a given group's PCA scores and the predominant air mass trajectories for the members of each group.  
271 They are (with the identities of samples making up each group listed in parentheses) as follows: 1) Primary Marine (N Am 6,7); 2)  
272 Aged Marine (Mar 5,6,7,9,12); 3) North American-Influenced (N Am 1,2,3,4,5); 4) North African-Influenced (N Afr  
273 9,10,11,12,13,14,15); 5) Mixed Source (Mar 4,8,10,11, N Am 8).

274 **3.3 Primary Marine OM samples.** Even with the removal of infrequently occurring molecular formulas, the PCA separates the two  
275 outlier samples, N Am 6 and N Am 7, into their own group highlighting their unique character relative to the other samples in this

276 dataset. While the air mass trajectories for N Am 6 and N Am 7 extend back to the North American continent, the WSOM molecular  
277 characteristics, specifically the abundance of N and P containing molecular formulas, for these two samples suggest this WSOM to  
278 have a primary marine biological source. Analysis of the magnitude-weighted average values for all of the PCA assigned sample  
279 groups show the Primary Marine group to have higher mean magnitude weighted percent abundances of CHON (54%) and CHONP  
280 (5.4%) formula groups than any of the other PCA groups (Table 1). The CHO and CHOS formula groups, noted above as ubiquitous  
281 components in all aerosol WSOM, still comprise quantitatively important portions of the spectral intensity (30% and 7%, respectively)  
282 but smaller portions than the other PCA differentiated groups. Marine phytoplankton and bacteria have higher nutritional requirements  
283 for both N and P than do terrestrial vegetation (e.g., Fagerbakke et al., 1996; Hewson and Fuhrmann, 2008; Bianchi and Canuel,  
284 2011), and both dissolved organic nitrogen and phosphorous have long been known to be enriched in the sea surface microlayer (e.g.,  
285 Williams, 1967; Williams et al., 1986) where surface active OM components accumulate after being entrained and brought to the  
286 surface with bubbles. The N- and P-enriched surface microlayer OM can then be emitted as sea spray, and marine biological  
287 components therefore represent a probable source of aerosol WSOM for this set of samples. Zamora et al. (2013), analyzing rainwater  
288 samples collected in Barbados, found higher dissolved organic P and N concentrations in sea spray derived rainwater relative to  
289 rainwater influenced by dust or biomass burning. The higher relative contributions of CHON and CHONP containing aerosol WSOM  
290 for this group of samples are thus consistent with a sea spray source of primary WSOM.

291 Patterns observed in the PCA loadings for the molecular formulas defining this sample group provide further evidence for a  
292 primary marine source of aerosol WSOM for these 2 samples and important molecular information for potential sea spray WSOM  
293 constituents. The PCA loadings defining this group are plotted together in a van Krevelen diagram (Figure 6a) with the 162 molecular  
294 formulas found in these samples but no others (and not included in the PCA). CHON formulas make up 85% of the formulas in Figure  
295 6a, and 38 of the remaining 59 formulas are made up by CHONP and CHONS formulas. The CHON formulas found to be defining for  
296 this Primary Marine sample group have O/C ( $0.15 < O/C < 0.45$ ) and H/C ( $1.5 < H/C < 2.0$ ) ratios that suggest potential peptide-like  
297 compounds, and several of the molecular formulas can be attributed to compounds with functionalized amino acids. These CHON  
298 molecular formulas form several Kendrick mass defect series with 1 to 4 nitrogen atoms in their molecular formulas (series of  
299 formulas differing by  $CH_2$  groups; Kendrick, 1963; Figure 7) that could represent biological compounds that have been degraded to  
300 different degrees in the water or during atmospheric transport. Figure 7 includes examples of potential amino acid containing  
301 compounds that correspond to these formulas. It is noted that the structures in Figure 7 are tentative and represent only some of many  
302 potential isomers that correspond to the assigned molecular formulas. LC/MS or a comparable technique is needed to verify the  
303 structures of the compounds that correspond to these formulas, but this is beyond the scope of this particular paper. Further, the  
304 CHONP molecular formulas defining this sample group have molecular formulas ( $H/C > 2.0$ ,  $O/P > 4$ ) consistent with phospholipid-  
305 like compounds, important structural components in biological cell membranes. The apparent importance of peptide-like CHON series

306 and the phospholipid-like CHONP formulas are an indication of a primary biological source for these compounds and to the WSOM  
307 in general.

308 Previous studies of marine-derived atmospheric OM have noted contributions from biological components such as amino acid  
309 and protein-like compounds (Kuznetsova et al., 2005; Altieri et al., 2012) and carbohydrates and polysaccharide compounds (Hawkins  
310 et al., 2010; Hawkins and Russell, 2010; Russell et al., 2010). Though we are unaware of studies that have identified phospholipids in  
311 aerosol OM from a sea spray source, they are consistent with a strong biological component of sea spray aerosol OM. It should be  
312 noted that carbohydrates and polysaccharide-like compounds previously found to be important components in sea spray aerosol OM  
313 (Hawkins et al., 2010; Hawkins and Russell, 2010; Russell et al., 2010) do not ionize efficiently via ESI due to a lack of ionizable  
314 polar functional groups and may have thus escaped the analytical window of ESI FTICR MS. The apparent biological contributions to  
315 this Primary Marine PCA group lend support for the role of sea surface biological composition as a determining factor in sea spray  
316 aerosol OM composition (e.g.; Aller et al., 2005; Schmitt-Koplin et al., 2012; Rinaldi et al., 2013; Gantt et al., 2013) and suggest the  
317 need to further explore how oceanographic conditions influence marine aerosol OM composition and impacts in the atmosphere.

318 **3.4 Aged Marine Samples.** A second PCA group comprised of 5 samples with marine air mass back trajectories and distinguished by  
319 high contributions from CHOS containing compounds was also identified and is hereafter referred to as the ‘Aged Marine’ samples  
320 based on their being characterized by an abundance of CHOS formulas consistent with organosulfate compounds formed via  
321 photochemical aging. CHO formulas were again the dominant formula type accounting for 43% of the spectral intensity (Table 1)

322 though the defining characteristic of these samples was quite clearly the abundance of CHOS formulas. On average, CHOS formulas  
323 accounted for 38% of the spectral intensity for the ‘Aged Marine’ samples (versus 7% in the Primary Marine samples), while CHON  
324 formulas made up just 5% of spectral intensity (versus 54% in the Primary Marine Samples, Table 1). Consistent with these average  
325 characteristics, the PCA loadings show more than 65% of the formulas defining the ‘Aged Marine’ samples to contain sulfur (246 out  
326 of 374) with the majority showing H/C ratios between 1.25 and 2.25, O/C ratios between 0.25 and 0.50 (Figure 6b), and O/S ratios  
327 greater than or equal to 4 suggesting that many of these formulas represent aliphatic organosulfate compounds. Organosulfate  
328 compounds have been identified in several studies examining rainwater and aerosol OM collected in terrestrial (e.g., Romero and  
329 Oehme, 2005; Reemtsma et al., 2006; Surratt et al., 2008; Wozniak et al., 2008; Altieri et al., 2009; Schmitt-Koplin et al., 2010) and  
330 marine (Claeys et al., 2010; Hawkins et al., 2010; Ovadnevaite et al., 2011) environments. Laboratory studies show organosulfate  
331 formation under both light and dark conditions with (e.g., Reemtsma et al., 2006; Surratt et al., 2007; Iinuma et al., 2007; Surratt et al.,  
332 2008; Minerath and Elrod, 2009; Minerath et al., 2009; Schmitt-Koplin et al., 2010) the acid-catalyzed ring opening reaction of  
333 epoxides formed from biogenic and anthropogenic precursors described by Iinuma et al. (2007) being the most kinetically favorable  
334 formation mechanism studied to date (Minerath and Elrod, 2009; Minerath et al., 2009). Thus, the abundance of organosulfate  
335 formulas in these samples can be attributed to secondary aging processes in the atmosphere and are indicative of aerosol WSOM that  
336 has been aged considerably relative to that in the Primary Marine samples.

337 Claeys et al. (2010) identified C<sub>6</sub>-C<sub>13</sub> organosulfates in aerosol samples collected on Amsterdam Island in the southern Indian  
338 Ocean with higher O/C ratios (0.46-1) than those identified as important to the Aged Marine samples here (0.25-0.5). The different  
339 O/C ratios likely relate to differences in the analytical windows of the techniques used in the two studies. Organosulfates in the Aged  
340 Marine group PCA loadings had negative ion nominal masses between 209 and 617 and contained 7-29 C atoms, while Claeys et al.  
341 (2010) detected negative ion masses up to 309 ( $\leq 13$  C atoms). The higher carbon chain lengths able to be detected here facilitates the  
342 detection of lower O/C ratio organosulfates, and they appear here as a defining characteristic for these Aged Marine samples. Sulfate  
343 is ubiquitous in the troposphere with strong marine and combustion sources, and the presence of the sulfate itself is not indicative of a  
344 particular source, however, the marine air mass trajectories and H/C and O/C ratios observed in these samples relative to those in  
345 samples with continentally-influenced air mass trajectories are strong evidence for a marine aerosol WSOM source.

346 Magnitude-weighted average H/C and O/C ratios for the Aged Marine (H/C = 1.57, O/C = 0.36, Table 1) group were slightly  
347 lower and higher, respectively, compared to those found for the Primary Marine (H/C = 1.66, O/C = 0.32, Table 1) group consistent  
348 with the Aged Marine samples having been processed in the atmosphere. Several studies have shown aerosol OM to increase in O  
349 content and decrease in H/C with photochemical degradation (e.g., Heald et al., 2010; Kroll et al., 2011; Sato et al., 2012). The  
350 Primary Marine and Aged Marine WSOM groups are distinguished from the continentally influenced groups by these relatively high  
351 H/C and low O/C magnitude weighted average values, indicative of a more aliphatic, less oxidized marine WSOM. A recent study of  
352 rainwater DOM similarly showed marine derived dissolved organic nitrogen compounds to have lower O/C ratios than continental

353 influenced dissolved organic nitrogen compounds (Altieri et al., 2012). Schmitt-Koplin et al. (2012) demonstrated that bubbles burst  
354 from surface water DOM are enriched in compounds with higher H/C and lower O/C ratios relative to that found in the surface water  
355 DOM. Aliphatic compounds with intermediate oxygen content appear to be the surface-active component within marine DOM that is  
356 emitted with sea spray aerosol, and their enrichment relative to the highly polar, more aliphatic WSOM signature typically found in  
357 continental and continentally-influenced aerosol WSOM are clear indicators of marine-derived aerosol WSOM. Our data further  
358 separates marine-derived aerosol WSOM into an N-rich peptide-like component that we propose represents a primary marine WSOM  
359 and a slightly more oxidized, S-rich organosulfur component that we propose represents aged marine WSOM.

360 **3.5 North American-Influenced Samples.** The North American-Influenced sample group was dominated by CHOS PCA loadings  
361 with higher O/C ratios than those for the Aged Marine group. The PCA loadings for this group show 134 and 36 of the 269 formulas  
362 to be CHOS and CHONS containing formulas, respectively. These S containing formulas have similar H/C range but a higher O/C  
363 range ( $1.3 < \text{H/C} < 2.0$ ;  $0.5 < \text{O/C} < 0.9$ ) than those for the Aged Marine group (Figure 6b and c). The majority (87 of 269) of the  
364 remaining formulas defining this group were CHO formulas plotting at H/C ratios between 1.0 and 1.6 and O/C ratios between 0.4 and  
365 0.75 (Figure 6c). The mean magnitude-weighted O/C ratio for these samples is 0.50, the highest of any of the sample groups, while the  
366 mean magnitude-weighted H/C ratio is 1.46, lower than the two marine groups but higher than the North African-Influenced sample  
367 group. Like the two marine groups, heteroatomic molecular formulas are important components to these 6 samples with CHOS and  
368 CHON formulas accounting for 26% and 14% of the spectral intensity, respectively, on average (Table 1).

369            Their high O/C ratios relative to the other sample groups suggests that these North American-influenced samples are  
370 characterized by a high degree of oxidation similar to the humic like substances (HULIS) described for many North American and  
371 European continental samples (e.g., Salma et al., 2010; Pavlovic and Hopke, 2012; Paglione et al., 2014) and reflects high  
372 contributions from sulfate, nitrate, and carboxylic acid functional groups. Highly oxygenated atmospheric HULIS has been attributed  
373 to SOA from various biogenic volatile precursors (e.g., Shapiro et al., 2009; Stone et al., 2009), fossil fuel and biomass combustion  
374 byproducts (e.g., Decesari et al., 2002; Stone et al., 2009; Salma et al., 2010; Pavlovic and Hopke, 2012), and the subsequent  
375 photochemical aging of these materials (e.g., Decesari et al., 2002; Pavlovic and Hopke, 2012). The North American-influenced  
376 samples (N Am 1-5) included in this group were those closest to the continent (Figure 1) where SOA formation and fossil  
377 fuel/biomass combustion emissions are highest, and we conclude that the importance of these high O/C CHO and CHOS compounds  
378 resulted from strong contributions from the North American continent to the WSOM in this group of samples.

379            The O/S ratios for the CHOS and CHONS formulas identified as important to these North American-influenced samples are  
380 consistent with those of organosulfate and nitrooxy organosulfate compounds ( $O/S > 4$ ) formed as discussed in the ‘Aged Marine’  
381 section. The major difference between the organosulfates in the North American-Influenced samples is the higher O/C ratio which  
382 likely relates to the organosulfate precursor compounds for these two sources. The O/C ratios for CHO formulas (which represent  
383 potential organosulfate precursors) in the North American-Influenced samples (Figure 6c) are considerably higher than those observed  
384 for the Aged and Mixed Source samples (Figure 6b and e). If these organosulfate compounds result from the acid-catalyzed reaction



385 of H<sub>2</sub>SO<sub>4</sub> with alcohol and carbonyl groups in these marine and North American-influenced CHO compounds of differing O/C ratios,  
386 the organosulfate products logically have differing O/C ratios. It thus appears that organosulfates from marine and continental  
387 combustion sources are molecularly distinct.

388 **3.5 North African-Influenced Samples.** The North African-Influenced group PCA loadings were dominated by contributions from  
389 CHO molecular formulas which represented 361 of the 408 molecular formulas defining the sample group. The North African-  
390 Influenced sample loadings were defined by having high O/C ratios ( $0.3 < O/C < 0.8$ ) relative to the marine groups and H/C ratios  
391 between 0.8 and 1.70 (Figure 6d). Average magnitude weighted abundances confirm that CHO formulas dominated the aerosol  
392 WSOM representing 76% of the spectral intensity (Table 1). This sample group also had the least aliphatic character as evidenced by  
393 having the lowest magnitude weighted H/C ratio (1.40) and highest magnitude weighted average  $AI_{mod}$  value (0.18, Table 1). Despite  
394 the high  $AI_{mod}$  value for the North African-Influenced samples, the WSOM compounds in these samples show little spectral  
395 contributions from formulas that could be considered black carbon, the highly condensed hydrocarbon byproduct of fossil fuel and  
396 biomass combustion. The areas of the van Krevelen diagram occupied by the molecular formulas characterizing the North African-  
397 Influenced samples are in the area where lignin molecules would plot (e.g., Sleighter and Hatcher, 2007). A study of dust deposited to  
398 a buoy in the northeast Atlantic off the coast of northwest Africa found lignin phenols to be a significant component of the dust OM  
399 further characterizing the lignin to have been highly altered and derived from non-woody angiosperms based on acid/aldehyde and

400 cinnamyl/vanillyl and syringyl/vanillyl ratios (Eglinton et al., 2002). The CHO compounds accounting for the molecular formulas in  
401 Figures 6d are also thus suggestive of a lignin source that has been highly altered via diagenesis in desert soils.

402 Desert dust contains OM that is highly processed within the soil and as a result has less aliphatic character. It also has less  
403 influence from anthropogenic N and S sources which explains the lesser contributions from heteroatom containing formulas for the  
404 North African-Influenced samples versus the North American-Influenced PCA group. Organosulfate formation is known to occur  
405 under acidic conditions such as those created by the emissions of nitrates and sulfates during fossil fuel combustion and was shown by  
406 Schmitt-Koplin et al. (2010) to be more efficient for compounds with higher H/C ratios. The lack of compounds with high H/C ratios  
407 further explains the relatively low contributions from CHOS compounds in these samples.

408 Compared to European and North American-influenced samples, aerosol OM influenced by Saharan dust is severely  
409 understudied, and considerably less is known about its detailed molecular composition. The data presented here demonstrate that  
410 samples with clear Saharan influence show a predominance of CHO aerosol WSOM compounds with less aliphatic character than  
411 typically found for aerosol WSOM influenced by the North American continent (e.g., Figure 6c and d; Wozniak et al., 2008) which  
412 experiences considerably more combustion influence known to both emit fossil fuel OM and stimulate secondary organic aerosol  
413 formation (e.g., de Gouw et al., 2008; Carlton et al., 2010). Fossil fuel combustion and secondary organic sources common to North  
414 American aerosol OM are comparatively minimal in North African source regions, and this is reflected in the differences in the North  
415 American-Influenced and North African-Influenced PCA group molecular characteristics. The defining molecular characteristics of

416 the North African-Influenced sample group are consistent with those of soil OM that has been highly degraded and is perhaps rich in  
417 aromatic compounds characteristic of oxidized soil humic material (Tan, 2003) and transported with Saharan dust as it is picked up  
418 with strong winds.

419 **3.6 Mixed Source Samples.** The remaining five aerosol samples which form the Mixed Source sample group showed molecular  
420 characteristics reflecting a mixture of marine and continental sources. The magnitude weighted O/C, H/C,  $AI_{mod}$ , and % contributions  
421 from CHO, CHON, CHOS, and CHONS formulas for the Mixed Source samples are all intermediate relative to the other sample  
422 groups (Table 1). The van Krevelen diagram for the PCA loadings for the Mixed Source samples (Figure 6e) are the most diverse in  
423 terms of elemental constituents, but CHO (51%), CHOS (20%), and CHOP (12%) formulas are the most abundant. The CHO formulas  
424 defining the Mixed Source sample have a higher O/C range (0.15-0.5) than the Aged Marine sample group (Figure 6b; O/C ~ 0.15-  
425 0.4) but do not extend to values as high as those defining the North American-influenced sample group (Figure 6c; O/C ~ 0.5-0.9).  
426 The CHOS formulas defining the Mixed Source sample show O/C ratios similar to both the Aged Marine and North American-  
427 influenced sample groups.

428 The diverse PCA loadings and intermediate magnitude weighted average molecular characteristics suggest that these samples  
429 do not have a singular dominant source to their aerosol WSOM but that they are influenced by both marine and continental sources.  
430 The Mixed Source samples consisted of four samples with marine air mass trajectories and one sample with a North American air  
431 mass trajectory, and of course, all five samples were collected over the marine environment. The lack of a dominant WSOM source to

432 these samples and the location of their collection over the middle of the ocean suggests a weak marine source to these samples and  
433 demonstrates the long range (in distance and time) transport of continentally derived WSOM.

#### 434 **4 Summary and Implications**

435 The analytical approach and transatlantic coverage in this study allowed the definition and confirmation of several source-  
436 specific aerosol WSOM characteristics that add to the body of literature obtained in marine aerosol OM studies using other techniques  
437 and/or sampling strategies. While, samples from similar air mass trajectories frequently showed similar molecular characteristics, air  
438 mass trajectories were not sufficient in describing the provenances of aerosol WSOM. PCA enabled the distinction of three types of  
439 marine aerosols defined by the degree to which they have been processed post-emission and their dilution with continental aerosol  
440 WSOM (Primary Marine, Aged Marine, and Mixed Source) and identified two samples with North American back trajectories as  
441 having primary marine sourced aerosol WSOM. These differences in air mass trajectory and PCA defined WSOM source illustrate the  
442 need to utilize multiple lines of evidence for determining aerosol OM provenance.

443 The PCA and FTICR MS results demonstrate that for samples collected over the ocean, aerosol WSOM having marine sources  
444 has lower O/C and higher H/C ratios than continentally-influenced WSOM, properties that derive from the characteristics of sea  
445 surface DOM and the bubble bursting process that emits that DOM as marine aerosols. The bubble bursting process known to produce  
446 sea spray aerosols has been shown in laboratory experiments to emit the more aliphatic (higher H/C) and less oxygenated (lower O/C)  
447 components within sea surface DOM (Schmitt-Koplin et al., 2012). The marine derived aerosol WSOM was further differentiated in

448 this study to describe samples that have been processed to different degrees in the atmosphere. The Primary Marine sample group  
449 showed molecular characteristics indicative of a marine biological component as demonstrated by the peptide and phospholipid-like  
450 CHON and CHONP containing molecular formulas present in the WSOM. The Aged Marine sample group is indicative of aerosol  
451 WSOM with a marine source that has been processed in the atmosphere as evidenced by the aliphatic (relative to the North American-  
452 Influenced samples) organosulfates that characterize these samples, and the Mixed Source sample group appears to show samples with  
453 WSOM from a mixture of aged, primary, and continental sources.

454         Among the continentally-influenced samples, the PCA clearly demonstrates the North American-Influenced samples to have  
455 higher H/C and O/C ratios and heteroatomic (N, S) content than the North African-Influenced samples. The higher N and S content  
456 and O/C ratios are likely due to the North American-influenced samples being oxidized in the atmosphere in the presence of  
457 combustion-emitted nitrates and sulfates in this more industrialized region. The lower H/C ratios observed for the North African-  
458 Influenced samples may be more of an indication of a lack of high H/C ratio compounds emitted from desert environments than a lack  
459 of low H/C ratio compounds emitted from North America and Europe. Combustion processes are well known to emit condensed  
460 aromatic compounds including black carbon, and tens to hundreds of condensed aromatic formulas were found in each North  
461 American-influenced sample (data not shown). It is likely, however, that the aliphatic, highly oxygenated compounds in the North  
462 American-Influenced samples dominated the signal in the electrospray source keeping these more condensed compounds at low  
463 abundance and therefore not considered in the PCA. Aerosols from the North African region, highly influenced by the Saharan desert

464 as evidenced by their orange coloration, carry OM from desert soils that have been subjected to degradation processes resulting in the  
465 loss of the aliphatic components of biomass. As a result, the lower H/C ratios in these samples are observed.

466         Though direct study of the samples' physical properties were not conducted, the defining molecular characteristics described  
467 here suggest some important source-specific environmental implications. UV and visible light absorption result from electron  
468 transitions, mainly  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions associated with C=C, C=O, C-O and aromatic rings (Andreae and Gelencser, 2006),  
469 and the higher average H/C ratios and lower average  $AI_{\text{mod}}$  values identified for the two marine aerosol WSOM sample groups suggest  
470 them to have a lesser radiative impact on a per carbon basis than aerosol WSOM from continental environments. This distinction  
471 between natural marine and continental (natural or anthropogenic) aerosol WSOM is an important factor to be considered in climate  
472 models attributing the direct effect on climate to various sources. Aerosol hygroscopicity has been related to cloud condensation  
473 nuclei formation with increased hygroscopicity leading to a higher indirect effect on climate via cloud formation. The higher O/C  
474 content observed in the continental aerosol WSOM similarly suggests continental aerosols to have a higher impact on hygroscopicity,  
475 which has been linked to oxygen content and climate, on a per carbon basis. The aerosol WSOM characteristics described here for this  
476 transatlantic transect of aerosol samples, therefore, provides important potential source-specific differences in climate relevant  
477 properties. Future work must link molecular characteristics and physical properties on aerosols collected at the same time to confirm  
478 these indications.

479 Finally, ESI FTICR MS, as demonstrated in this study, is a powerful technique providing extensive aerosol WSOM molecular  
480 characterization, but it does have a specific analytical window, and a great many compounds present in aerosol WSOM elude  
481 detection using this technique. For example, carbohydrates have been identified as a major constituent of primary marine aerosol OM  
482 but do not ionize well in the ESI source. As such, the current work is not comprehensive and should be viewed (as should all studies  
483 of OM characterization) in the context of its methodological approach. With that in mind, the WSOM FTICR MS data presented here  
484 make a significant contribution to the characterization of aerosol OM in remote marine aerosols influenced by continental sources to  
485 varying degrees. Future work combining online and offline OM characterization techniques will enable the comprehensive  
486 characterization needed to fully understand the link between OM sources and transformations, molecular characteristics, and impacts  
487 in the environment.

488

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496

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705

706 **Table 1.** PCA group magnitude weighted average elemental formula characteristics and elemental formula percent compositions.

707

<b>PCA Group</b>	<b>O/C</b>	<b>H/C</b>	<b>AI<sub>mod</sub></b>	<b>CHO</b>	<b>CHON</b>	<b>CHOS</b>	<b>CHONS</b>	<b>CHOP</b>	<b>CHONP</b>	<b>CHOSP</b>
Primary Marine	0.32	1.66	0.09	30%	54%	6.9%	1.9%	2.5%	5.4%	0%
Aged Marine	0.36	1.57	0.14	43%	5.2%	38%	3.6%	6.4%	3.2%	0.5%
North American-Influenced	0.50	1.46	0.14	50%	14%	26%	4.6%	3.6%	0.7%	0.1%
North African-Influenced	0.45	1.40	0.18	76%	9.3%	8.3%	0.6%	4.8%	0.8%	0.08%
Mixed Source	0.37	1.52	0.15	54%	6.3%	24%	2.7%	8.0%	3.2%	1.8%

708 **Figure Captions**

709 **Figure 1.** Aerosol particulate collection locations during the 2011 US GEOTRACES cruise. Arrows pointing to a dot were collected  
710 on station. Arrows pointing to the line were collected in transit. Samples labeled as “N Am”, and “N Afr” showed a majority of 5 day  
711 ensemble air mass back trajectories extending back to the North American and African continents. Samples labeled “Mar” showed 5  
712 day ensemble air mass back trajectories that had minimal continental influence.

713 **Figure 2.** Representative ensemble air mass back trajectories for samples influenced by a) North American, b) North African sources,  
714 and c) Marine (minimal recent continental influence).

715 **Figure 3.** van Krevelen diagrams for aerosol WSOM molecular formulas assigned to greater than a) 75% (at least 18 samples) and b)  
716 90% (at least 22 samples) of the 24 aerosol samples. Data points are color coded for molecular formula elemental composition as  
717 described in the figure key.

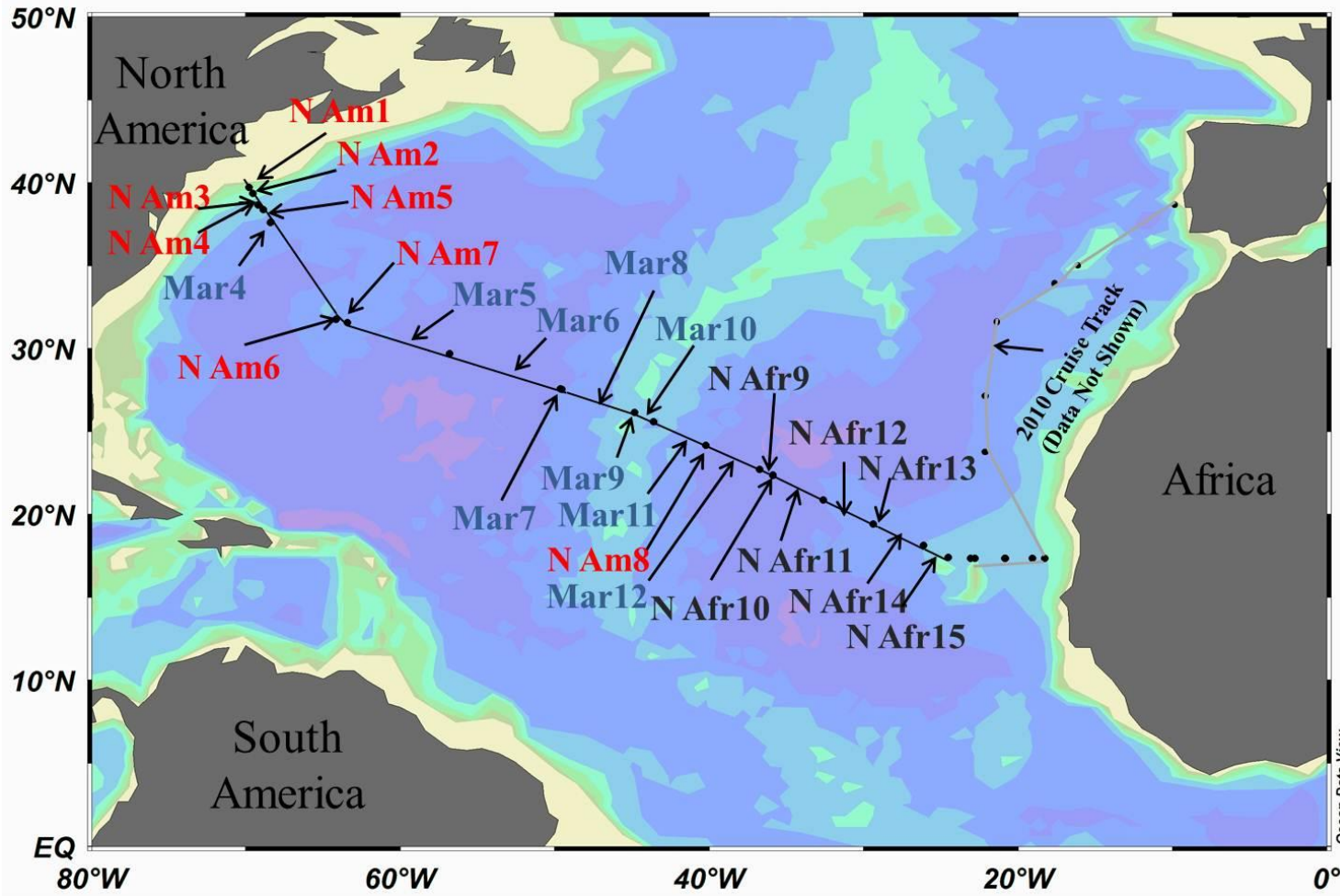
718 **Figure 4.** van Krevelen diagram for the 2408 aerosol WSOM molecular formula input variables to the Principal Component Analysis.  
719 Data points are color coded for molecular formula elemental composition as described in the figure key.

720 **Figure 5.** Three dimensional plots showing the a) sample scores and b) variable (molecular formulas) loadings for the first three  
721 principal components accounting for 51% of the variance in the dataset. Sample data points with similar PC scores are color coded for  
722 classification of samples into sample groups with similar molecular characteristics. The loadings assumed to be important components  
723 of each group are similarly color coded.

724 **Figure 6.** van Krevelen diagrams corresponding to the WSOM loadings for the sample groups assigned by the PCA and classified as  
725 a) Primary Marine, b) Aged Marine, c) North American-Influenced, d) North African-influenced, and e) Mixed Source samples. Data  
726 points are color coded for molecular formula elemental composition as described in the figure key in the top right panel.

727 **Figure 7.** Kendrick mass defect series (CH<sub>2</sub>) for a) CHON formulas containing 1-4 nitrogen atoms identified for samples N Am 6 and  
728 N Am 7 which make up the Primary Marine sample group. The molecular structures represent potential amino acid containing isomer  
729 compounds corresponding to several identified molecular formulas. The red portions of the molecular structures represent the amino  
730 acid portions of the compounds.  
731

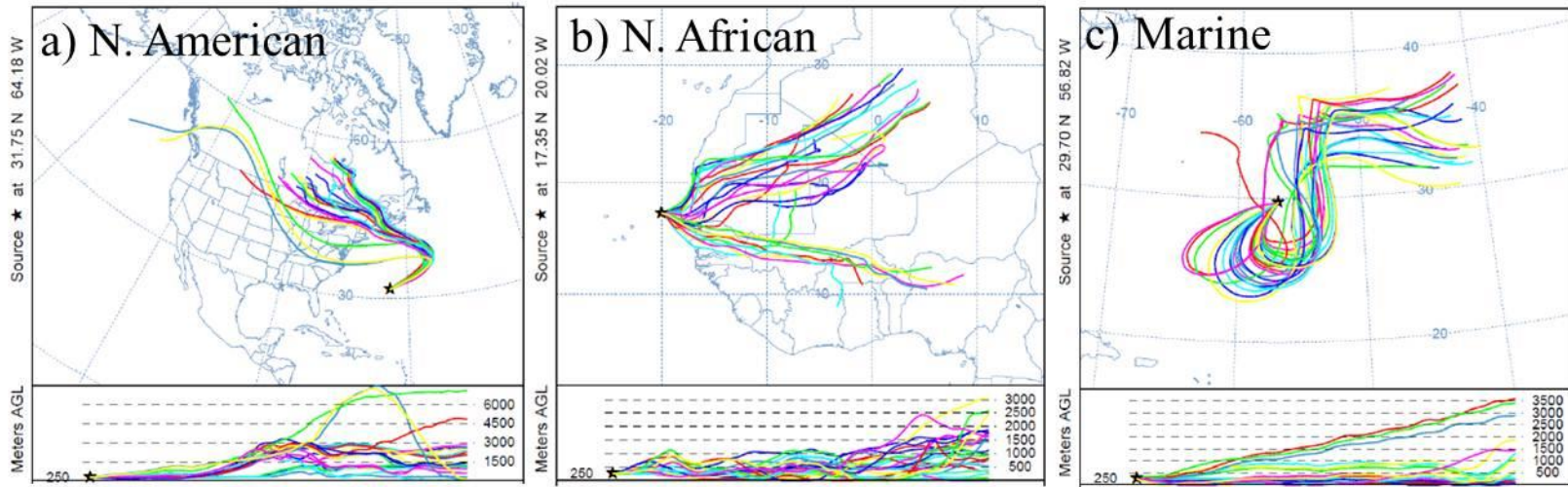
732 Figure 1.



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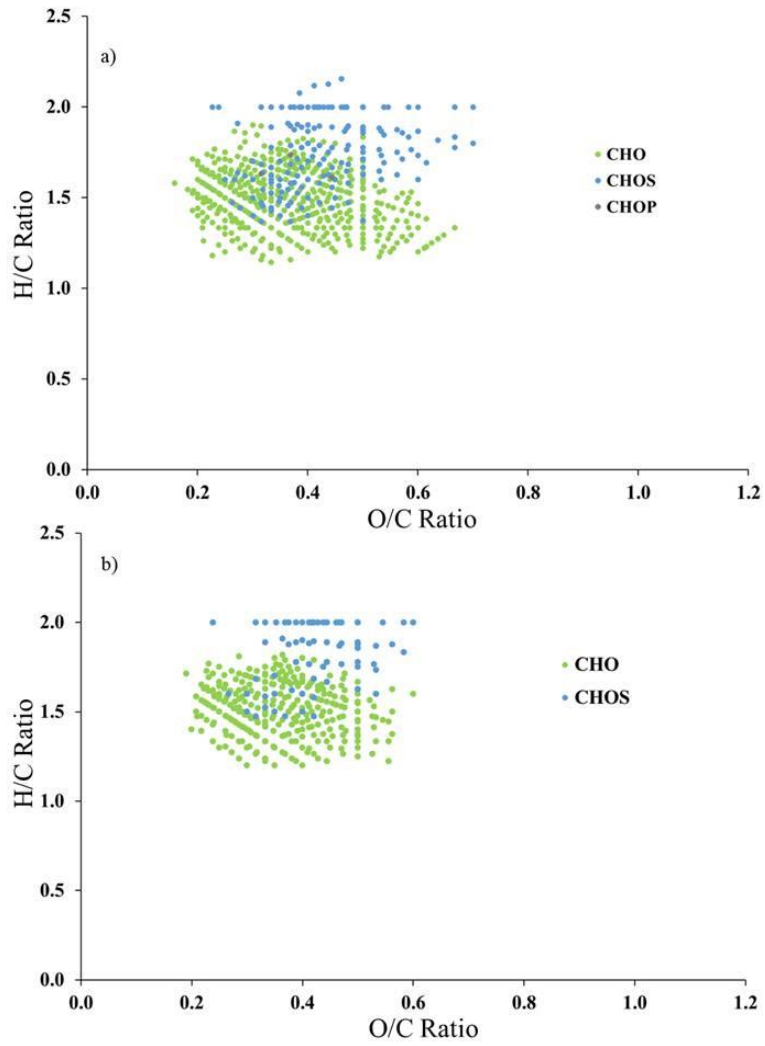
735 Figure 2.



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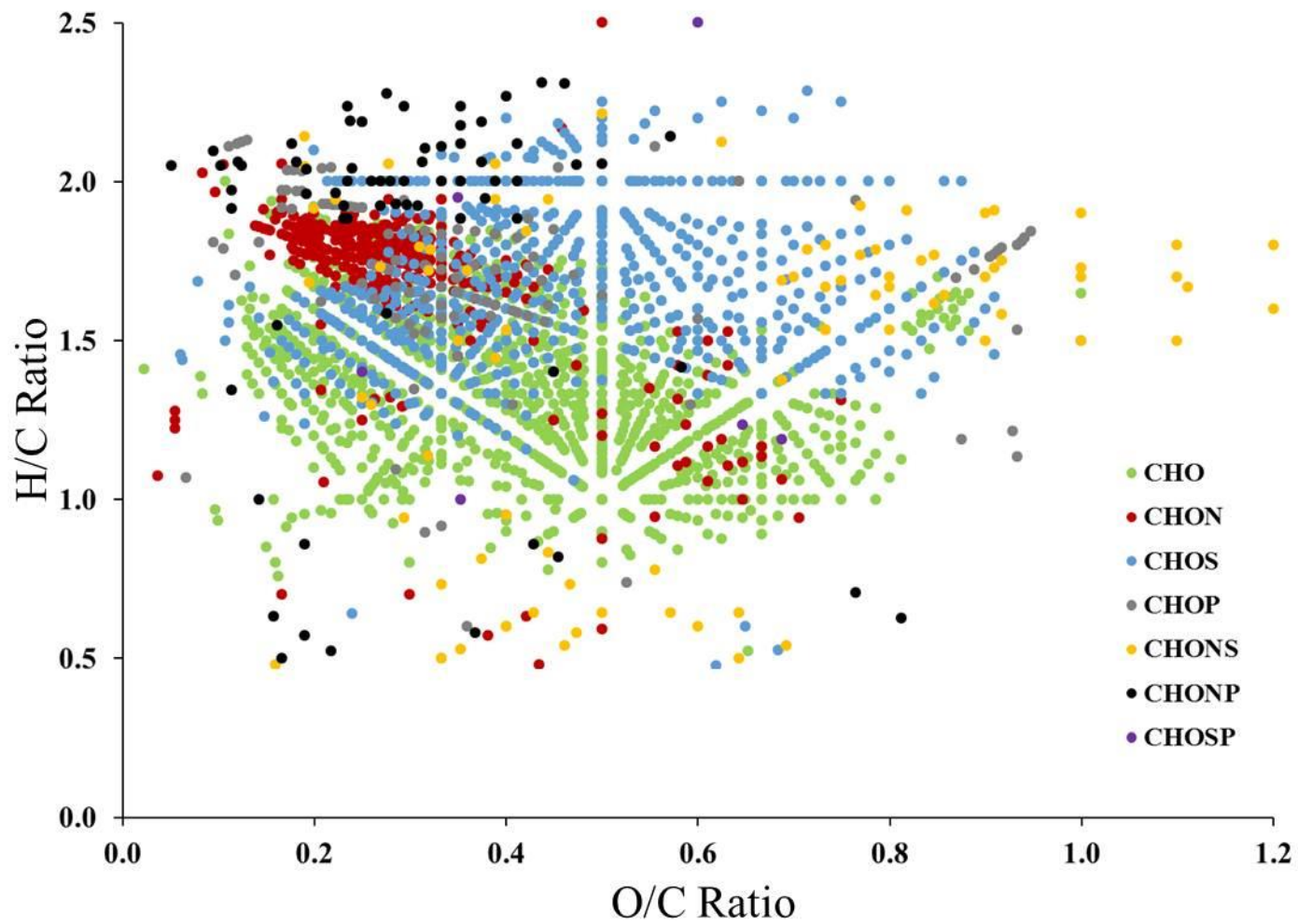
738 Figure 3.



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741 Figure 4.

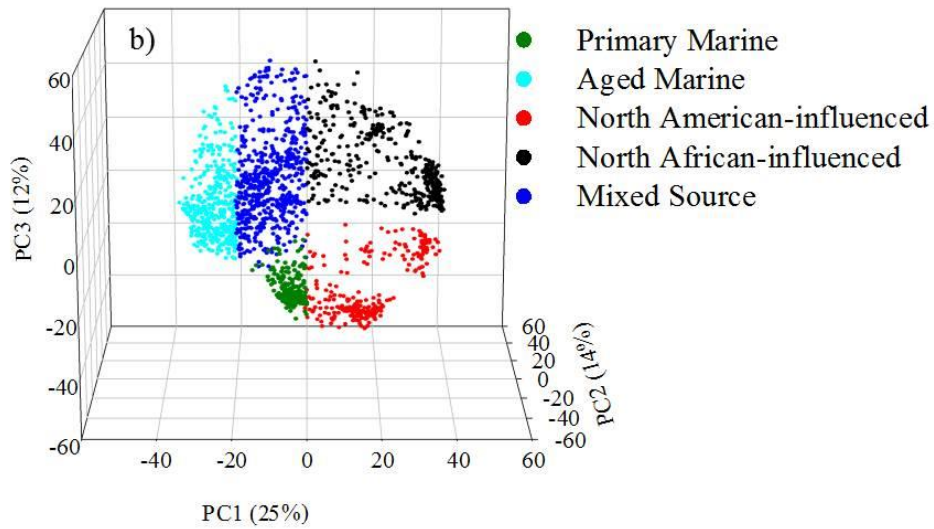
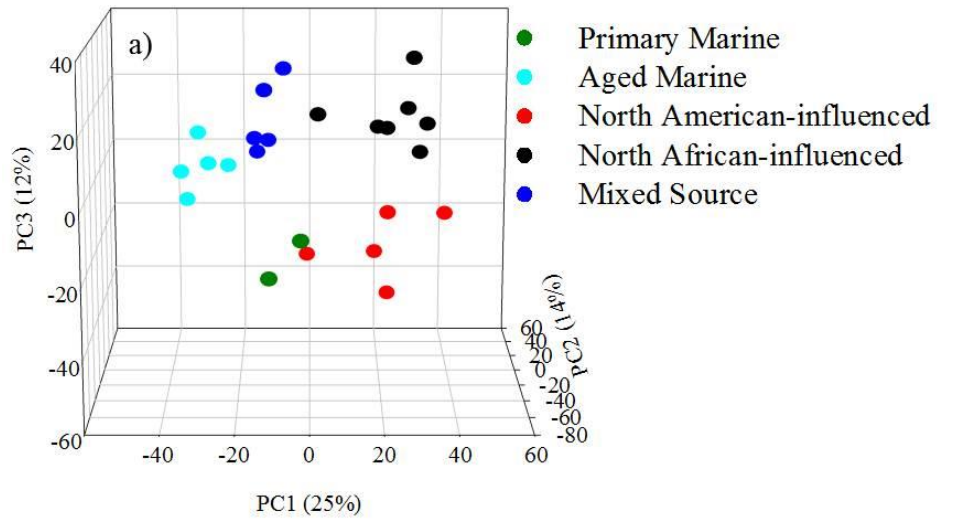


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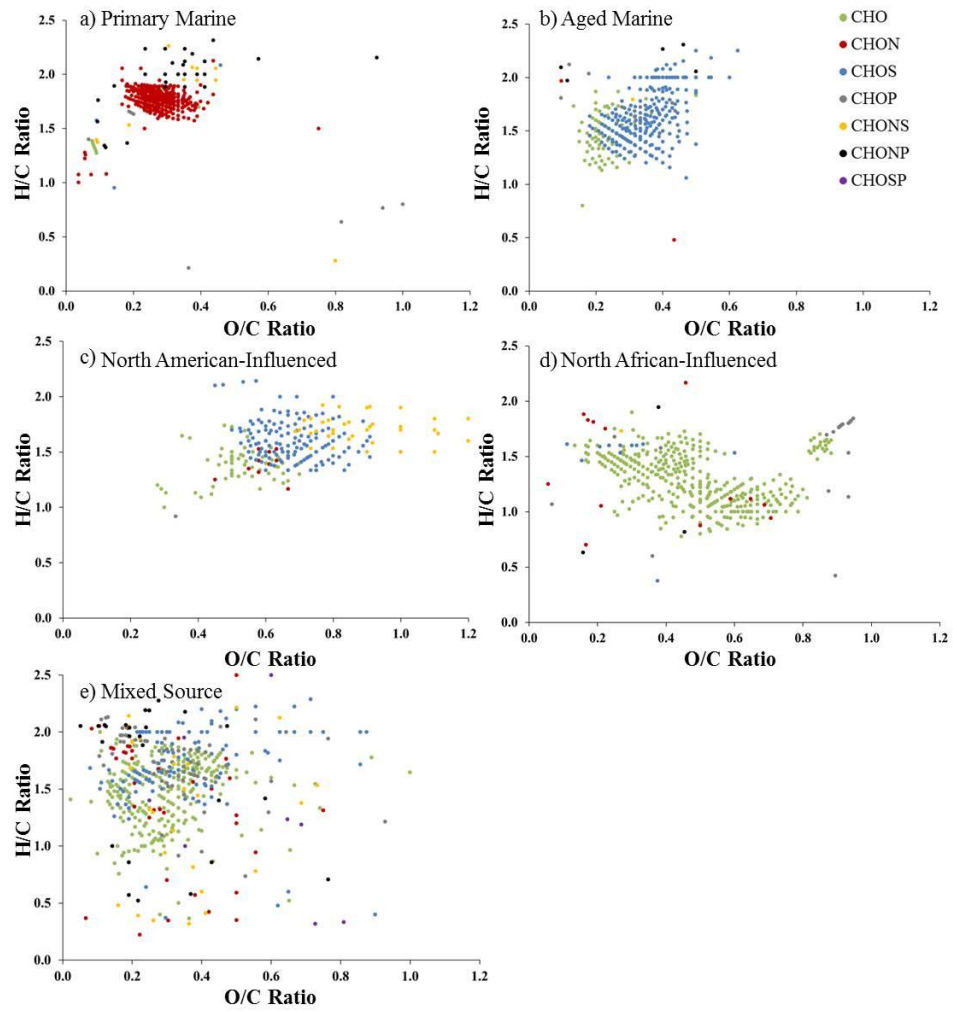


744 Figure 5.



745

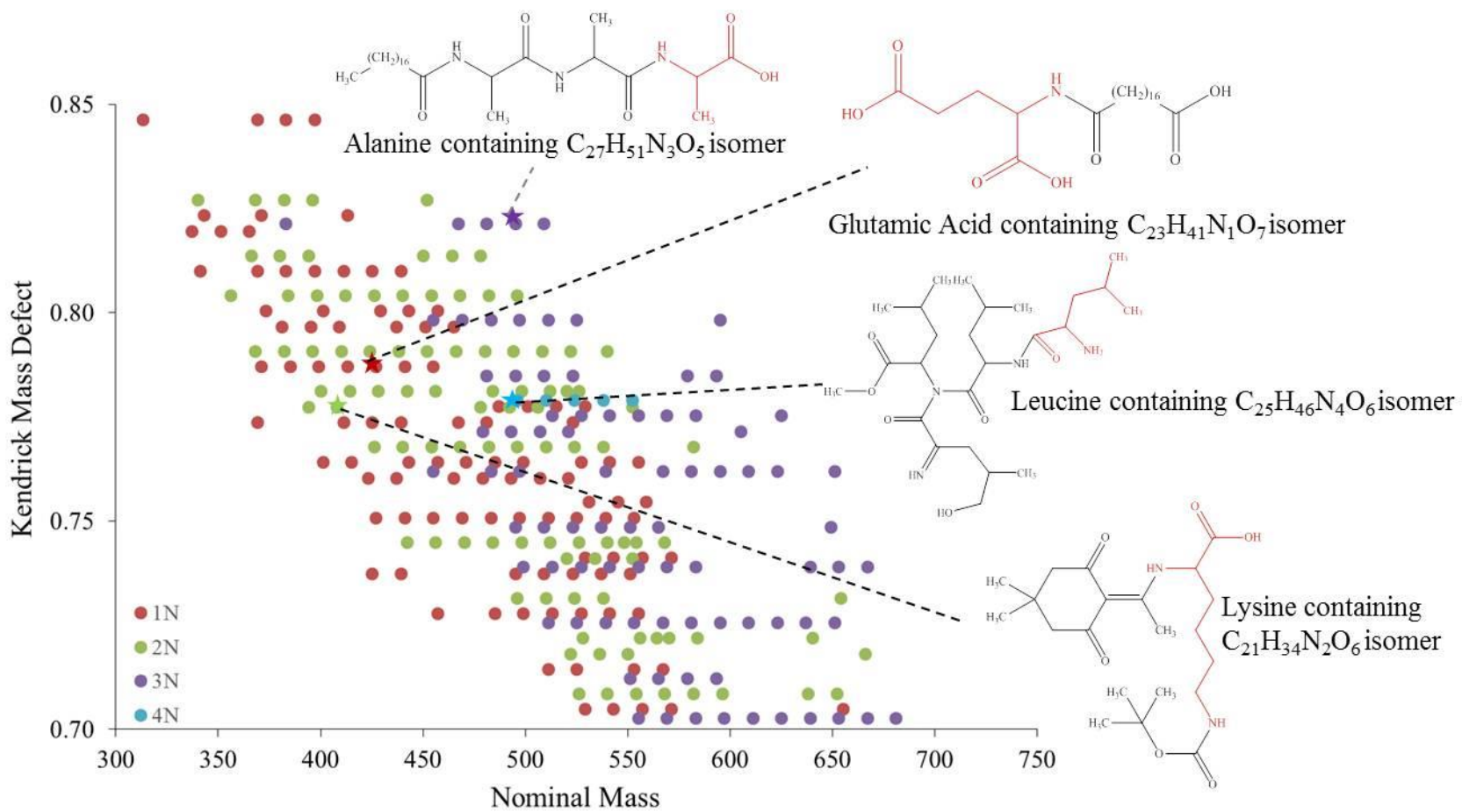
746 Figure 6.



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749 Figure 7.



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