

1 **Size resolved characterization of the polysaccharidic and**
2 **proteinaceous components of Sea Spray Aerosol**

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20 **Keywords.**

21 Sea surface microlayer, transparent exopolymer material, protein-containing gel particles, sea
22 spray aerosol, MOUDI

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26 ABSTRACT

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Dissolved organic polymers released by phytoplankton and bacteria abiologically self-assemble in surface ocean waters into nano- to micro-sized gels containing polysaccharides, proteins, lipids and other components. These gels concentrate in the sea surface microlayer (SML), where they can potentially contribute to sea spray aerosol (SSA). Sea spray is a major source of atmospheric aerosol mass over much of the earth's surface, and knowledge of its properties (including the amount and nature of the organic content), size distributions and fluxes are fundamental for determining its role in atmospheric chemistry and climate. Using a cascade impactor, we collected size-fractionated aerosol particles from ambient air and from freshly generated Sea Sweep SSA in the western North Atlantic Ocean together with biological and chemical characterization of subsurface and SML waters. Spectrophotometric methods were applied to quantify the polysaccharide-containing transparent exopolymer (TEP) and protein-containing Coomassie stainable material (CSM) in these particles and waters. This study demonstrates that both TEP and CSM in surface ocean waters are aerosolized with sea spray with the greatest total TEP associated with particles < 180 nm in diameter and > 5000 nm. The higher concentrations of TEP and CSM in particles > 5000 nm most likely reflects collection of microorganism cells and/or fragments. The greater concentration of CSM in larger size particles may also reflect greater stability of proteinaceous gels compared to polysaccharide-rich gels in surface waters and the SML. Both TEP and CSM were measured in the ambient marine air sample with concentrations of $2.1 \pm 0.16 \mu\text{g Xanthan Gum equivalents (XG eq.) m}^{-3}$ and $14 \pm 1.0 \mu\text{g bovine serum albumin equivalents (BSA eq.) m}^{-3}$. TEP in Sea Sweep SSA averaged $4.7 \pm 3.1 \mu\text{g XG eq. m}^{-3}$ and CSM $8.6 \pm 7.3 \mu\text{g BSA eq. m}^{-3}$. This work shows the transport of marine biogenic material across the air-sea interface through primary particle emission and the first demonstration of particle size discriminated TEP and CSM characterization of SSA and ambient aerosol under field conditions.

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1. Introduction

75 A direct link between marine aerosol particles and surface water composition, which in turn is
76 affected by the metabolic activities of planktonic microorganisms, has been postulated for over
77 half a century (e.g. Zobell and Mathews, 1936; Stevenson and Collier, 1962; Blanchard, 1964;
78 Wallace et al., 1972; Hoffman and Duce, 1974; Middlebrook et al., 1998; O'Dowd et al., 2004;
79 Kuznetsova et al., 2005; Leck and Bigg, 2005a, b; Ceburnis et al., 2008; Facchini et al., 2008;
80 Hawkins and Russell, 2010; Orellana et al., 2011; Ovadnevaite et al., 2011; Schmitt-Kopplin et
81 al., 2012; Ovadnevaite et al., 2014). The sea-surface microlayer (SML), tens to hundreds of μm
82 thick and comprising the ubiquitous uppermost layer, links the hydrosphere with the atmosphere,
83 and is central to a range of global biogeochemical and climate-related processes (Lewis and
84 Schwartz, 2004; Cincinelli et al., 2005; Cunliffe et al., 2012; de Leeuw et al., 2011; Gantt et al.,
85 2011; Schill et al., 2015; Quinn et al., 2015; Burrows et al., 2016; Laskin et al., 2016). Like bulk
86 seawater, the SML contains a complex mixture of inorganic particles, particulate organic matter
87 in the form of microorganisms, debris (including bacterial cell walls and fragments of
88 phytoplankton), as well as semitransparent organic particles and dissolved organic material
89 (DOM) of phytoplankton and bacterial origin, some of which may adsorb onto inorganic
90 particles. Recently, we have shown that phytoplankton cells and exudates can nucleate ice under
91 tropospheric conditions with potential major implications for cloud formation, precipitation, the
92 hydrological cycle, and climate (Alpert et al., 2011 a and b; Knopf et al., 2011, Wilson et al.,
93 2015, Ladino et al., 2016).

94 Compared with bulk waters, the physical, chemical, and biological processes which lead to
95 the spontaneous formation of suspended particles, "highly hydrated loose gels of tangled
96 macromolecules and colloids" (Sieburth, 1983), are more intense in the SML because of its
97 enrichment in surface-active polysaccharides (Wurl and Holmes, 2008). Polysaccharides are the
98 dominant gel component, accounting for ~30% of the DOM in the SML (Sieburth, 1983), and
99 those $> 0.4 \mu\text{m}$ in radius are referred to as transparent exopolymer material (TEP) (e.g. Alldredge
100 et al., 1993). Proteinaceous materials, which make up to ~16% of the SML DOM (Sieburth,
101 1983), can also form gels or can be mixed with TEP and smaller polysaccharide-rich particles
102 (Kuznetsova and Lee, 2001; Matrai et al., 2008; Cisternas-Novoa et al., 2015). Semi-quantitative
103 methods of measuring the mass of particular gel types are available, but due to methodological
104 limitations, gel size and state of mixing with other organic and inorganic materials in particles
105 have not been well quantified, nor is gel formation well understood. This is partly because the
106 most abundant gels are sub-micrometer in size (colloidal nanogels), although super-micrometer
107 size gels (colloidal microgels) can also form (Passow, 2002; Verdugo et al., 2004; Verdugo et al.,
108 2008; Verdugo and Sanchi, 2010; Verdugo, 2012). Current methods of measuring polysaccharide
109 and proteinaceous materials in ocean waters involve staining with dyes that react with
110 components of these materials, followed by 1) light microscopy or flow cytometry-based
111 counting and measurement of stained particles, or 2) spectrophotometric determination of the
112 total content of stainable material (TEP or Coomassie stainable material, for which we propose
113 the term CSM to distinguish it from Coomassie stainable particles, which may or may not consist
114 entirely of CSM) obtained by filtration of a known volume of liquid. Neither method, however,
115 allows determination of the TEP or CSM content of individual particles in different size ranges.
116 Nor can they tell anything about mixtures of polysaccharides with other macromolecules,
117 including proteins and lipids, which may influence gel microstructure, formation, mixing, and

118 size. Furthermore, field measurements often only calculate enrichment factors, thus avoiding the
119 technical difficulties inherent to generating standard curves.

120 Overall productivity of surface waters, as well as the composition of the phytoplankton
121 community, would be expected to influence abundances of polysaccharide-rich and protein-rich
122 particles in the SML, with eutrophic waters differing from oligotrophic waters (e.g. Matrai et al.,
123 2008; Gao et al., 2012). Productivity may also affect aerosol composition (O'Dowd et al., 2004).
124 Although both types of particles form in ocean waters, they appear to have distinct
125 characteristics and behaviors. Not only can the relative abundances vary with the dominant
126 bloom species, but they can change during different phases of blooms and as the composition of
127 the phytoplankton changes seasonally (e.g. Grossart et al., 1997, Berman and Viner-Mozzini,
128 2001; Cisternas-Novoa et al., 2015). These differences may translate into differences in the
129 production flux of total SSA, the amount of organic material, and the chemical characteristics of
130 the aerosolized organic component as shown by Alpert et al. (2015) and Cochran et al. (2016).
131 We report on the links between exudate production in the SML, the size of SSA, and their
132 polysaccharide and protein content which we are able to follow by modifying existing
133 spectrophotometric methods for use with SSA which had been size fractionated by means of a 13
134 stage Multi Orifice Uniform Deposition Impactor (MOUDI Model 122R, MSP Corporation,
135 Minneapolis, MN) Cascade impactor. Participation in the Western Atlantic Climate Study II
136 (WACS II) provided the opportunity to test our approach, allowing us to collect SSA directly
137 emitted from the ocean without interference of secondary processes such as the condensation of
138 organic material from the gas phase. This was achieved by the use of an in situ particle
139 generator, the Sea Sweep (Bates et al., 2012). In addition, we collected ambient particles in the
140 same general ocean sampling area, but which briefly passed over Newfoundland and the
141 biologically productive waters of Georges Banks and may have been affected by secondary
142 processes during atmospheric transport.

143 The driving force behind this study was the need to better understand the chemical diversity
144 of sea surface microlayers and associated SSA, which serve as the natural background marine
145 source of atmospheric organic aerosols and are not well understood (e.g. Andreae, 2009; Ault et
146 al., 2013, Frossard et al., 2014; Burrows et al., 2014). Specifically, size resolved characterization
147 of aerosolized particles will allow us to better quantify the relative contribution of marine
148 biologically derived organics to the total SSA mass. As far as we are aware, this is the first
149 demonstration of aerosol particle size discriminated characterization of TEP and CSM for SSA
150 and ambient aerosol under field conditions.

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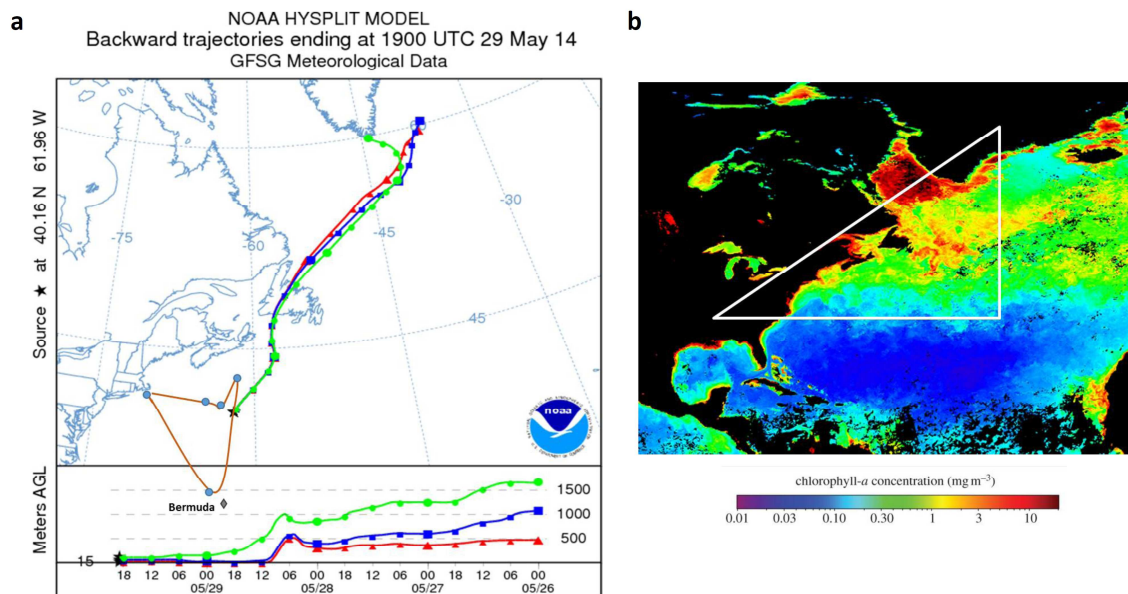
152 **2. Materials and methods**

153 *2.1 Sampling Stations*

154 Subsurface water, SML samples, freshly emitted SSA and ambient aerosol were collected
155 off the R/V Knorr during the WACS II cruise in May 2014, which sampled both northern,
156 colder, moderately productive waters of the western North Atlantic and the warmer waters of the
157 Sargasso Sea, a region of typically low productivity (Table 1 and Fig. 1). Station numbers 1, 2, 3,
158 4, and 5 were officially designated sampling locations. A location which we sampled on the day
159 after the ship departed Station (Sta.) 1 was designated "1.1", and ambient air was sampled at
160 "2/3", during transit between Stas. 2 and 3. Fluorometric measurements of maximum

161 photosynthetic efficiency, a surrogate for potential primary productivity, were highest at northern
 162 stations (Stas. 1, 1.1, and 2) where the phytoplankton community was dominated by
 163 coccolithophores with dinoflagellates and green algae as lesser components. Of the stations we
 164 sampled, the lowest biological activity was found at Sta. 4, just west of Bermuda, where
 165 picocyanobacteria and small green algae predominated.

166 To assess the source of the ambient air sampled, 5 day back trajectories at 30, 50, and 100 m
 167 (approximate sampling height above sea level) were calculated from Sta. 2/3 using the Hybrid
 168 Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2015;
 169 Rolph, 2015) (Fig.1). The 5 day back trajectories extend up to waters off southern Greenland at
 170 ~63°N latitude, and indicate that the air mass ultimately sampled at Sta. 2/3 stayed in the marine
 171 boundary layer over open ocean western North Atlantic waters for several days, rapidly crossed
 172 over Newfoundland and had been over open ocean waters again for the 1.5 days before
 173 collecting the aerosol particles. Wide Field-of-view Sensor (SeaWiFS) (NASA; 25 May 2014)
 174 images covering the backward trajectories region during the same period show ocean water Chl *a*
 175 concentrations in the moderate to productive range varying along the trajectory from at least 3
 176 $\mu\text{g/L}$ off Greenland to 0.5 $\mu\text{g/L}$ in waters off southwest of Newfoundland. Together these data
 177 suggest the potential for long distance transport of marine particles impacted by biological
 178 activity carried aloft by winds passing over ocean waters.



199 **Fig. 1.** Sampling locations during WACS II campaign, backward trajectories, and chlorophyll
 200 *a* concentrations. (a) WACS II cruise track (brown line) with location of sampled stations.
 201 The HYSPLIT model air mass regime for the ambient air collection period is also shown, as
 202 calculated from 5-day back trajectories from Sta. 2/3 (indicated by the star at altitudes of 30,
 203 50, and 100 m above sea level). (b) SeaWiFS (NASA; 25 May 2014) image at 9 km over the
 204 back trajectories region show ocean water Chl *a* concentrations in the moderate to productive
 205 range varying along the trajectory from 0.5 to at least 3 $\mu\text{g/L}$ south off Greenland.
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207 *2.2 Collection and shipboard processing of water and SML samples*

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209 Subsurface water, either from the ship's uncontaminated sampling intake at 5 m water depth
 210 or from a container lowered over the side of the ship to a depth of 0.5 m, was collected into acid
 211 washed 250 and 500 ml collapsible LDPE cubitainers (Thermo Fisher Scientific, Inc.). Aliquots
 212 for the various analyses were removed before the remaining water was preserved with 10 µl of
 213 50% w/v ZnCl₂.

214 Sea state dictated the modes of sample collection and sometimes restricted the use of the
 215 rotating drum for SML sampling. Even direct contact with the ocean surface was limited at some
 216 stations, further complicating collection of the SML. Consequently, complete sample sets are not
 217 available for all stations.

218 Sea state permitting, SML samples were collected from the hydrophilic Teflon film coating of
 219 a rotating drum sampler mounted on the 'Interface II' battery operated remote-controlled
 220 catamaran (Wilson et al., 2015) modified from Harvey (1966) and Knulst et al. (2003). Due to
 221 the sea state during the WACS II campaign, the Interface II was tethered to the CTD arm of the
 222 R/V Knorr on the starboard side of the ship during microlayer sampling. When the drum sampler
 223 was brought back onboard, accumulated microlayer water was transferred into 250 ml
 224 cubitainers. Before and after sampling at each location, subsurface seawater from the ship's
 225 uncontaminated supply was flushed through the catamaran sampling system to clear any
 226 previously collected SML. Alternately, SML was collected on shipboard by the glass plate
 227 dipping method after Harvey and Burzell (1972), from a 250 gal tank filled with sea water from
 228 the ship's intake line, and then allowed to stand for an hour to establish a microlayer. It should be
 229 noted that the rotating drum sampler and the glass dipping method probe different thicknesses of
 230 the SML (e.g. Agogue et al., 2004; Cunliffe et al., 2011), thus making comparison difficult.

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232 **Table 1.** Station locations, fluorometric Chl *a* values from underway sampling of surface waters
 233 (generally 2-5 m below ocean surface), and relative non-chlorophyll *a* light absorbing accessory
 234 pigment concentrations. Seawater samples for accessory pigments were collected within the
 235 upper mixed layer between 5 and 20 meters depth at the same locations as other data for stations
 236 1, 1.1, 2, and 3, but were collected 71 km to the northwest of station 4, and 43 km to the
 237 southeast of station 5, both within a few hours. n = samples taken.

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Station	Latitude (N)	Longitude (W)	Chl <i>a</i> (µg /L ± 1 sd)	Accessory Pigments (relative to Chl <i>a</i>)
1	40.38192	63.15497	0.331±0.084 (n=5)	Fuco > Zea > Hex-fuco
1.1	40.41558	62.33802	0.275±0.154 (n=8)	Zea > Fuco > Hex-fuco
2	42.48608	61.56345	2.219±0.226 (n=4)	Peri > Hex-fuco > Zea
3	40.16405	61.95833	0.429±0.207 (n=4)	Fuco > Hex-fuco > Zea
4	33.26817	62.90572	0.100±0.069 (n=4)	Zea > Hex-fuco > But-fuco
5	40.62100	70.40621	0.675 (n=1)	Hex-fuco > Fuco = Zea

247 Abbreviations: Fuco = fucoxanthin; Zea = zeaxanthin; Hex-fuco = 19'-Hexanoyloxyfucoxanthin;
 248 But-fuco = 19'-Butanoyloxyfucoxanthin; Peri = peridinin.

249 Accessory pigment determinations and ratios to Chl *a* ratios allow for discrimination between
250 phytoplankton classes (Mackey et al., 1996). Accessory pigment analyses were done on 0.75 to
251 2.2 L of seawater collected for high-performance liquid chromatography (HPLC) analyses from
252 Niskin bottles or the ship's underway line and filtered through 25 mm Whatman® Glass
253 microfiber filters, Grade GF/F filters at vacuum pressure of 150 mm Hg. Filters were
254 subsequently folded in half, wrapped in aluminum foil, and stored in a liquid nitrogen dewar
255 until shipped to the Goddard Space Flight Center HPLC laboratory (Greenbelt, MD) where the
256 samples were extracted, separated, and quantified according to Van Heukelem and Thomas
257 (2001), further described in Claustre et al. (2004).

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259 *2.3 Analysis of seawater and SML samples*

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261 Subsurface and microlayer water samples were sampled for quantification of TEP, CSM,
262 dissolved organic carbon (DOC), particulate organic carbon (POC), particulate organic nitrogen
263 (PON), and numbers of bacteria and algal cells. Duplicate 20 mL seawater samples were
264 preserved either with Lugol's iodine (Thronsen, 1978) or neutralized sodium borate buffered
265 formaldehyde solution (3% final concentration) for enumeration of bacteria and phytoplankton.
266 Bacterial and phytoplankton abundances were assessed using epifluorescence microscopy after
267 staining with Acridine Orange (after Hobbie et al., 1977; Watson et al., 1977). Counting
268 precision was better than 5%. Phytoplankton were identified using light microscopy, enumerated
269 and classified into broad taxonomic algal groups. Recorded volumes of seawater were passed
270 through precombusted and preweighed GFF filters (nominal pore size 0.7 µm) for POC and PON
271 analyses. Filters were kept frozen until analyzed. For DOC analyses, 40 mL samples of the
272 filtered seawater were retained in precombusted glass vials and acidified to pH 1 via dropwise
273 addition of concentrated HCl. Vials were then sealed with Teflon lined caps and stored at 4 °C
274 until analysis. Acid cleaned glassware and filtration apparatus and precombusted (550 °C) quartz
275 fiber filters were used to collect and process all DOC and POC samples.

276 Dissolved organic carbon concentrations in water and SML samples were determined using
277 a Shimadzu TOC-5000 DOC analyzer (1% precision). Total C and N were measured using a
278 Carlo-Erba 1102 CHNOS elemental analyzer (precision: C: 1–2%; N: 2–3%).

279 For measurements of TEP in SML and seawater, duplicate samples (50 to 250 ml as needed)
280 were filtered at low, constant vacuum (< 200 mm Hg) onto 25 mm diameter 0.4 µm
281 polycarbonate filters and stained with 500 µl of 0.02% Alcian Blue in 0.06% acetic acid (pH 2.5)
282 solution for 5 seconds, following the procedure of Passow and Alldredge (1995) as modified by
283 Engel (2009) and Cisternas-Novoa et al. (2014). A Sartorius model 16315 filtration apparatus
284 with a fluorocarbon-coated steel screen filter support was used. Stained filters were rinsed with 1
285 ml ultrapure water three times to remove excess dye and frozen until analysis in the laboratory.
286 Samples for CSM quantification were similarly filtered, stained with 1 ml of 0.04 % Coomassie
287 Brilliant Blue (CBB-G 250) dye at pH 7.4 for 30-60 seconds, rinsed, stored frozen, and analyzed
288 according to the procedure of Cisternas-Novoa et al. (2014).

289 Filters with stained TEP from water and the SML were extracted, a calibration curve
290 constructed, and the results interpreted by the method described by Passow and Alldredge (1995)
291 as modified by Engel (2009) and Cisternas-Novoa et al. (2014). The Alcian Blue solution used
292 on shipboard was calibrated using a suspension of Xanthan Gum (XG). Filters with stained CSM
293 from the SML or from seawater were analyzed and the results interpreted by the method of
294 Cisternas-Novoa et al. (2014), using bovine serum albumin (BSA) as the standard for calibration

295 of the Coomassie Blue solution used on shipboard. When making up new Alcian Blue or
296 Coomassie Brilliant Blue dyes, new calibration curves have to be determined. Optical densities
297 of samples, blanks (unexposed filter), and standards were measured at 787 nm using a Unico
298 2802 UV/Vis spectrophotometer and a cell with a 1 cm path length. A Mettler XP6U ultra micro
299 balance equipped with a U-Electrode Antistatic System was used for dry weight determinations
300 on XG standards. TEP concentrations were reported in micrograms of XG equivalents per liter of
301 air or nanograms per ml water. CSM concentrations were reported in micrograms of BSA
302 equivalents per liter of air or nanograms BSA equivalents per mL water.

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304 *2.4 Measurement of Aerosol Size Distributions*

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306 Ambient aerosol particles were sampled from the inlet via a stainless steel tube on the mast
307 extending ~18 m above the sea surface. The mast was capped with a cone-shaped 5 cm diameter
308 inlet nozzle that was rotated into the wind to maintain nominally isokinetic flow and minimize
309 the loss of supermicron particles as described in Bates et al. (2012). Air was drawn through the
310 inlet nozzle at $1 \text{ m}^3 \text{ min}^{-1}$ to the lower 1.5 m of the tubing where it was heated for ~2 sec to $24 \pm$
311 0.5° C to dry the aerosol to an RH of ~60% (Bates et al., 2005).

312 SSA particles were generated by the in situ Sea Sweep nascent particle generator system
313 designed by Bates and colleagues (Bates et al., 2012) which was deployed leeward of the R/V
314 Knorr. This device's curtained frame protected a ~0.5 m^2 sea surface area from ambient air and
315 aerosol particles. SSA particles were directly emitted from the ocean surface by bursting of
316 bubbles generated 0.75 m below the water surface with particle-free air. A 5.1 cm ID NutriFLEX
317 Pliovic™ hose attached to the top of the Sea Sweep brought SSA particles to the MOUDI and
318 the scanning mobility particle sizer at a flow rate of $1 \text{ m}^3 \text{ min}^{-1}$. Similar to sampling from the
319 mast, in the lower 1.5 m of the tubing the aerosol was heated for ~2 sec to $24 \pm 0.5^\circ \text{ C}$ to dry the
320 aerosol to a RH of ~60% (Bates et al., 2005). Sampling times for particle collection by the
321 MOUDI at each station are listed in Table 2. It should be noted that because bubble capture and
322 flow rates can vary, absolute particle number concentrations from Sea Sweep generated SSA
323 cannot be compared between stations.

324 The aerosol size distributions at 60% RH generated by the Sea Sweep and sampled from
325 ambient air were determined using a Differential Mobility Particle Sizer (DMPS) equipped with
326 a differential mobility particle sizer (Aitken-DMPS), a medium column differential mobility
327 particle sizer (Accumulation-DMPS) and an aerodynamic particle sizer (APS model 3321, TSI,
328 St. Paul, MN) in the aerodynamic particle diameter range from 0.02 to 11.38 μm having an
329 aerosol inlet with 10 μm 50% cut-point. Both instruments were operated at $55 \pm 10\%$ RH and
330 aerosol distributions were collected every 5 min and gridded in 96 size bins. The transmission
331 efficiency for particles < 6.5 μm (aerodynamic diameter) has been determined to be 95% (Bates
332 et al., 2002). Simultaneous measurements of the aerosol number size distribution made directly
333 at the top of the Sea Sweep and at the base of the sampling mast showed no measurable loss of
334 particles (Bates et al., 2012). The size distributions are a combination of DMPS and APS data
335 where the APS aerodynamic diameters were converted to geometric diameters using densities
336 calculated with the thermodynamic model, AeRho (Quinn and Coffman, 1998). The model uses
337 inorganic ion and total organic carbon data from in-parallel running 7-stage impactors to
338 estimate the density of the aerosol and the amount of water that is associated with the inorganic
339 compounds at the measurement temperature and RH. The diameter channels in the overlap
340 region of the DMPS and APS were chosen in the following manner: the last DMPS channel was

341 discarded and the first APS diameter channel that was larger than the last valid DMPS channel
342 was chosen as the first APS channel (Quinn et al., 1998; Quinn et al., 2002; Quinn et al., 2004).
343 We report aerosol number and mass size distributions as a function of aerodynamic diameter for
344 derivation of the total particulate mass sampled by the MOUDI as outlined below.

345
346 Table 2. MOUDI SSA sampling times at Sea Sweep stations during the 2014 WACS II cruise
347 and of ambient air between Stations 2 and 3 which was sampled as the ship was underway (UTC-
348 Coordinated Universal Time).

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Station	Sampling times (UTC)	Sampling times (min)
1	142.6389-142.9063	250
1.1	143.5764-143.7813	490
2	146.5938-146.9514	485
4	152.7779-153.3757	840
5	155.8368-156.5521	660
2/3 Ambient	148.8646-148.9965	405

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The aerosol number and mass size distributions in Figure 2 include the uncertainty due to the variation of the distribution during the sampling period (left panels) which represents $\pm 1\sigma$ variation from the mean and the uncertainty due to the instrument counting statistics given by the counting statistics. Above $1\ \mu\text{m}$ the error is estimated to be 10% (Bates et al., 2012, Pfeifer et al., 2016) while below $1\ \mu\text{m}$ counting statistics can yield an error which can be $>10\%$. For the remainder of the document the combined uncertainties (sampling variability and counting are applied in the data analysis. This yields the most conservative error. As discussed below aerosol mass size distributions shown in Fig. 2 are used to derive the total particle mass (TPM) and its uncertainty for each stage sampled by MOUDI.

2.5 Aerosol sampling with the cascade impactor MOUDI

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The MOUDI was kept in a humidity controlled instrumentation chamber at the base of the ship's mast. Inside the instrumentation chamber, a portion of the air was directed to the MOUDI at a flow rate of $30\ \text{L}\ \text{min}^{-1}$. For analysis of particulate TEP and CSM concentrations as a function of aerosol particle size, replicate 13 mm diameter $0.2\ \mu\text{m}$ pore size polycarbonate filters were placed on each of the 9 uppermost stages of the MOUDI. Table 3 displays the corresponding cut-point diameters ranging from 100 to 10000 nm aerodynamic diameters.

As the 13 mm filters will only receive a fraction of the total number of deposited particles on a given stage and because the aerosol impaction area varies with the stage, the actual area of impaction for each stage was directly determined. Atomized sea salt particles were collected by the MOUDI onto foil liners covering each stage. The deposition area on each stage measured (Table 3) and confirmed by comparison with diameters given by Mason et al. (2015). The scaling factor, S_{corr} , given in Table 3 reflects the difference between the area of particles

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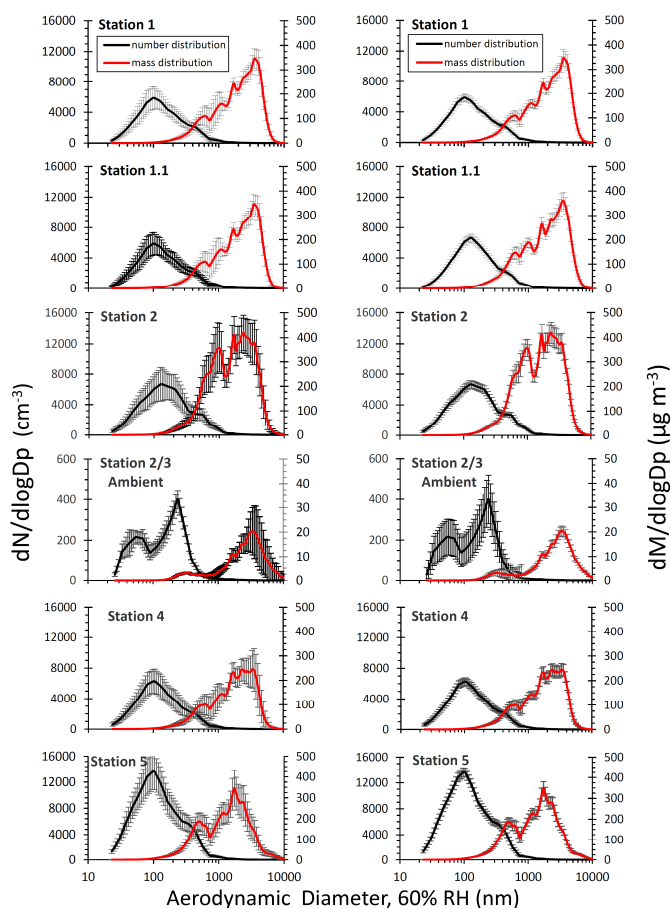


Fig. 2. Aerosol number (black line) and mass distribution (red line) as a function of aerodynamic diameter at 60% RH derived from DMPS and APS measurements for Sea Sweep stations and ambient air collected at Sta. 2/3. Aerosol distributions are time-averaged at 5 min intervals, but only data acquired during MOUDI™ sample collection periods were considered (Table 2). Vertical error bars in the left column reflect sampling variability and represent 1 standard deviation. Error bars in distributions shown in the right column illustrate the uncertainty due to the DMPS/APS instrument counting.

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was impacted onto filters which could be stained for TEP and CSM determination and the total impactation area of a given stage. This correction allowed for comparison of airborne TEP and CSM concentrations with TPM concentrations.

Table 3. MOUDI particle collection characteristics of each stage expressed as midpoint cut-point diameters given as equivalent aerodynamic diameters. The maximum uniformly impacted area per stage is given with corresponding scaling factor for the 9.5 mm diameter area of the 13 mm diameter filters where impacted particles were actually stained.

Stage	50% Cut-point (nm)	Deposit Area (nm ²)	Scaling Factor, S _{corr}
Inlet			
1	10000	424.6	5.99
2	5600	424.6	5.99
3	3200	541.2	7.63
4	1800	541.2	7.63
5	1000	541.2	7.63
6	560	604.8	8.53
7	320	583.2	8.23
8	180	583.2	8.23
9	100	583.2	8.23

429 Sampling at 60% RH with the MOUDI was chosen to reduce particle losses due to
430 bouncing, though we were not able to quantify this impact. MOUDI particle loss for liquid and
431 solid particles is specified as follows (Marple, 1991). Between stages 3 and 8, particle loss is
432 below 2%. Particle loss increased towards ~8% for stage 10. The greatest particle losses are for
433 the largest particle sizes, i.e. stages 1 and 2, reaching ~20%. The actual particle loss for the
434 particles sampled in this study is not known. Therefore, the data analysis does not account for
435 these losses. However, the data analysis presented below indicates similar or larger uncertainties
436 in measured particle mass due to sampling of TPM and in TEP and CSM mass determination.
437 Therefore, potential particle losses can be assumed to have a minor impact on presented data
438 analysis.

439 No filters were placed on stages 10-13 (cut-point diameters 56, 32, 18, 10 nm) since TEP
440 and CSM measurements on these small particles cannot yet be made as outlined below.

441

442 *2.6 Particulate TEP and CSM Measurements*

443

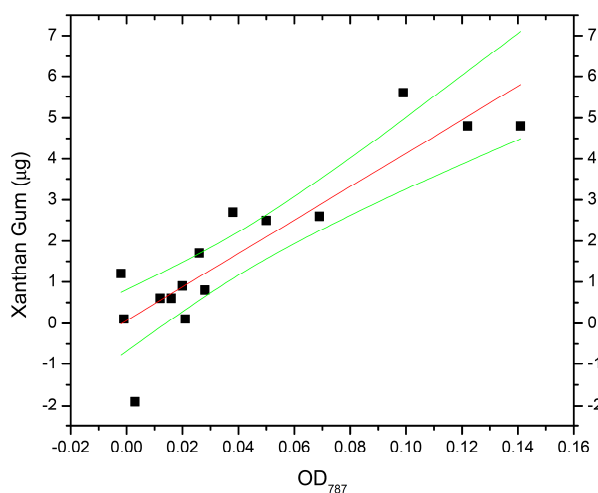
444 Polycarbonate filters were used to collect size fractionated SSA and ambient air samples for
445 TEP and CSM analysis. These samples were stained on shipboard as described above for water
446 samples. The 0.2 μm pore size filters were removed from each stage of the MOUDI and
447 immediately stained with 0.25 – 0.5 mL of 0.1 μm filtered Alcian Blue or Coomassie Blue
448 solutions for 5 sec or 30 s, respectively (the same time used for seawater samples), rinsed with 2
449 mL, 0.1 μm filtered distilled water, and stored at -20°C . Particle-free filters were stained and
450 rinsed along with each set of samples to serve as controls. For staining and rinsing of filters, a 13
451 mm glass filtration unit (Advantec KG13AA) was modified by replacement of the glass frit with
452 a polypropylene filter support and the addition of an acrylic plate to restrict the staining/filtration
453 area to 9.5 mm. The current lower size limit of aerosol particles for TEP and CSM determination
454 is about 100 nm. Smaller particles, even if they swell during dying and rinsing, may not be
455 sufficiently retained in the filter to assure accurate mass measurements.

456 Because of the small diameter of MOUDI stages and the need for simultaneous collection of
457 other sample types, only three filters could be placed on any one stage, so two were used to
458 collect particles for TEP analyses and one for CSM analysis. We therefore did not attempt
459 multivariate statistical analyses of the data.

460 In order to determine the TEP portion of total aerosol mass we measured Alcian Blue-stained
461 samples and reagent blanks on 13 mm filters, by modifying the colorimetric method of Passow
462 and Alldredge (1995) as follows. Each aerosol sample on a 13 mm filter was extracted in a 10
463 mL borosilicate glass beaker for 2 h using 1.5 mL of 80% sulfuric acid, with swirling every 15
464 min. Optical densities were then measured at 787 nm against a distilled water instrument blank
465 using a UV/Vis spectrophotometer and a semi micro cell with a 1 cm path length. To convert the
466 measured absorbance into mass of TEP, the absorbance was calibrated using XG as a standard.
467 Although the same Alcian Blue solution was used for all samples (seawater, SML, aerosol), the
468 aerosol samples processed using our modified filtration apparatus required preparation of a
469 separate calibration curve using 13 mm diameter, 0.2 μm polycarbonate filters (Fig. 3). Our
470 working solution was a tenfold dilution (in 0.1 μm filtered distilled water) of XG standard which
471 had been freshly prepared according to Cisternas-Novoa et al. (2014). Filters for dry weight
472 measurements were prewashed, dried at 40°C , and cooled in a desiccator prior to weighing to a
473 constant weight. The use of the ultra-micro balance and an antistatic system was critical to the

474 successful generation of calibration curves due to the very low sample masses and substantial
 475 static charge issues.

476 A calibration curve for XG weights up to 0.12 μg was constructed as follows. For calibration
 477 of each XG mass, three samples of a known volume of the XG working solution were divided
 478 into replicate aliquots. One aliquot for XG mass determination was collected on a preweighed
 479 filter, dried and weighed to a constant weight. The second aliquot was collected on a filter, dyed,
 480 extracted for 3 hr in 80% H_2SO_4 and the adsorption of the resulting solution measured at 787 nm.
 481 In parallel to account for slight changes in dye retention from filter to filter, blank filters without
 482 XG were washed and dried, were dyed, extracted, and after 3 hours the adsorption of the
 483 resulting solution measured at 787 nm. The mass of XG is then plotted against the difference in
 484 absorbance between the replicate filter containing XG and corresponding blank filter giving the
 485 net absorbance. From this procedure we were able to produce a calibration curve that is linear
 486 between 0 and 0.12 μg XG (Fig. 3). For the lowest or zero XG masses, slightly negative optical
 487 density reading are possible due to slight retention of the dye within a filter even without the
 488 addition of XG, resulting in some absorbance.



489
 490
 491 **Fig. 3.** An example of a TEP calibration curve (red) with 95%
 492 confidence bands ($\pm 1\sigma$, green)
 493 using xanthan gum as surrogate
 494 material and stained by Alcian
 495 Blue using a 13 mm diameter filter
 496 apparatus.

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 504 The calibration curve was not forced through the origin of the plot. The concentration of TEP
 505 determined in aerosol samples is then corrected for the fractional coverage of the MOUDITM
 506 stage area (Table 2), normalized by the volume of air sampled, and expressed in micrograms of
 507 XG equivalents per liter of air ($\mu\text{g XG eq. L}^{-1}$) as calculated by the equation:

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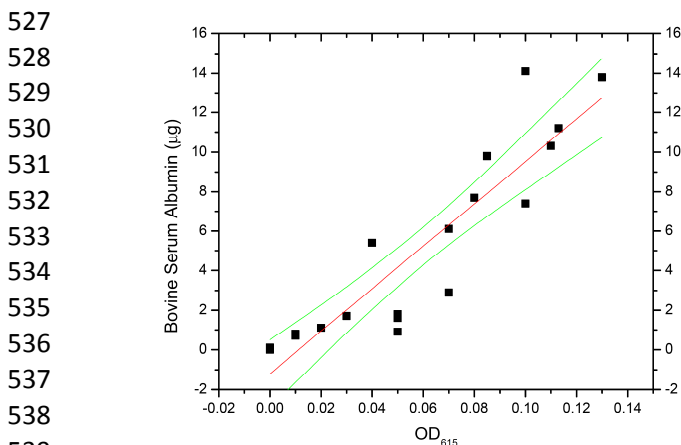
$$TEP (\mu\text{g XG eq L}^{-1}) = (TEP^{sample} - TEP^{blank}) / V^{air} \times S_{corr} \quad (1)$$

510 where TEP^{sample} is the TEP mass in μg of the aerosol, TEP^{blank} is the TEP mass in μg of the blank
 511 filter (both derived from Fig. 3), and V^{air} is the volume of air in liters which passed through the
 512 MOUDI. In cases where there were limited numbers of stainable particles in a given size bin,
 513 $TEP^{sample} - TEP^{blank} \approx 0$, representing our detection limit.

514 For CSM measurements from aerosol samples, 1 mL of 3% SDS in 50% isopropyl alcohol
 515 was added to the 5 mL cryo tubes used to store the stained filters. The samples were placed in a
 516 Fisher Scientific FS30H ultrasonic bath for 2 hr at 37 °C. Absorption of the eluted dye from

517 samples and filtered seawater blanks was determined spectrophotometrically at 615 nm in a 1 cm
 518 path length semi micro cell against particle-free distilled water.

519 The Coomassie Brilliant Blue solution used on shipboard was calibrated for use with our
 520 method in the same manner employed for the Alcian Blue calibration for the TEP analysis
 521 described above. A BSA standard prepared according to Cisternas-Novoa et al. (2014) was
 522 diluted tenfold with 0.1 μm filtered distilled water for generating a standard curve using 13 mm
 523 diameter, 0.2 μm pore size filters. The calibration curve for CSM mass derivation is shown in
 524 Fig. 4. The calibration curve was not forced through the origin of the plot. As for the Alcian Blue
 525 standardization the dry weight (in μg) of the BSA retained by filters was related to the
 526 Coomassie Brilliant Blue absorbance.



527
 528
 529 **Fig. 4.** An example of a CSM calibration curve (red) with 95% confidence bands
 530 ($\pm 1 \sigma$, green) using bovine serum albumin as surrogate material and stained
 531 by Coomassie Brilliant Blue dye using a 13 mm filter apparatus.
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 539 Results are expressed in micrograms of BSA equivalents per liter air using the equation:

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 541
 542
$$CSM (\mu\text{g XG eq L}^{-1}) = (CSM^{sample} - CSM^{blank}) / V^{air} \times S_{corr} \quad (2)$$

543 where CSM^{sample} is the CSM mass in μg of the aerosol, CSM^{blank} is the CSM mass in μg of the
 544 blank filter (both derived from Fig. 4), and V^{air} is the volume of air in liters which passed through
 545 the MOUDI. In cases where there were limited numbers of stainable particles in a given size bin,
 546 $CSM^{sample} - CSM^{blank} \approx 0$, representing our detection limit.

547 Application of Equations 1 and 2 yields the amount of TEP and CSM in collected aerosol
 548 particles, respectively, as a function of particle size given by respective MOUDI stage or when
 549 summed over all stages as total airborne TEP and CSM concentrations. Neglecting particle losses
 550 in MOUDI, the dominant uncertainty in derived TEP and CSM concentrations is due to
 551 calibration uncertainties as depicted in Figs. 3 and 4. In the typical TEP and CSM concentration
 552 range present on the MOUDI stages, the mass uncertainty is about 25 and 20 %, respectively.

553
 554 **2.7 Estimation of TEP and CSM Concentrations in Collected Aerosol Particles.**
 555

556 Assessment of the mass concentration of TEP and CSM in sampled aerosol particles as a
 557 function of size requires determination of TPM in each MOUDI stage. Since TPM for each
 558 MOUDI stage could not be determined independently, the continuously measured DMPS/APS
 559 aerosol mass size distributions are applied to give an estimate of TPM. To improve future
 560 analysis we recommend using two MOUDI setups in parallel, isokinetically sampling with same

561 cut-point diameters, one collecting particles for determination of TEP and CSM and the other
562 one to determine TPM per sampling stage.

563 To estimate the collected TPM, we first represent the MOUDI collection efficiency curves
564 (Marple, 1991) by lognormal functions extending those beyond the given cut-point by $\pm 4\sigma$ to
565 assess the particle masses that are being collected per stage. As mentioned above, particle losses
566 in MOUDI are not included in this analysis and will very likely have only a minor effect on the
567 overall data uncertainty. The time averaged 96 binned DMPS/APS mass distribution data (Fig. 2)
568 are sorted into the size range of individual MOUDI stages (Table 2) where overlaps in the
569 collection efficiency curves have been accounted for. For example, a DMPS/APS size bin
570 smaller than the cut-point diameter will result in 50% and less of the particles being collected in
571 that stage but more than 50% in the stage with smaller cut-point diameter. Subsequently, the
572 derived aerosol particles masses for each bin representing the respective MOUDI stage are
573 summed to yield TPM per impaction stage. We used the combined errors presented in Fig. 2 per
574 size bin to yield, by application of the root of sum of squares, the uncertainty of the TPM per
575 stage. MOUDI sampling time is accounted for by the 30 L min^{-1} instrument input flow. This
576 finally yields the TPM for each MOUDI stage that can then be compared with the TEP and CSM
577 concentrations per stage.

578 Below we report the mass ratio of TEP or CSM to TPM for each MOUDI stage and in sum
579 for all stages, i.e. total sampled TEP or CSM over total TPM. The uncertainty of these ratios
580 results from the uncertainties in TEP and CSM measurements and the uncertainties in TPM
581 measurements.

582

583 3. Results and discussions

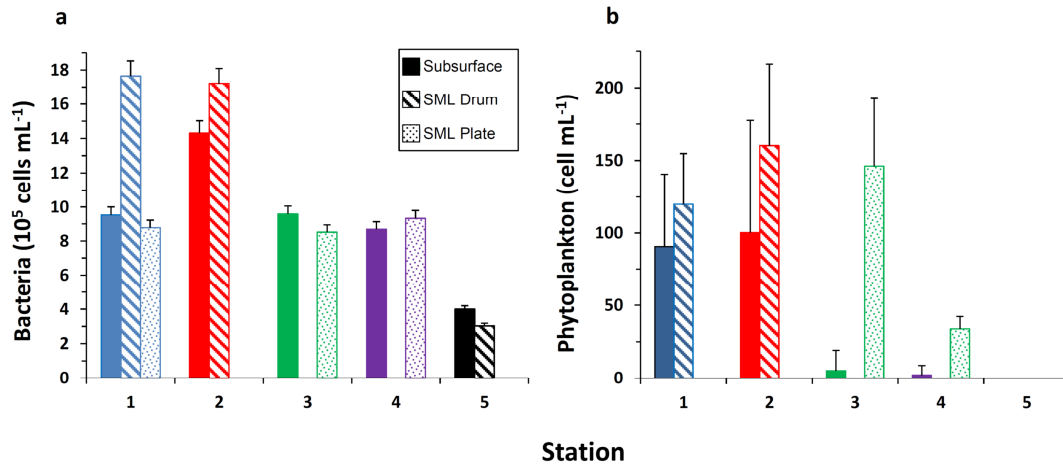
584 3.1 Ocean Water Characteristics.

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586 Concentrations of Chl *a* in subsurface waters collected at 5 m depth varied by 2 orders of
587 magnitude between ~ 0.1 and $2.2 \mu\text{g/L}$ over the entire cruise area, indicating relatively low algal
588 biomass. The highest mean Chl *a* levels were recorded at the northernmost station (Sta. 2) and
589 the lowest Chl *a* levels occurred at Station 4. The relative abundances of the dominant
590 phytoplankton taxa can be estimated based on the relative concentrations of specific taxonomic
591 indicator accessory pigments (Jeffrey et al., 1999). The most commonly found carotenoid
592 pigments within the study region were fucoxanthin, zeaxanthin, 19'-Hexanoyloxyfucoxanthin,
593 19'-Butanoyloxyfucoxanthin and peridinin (Table 1). These indicate the presence of several
594 major taxonomic groups of phytoplankton. Fucoxanthin, although present in many golden-brown
595 taxa of phytoplankton, is most commonly associated with the presence of diatoms. Zeaxanthin,
596 another accessory pigment common to several classes, indicates high concentrations of
597 cyanobacteria (e.g., *Synechococcus* sp. and *Prochlorococcus* sp.) present at all stations (Jeffrey
598 & Wright, 1997; Goericke & Repeta, 1992). The compounds 19'-hexanoyloxyfucoxanthin and
599 19'-butanoyloxyfucoxanthin are indicators of the presence of coccolithophorids and
600 pelagophytes, respectively (Zapata et al., 2004; Jeffrey & Wright, 1997). Of particular note is the
601 high concentration of peridinin at station 2, indicating that dinoflagellates were a dominant
602 phytoplankton present here (Jeffrey & Wright, 1997).

603 SML samples collected by the rotating drum were enriched in bacteria compared to
604 subsurface waters at both Stas. 1 and 2, but not at Sta. 5 where subsurface bacterial numbers
605 were the lowest (Fig. 5). Phytoplankton numbers may follow a similar pattern to bacterial
606 numbers at Stas. 1 and 2, but data are lacking at Sta. 5. When SML samples were taken using the

607 plate method, numbers of phytoplankton were substantially higher in the SML at Stas. 3 and 4,
 608 but numbers of bacteria were not.



624 **Fig. 5.** Bacterial (a) and phytoplankton (b) concentrations in subsurface and SML
 625 waters of varying thickness collected by rotating drum and by the plate method. Gaps
 626 represent points where conditions precluded sample collection or insufficient sample
 627 was available.

630 **Table 3.** Particulate organic carbon, particulate organic nitrogen, and dissolved organic carbon
 631 in bulk seawater and SML samples. Instrument precision is 5% for C and 2% for N.

Station		DOC (μM)	POC (μM)	PON (μM)
1	Subsurface			
	SML drum	289	207	10.8
	SML plate			
2	Subsurface	134	515	12.8
	SML drum	205	182	8.7
	SML plate			
3	Subsurface			
	SML drum			
	SML plate	386	<2	<1.8
4	Subsurface	137	<2	<1.8
	SML drum			
	SML plate	140	<2	<1.8
5	Subsurface	146	<2	<1.8
	SML drum	185	<2	<1.8
	SML plate			

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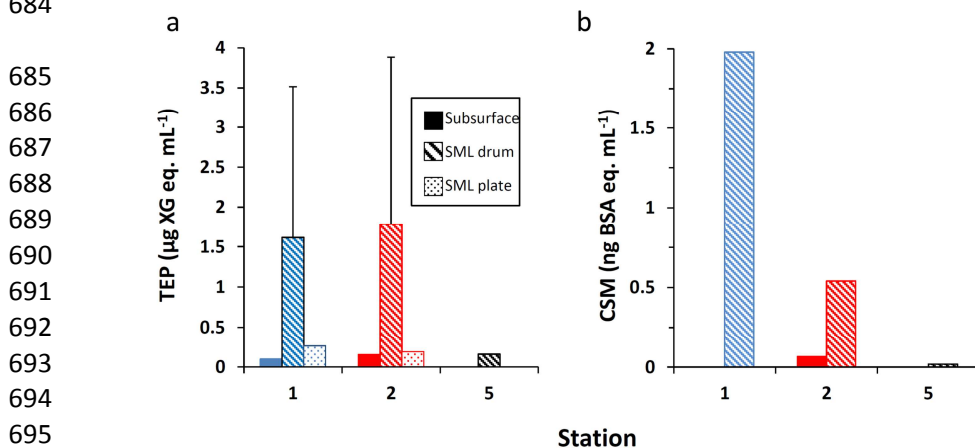
654 Subsurface water chemistry data are available only for Stas. 2, 4, and 5 (Table 3). As
 655 expected, subsurface POC and PON levels (Table 2) were highest at Sta. 2, where Chl *a* levels
 656 and microbial numbers were highest (Table 1, Fig. 5). Subsurface water from Stas. 2, 4, and 5,
 657 however, had similar DOC levels (Table 2) perhaps reflecting a balance between DOC
 658 production and its consumption by heterotrophs.

659 Although drum-sampled SML water was enriched in bacteria at Sta. 2, POC and PON show
 660 no enrichment, but DOC is enriched (Fig. 5 and Table 3). At Sta. 5, where drum-sampled SML
 661 water was not enriched in bacteria, POC and PON again showed no enrichment, but DOC levels
 662 were slightly higher in the SML. At Sta. 4, where the SML was sampled on shipboard by means
 663 of a plate, phytoplankton were enriched in the SML, but levels of bacteria, DOC, POC, and PON
 664 showed no difference between SML and subsurface waters. One explanation for these differences
 665 is simply the natural variability in water mass characteristics. Apparent differences between
 666 stations may also be due to differences in sampling technique with the drum collecting a thinner
 667 microlayer than the plate.

668 It is well known that DOC concentrations, even when collected at the same geographic
 669 location and depth below the surface, can vary widely, reflecting small scale temporal and spatial
 670 variability. Measured in water collected at 5 m below the surface during WACS II, DOC
 671 concentrations (134-146 μM) were higher than measured during the WACS 2012 cruise to the
 672 same general area in late August 2012 (70-95 μM). Complicating general comparisons of DOC
 673 concentrations in surface oceanic waters with other studies, including many in North Atlantic
 674 and Sargasso Sea waters, is the fact that the definition of ‘surface’ waters which can range from
 675 the top 50 to 100 m (Hansell et al., 2001) to 2 m (Carlson, 1983; Alldredge, 2000), 5 m (Quinn
 676 et al., 2014, this study), or 10 m (Hedges et al., 1993).

677 TEP and CSM measurements were carried out at Stas. 1, 2, and 5 (Fig. 6) where the SML was
 678 collected by the rotating drum sampler. Subsurface TEP values were typical for open ocean
 679 waters (see e.g. Bar-Zeev, 2015). The data suggest that the SML at Stas. 1 and 2 was
 680 considerably enriched in TEP. A sample collected by the plate method at Sta. 1 also showed TEP
 681 enrichment, but to a lesser degree, which would be expected given that the glass plate samples a
 682 20-150 μm thick layer, while the drum sampler collects the upper 50 μm (Cunliffe et al., 2013).
 683 CSM was enriched in the SML at Sta. 2, but to a lesser extent than TEP.

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Fig. 6. Concentrations of (a) TEP and (b) CSM in subsurface and SML waters for stations in cruise area. Stations 3 and 4 are not shown since no data are available. Error bars for TEP data represent standard deviations of triplicate samples. CSM data is for one sample each. Gaps represent points where conditions precluded sample collection.

3.2. Aerosol Number and Mass

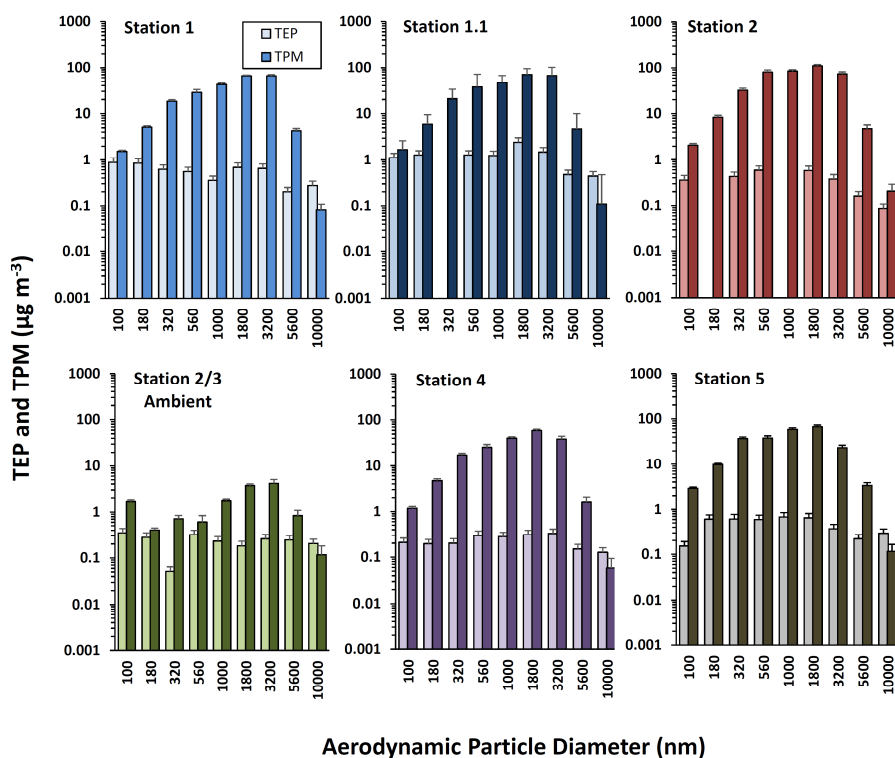
706 The primary mode diameter of the number size distributions for Sea Sweep generated
707 aerosol particles averaged over the corresponding period of MOUDI aerosol collection varied
708 very little between stations peaking around 100 nm (60% RH) (Fig. 2), reflecting the frit size of
709 the diffusion stones used to generate the sea spray (Bates et al., 2012). Particle number
710 concentrations recorded for the ambient air collected at Station 2/3 averaged 263 ± 29 particles
711 cm^{-3} , a value similar to data reported for background marine conditions of 200-300 particles
712 cm^{-3} in subtropical and equatorial regions (e.g. Covert et al., 1996; Quinn et al., 2002; Bates et al.,
713 2002).

3.3. Particulate TEP and CSM

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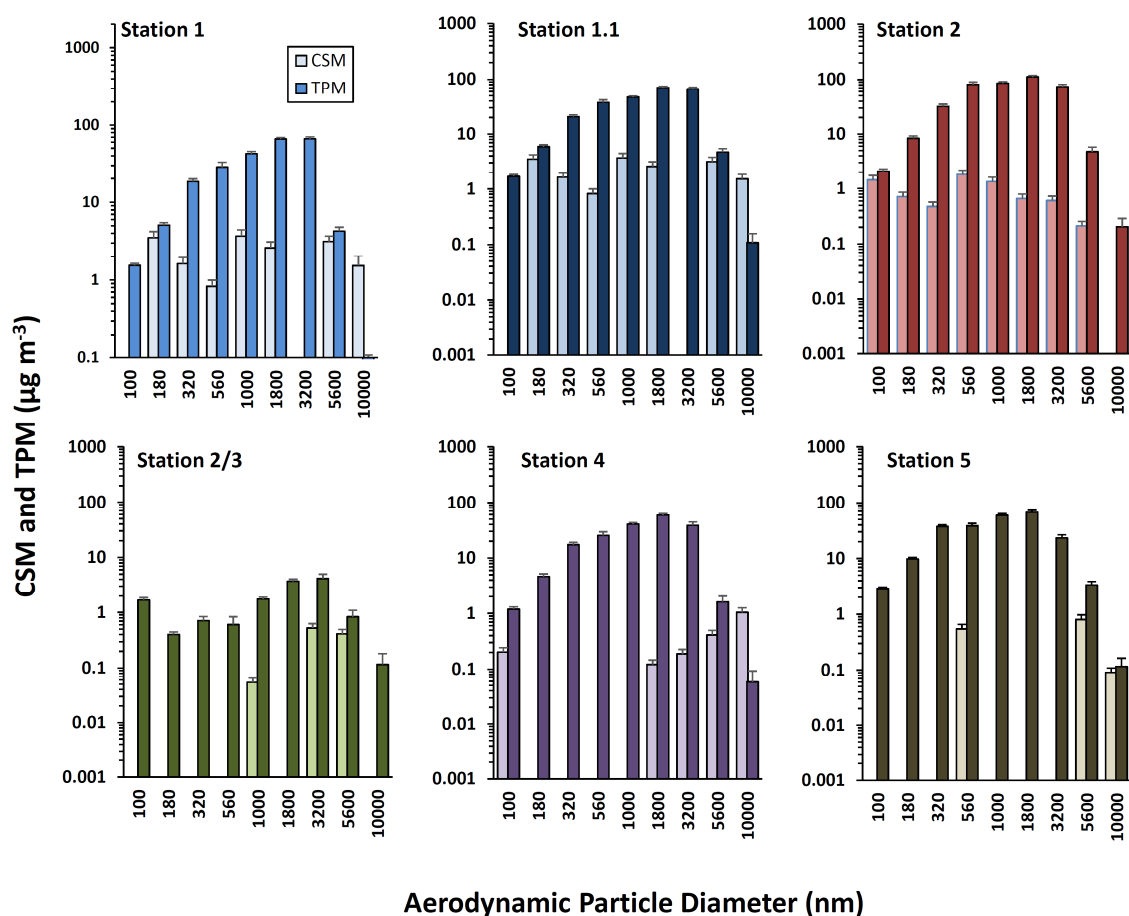
715 The size fractionated mass of TEP and CSM derived from MOUDI relative to corresponding
716 size fractionated TPM derived from Sea Sweep and ambient air are shown in Figs. 7 and 8,
717 respectively. Note that these are total mass values per stage based on the total sampled air
718 volume at each station. Highest SSA mass concentrations sampled by MOUDI are found for
719 supermicron particle sizes. The highest concentrations of TEP across the different stations are
720 not as clear but in most cases also coincide with supermicron particles, however, their variation
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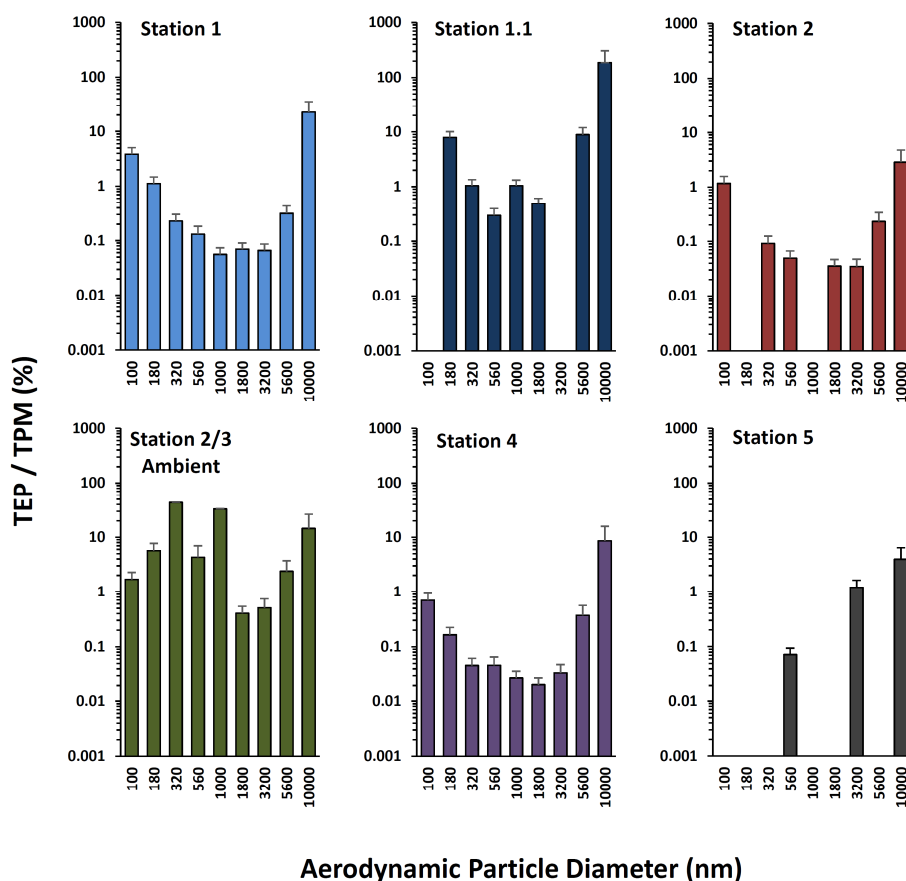
745 **Fig. 7.** Airborne TEP mass and corresponding TPM for each MOUDI stage collected from
 746 Sea Sweep generated SSA and ambient air (Station 2/3). TEP values are the mean of 2
 747 replicates. Error for TEP measurements is ~25% and error for TPM data represents the total
 748 uncertainty due to natural variability and counting statistics. The absence of data means that
 749 TEP values were below *detection* ($TEP^{sample} - TEP^{blank} \approx 0$).
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752 is much less compared to TPM. In general, TEP mass per stage is always much lower than
 753 corresponding TPM except for the largest particles collected by MOUDI (> 10,000 nm), where
 754 TPM is underestimated due to the limitation of sampled maximum particle size by APS
 755 measurements.
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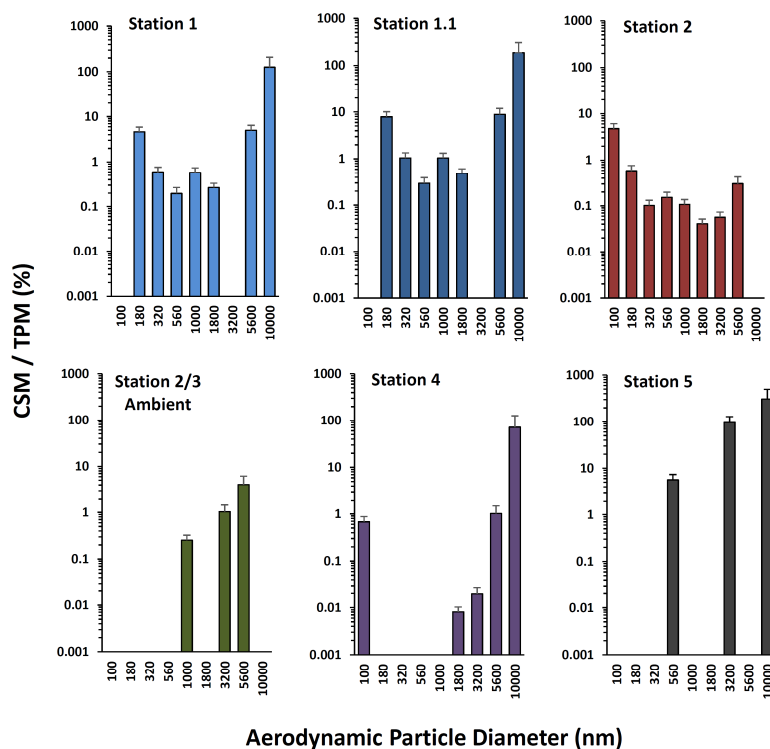
757 **Fig. 8.** Airborne CSM mass and corresponding TPM collected by MOUDI for each stage from
 758 all Sea Sweep stations and ambient air (Sta. 2/3). Error for CSM measurements is ~20%. The
 759 TPM data are the same as in Fig. 7. The absence of data means that CSM values were below
 760 detection ($CSM^{sample} - CSM^{blank} \approx 0$).
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765 To determine the fraction of TEP and CSM mass relative to TPM in Sea Sweep generated
 766 SSA and ambient aerosol particles, the TEP or CSM concentration at each MOUDI stage was
 767 divided by the TPM for the corresponding size range (Figs. 9 and 10). The uncertainty of the
 768 mass ratio is derived from the sum of the relative errors associated with TEP or CSM and TPM.
 769 As explained above, the higher mass ratios of TEP and CSM in particles > 10,000 nm is likely
 770 artificial, since not all of these particles are sampled by the APS, implying that TPM mass for
 771 this MOUDI stage is underestimated. It should also be remembered that the amounts of TEP and
 772 CSM are expressed as equivalent masses of XG or BSA, and that differences in chemical
 773 composition of marine polymeric gels might cause them to respond differently to staining,
 774 resulting in additional uncertainty, likely giving the lower limits for TEP and CSM masses and
 775 thus concentrations. Finally, differences in the viscosity of SSA and ambient particles could
 776 potentially influence their properties and therefore adhesion probability in the MOUDI
 777 influencing their stage distribution. For example, if the ambient aerosol particles had higher
 778 viscosity than those collected from the Sea Sweep, they would have been more prone to
 779 bouncing and therefore likely to be accumulated on MOUDI stages with smaller cut-point
 780 diameters (e.g. Marple et al., 1991; Ivosevic et al., 2006).



807 **Fig. 9.** Size fractionated TEP mass concentration in TPM at each station from Sea Sweep
 808 generated SSA and ambient air Station 2/3. The absence of data means that TEP values were
 809 below detection ($TEP^{sample} - TEP^{blank} \approx 0$).

812 The data displayed in Fig. 9 demonstrate that aerosol particles in the submicron size
 813 fractions contained more TEP on average than did larger particles. This effective transfer of
 814 organic matter into the fine aerosol fraction corroborates earlier findings, of a dramatic increase
 815 in organic matter content of smaller particles in nascent sea spray (Middlebrook et al., 1998;
 816 Oppo et al., 1999; O'Dowd et al., 2004; Keene et al., 2007; Facchini et al., 2008; Ault et al.,
 817 2013; Prather et al., 2015; Quinn et al., 2015). Previous studies found that heating freshly emitted
 818 SSA generated at the ocean surface by use of Sea Sweep to 230 °C only resulted in a < 15%
 819 decrease in particle number concentration (Quinn et al., 2014) and volatilization of < 10% of the
 820 organic carbon (Quinn et al., 2015) which can be attributed to the colloidal nature of the organic
 821 carbon components that are present in seawater and their chemical and physical stability (de
 822 Gennes and Léger, 1982; Chin et al., 1998; Verdugo et al., 2008.) This is consistent with the
 823 thermal stability of polysaccharide- and proteinaceous-rich material until > 250 °C (Yun and
 824 Park, 2003) and > 280 °C (White, 1984; Creighton, 1993), respectively. Estimates of TEP
 825 content in the smallest particles were high at all stations including the ambient air sample (Fig.
 826 9). The elevated TEP for supermicron particles sizes of >5600 nm could reflect the
 827 aerosolization of TEP attached to phytoplankton cells or fragments of frustules. Such particles
 828 were observed previously in Arctic air samples (e.g. Leck and Bigg, 1999 and Bigg and Leck,
 829 2001) and were similar to particles found in the SML between ice floes (Bigg et al. 2004; Leck et
 830 al., 2005). On the other hand, although nanogels are the most abundant in seawater, multiple
 831 annealing steps and mixing of gels with longer undegraded polymers produce larger and more
 832 stable gels (Passow, 2000).



855 **Fig. 10.** Size fractionated CSM mass over TPM at each station from Sea Sweep
 856 generated SSA and ambient air Station 2/3. The absence of data means that CSM values
 857 were below detection ($CSM^{sample} - CSM^{blank} \approx 0$).

858

859 Figure 10 shows the particle size-resolved mass ratio of protein-rich CSM to TPM generated
860 by the Sea Sweep and collected from the ambient air. Like TEP-containing particles, CSM
861 ranges in size from a few nm (nanogels) to a few microns (microgels) (Verdugo 2012). One
862 explanation for the presence of high CSM mass in larger aerosol particles might be that large
863 CSM-containing particles (i.e. gels) in surface waters may be more stable relative to small ones.
864 In fact, this matches with observations that in the SML, CSM generally includes bigger particles
865 than TEP (e.g. Galgani and Engel, 2013). Observations of higher bacterial densities associated
866 with CSM compared with TEP (Berman and Viner-Mozzini, 2001) introduce the possibility that
867 the protein-rich gel particles are larger because they include bacteria or bacterial fragments
868 which average 1-3 μm in size. There is little information about CSM production by different
869 phytoplankton species or about how algal growth phase or bacterial abundance influence CSM
870 concentrations and size, but our findings are consistent with observations that TEP and CSM are
871 different particles with different characteristics and behavior in surface waters, and may be
872 differently affected by the nature of the dominant phytoplankton group and the activities of
873 associated bacteria (Long and Azam, 1996; Berman and Viner-Mozzini, 2001; Cisternas-Novoa
874 et al., 2015). These differences may also affect the efficiency with which they are aerosolized.

875 The enrichment trend for smaller particles in this case is not as clear as for TEP since in
876 some instances CSM could not be detected. This may imply that the concentration of CSM in
877 general is lower in SSA compared to TEP. As in the case of TEP, most stations demonstrate a
878 strong enrichment of CSM in supermicron size particles. Proteinaceous materials include cells
879 and cell fragments, and thus the elevated CSM values at larger particles sizes could be due to
880 aerosolization of phytoplankton or bacterial cells or fragments. Alternately or additionally, this
881 could be related to the observed greater stability of Coomassie stainable gels compared to TEP in
882 surface waters (e.g. Passow, 2000). This difference in behavior might enable the persistence and
883 availability for aerosolization of relatively large CSM-containing particles.

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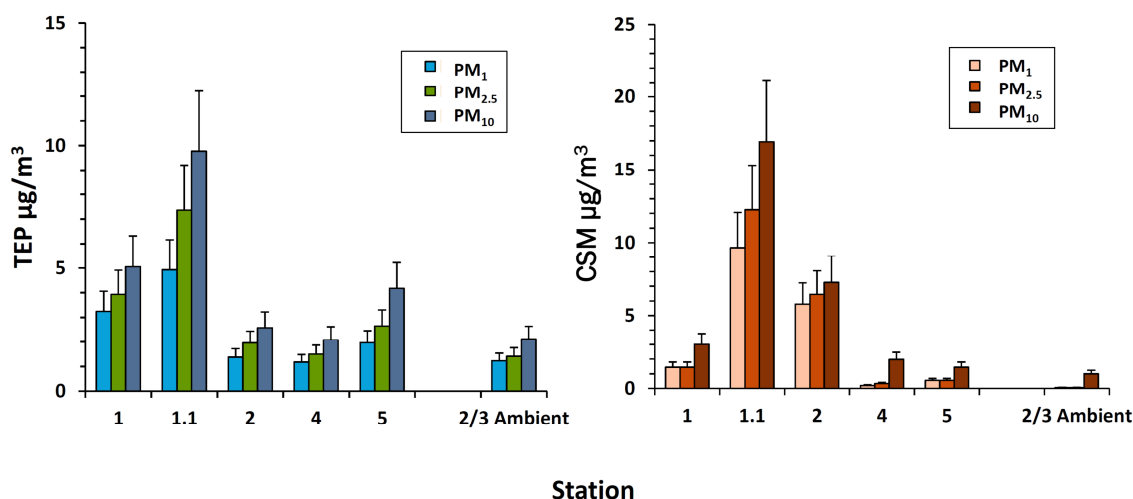
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900 **Fig. 11.** Particulate mass PM_{10} , $\text{PM}_{2.5}$ and PM_1 of TEP and CSM generated by Sea Sweep
901 and collected in the ambient air sample.
902
903

904 Figure 11 presents the estimated total TEP and CSM concentrations associated with PM₁,
905 PM_{2.5} and PM₁₀ derived from particles impacted onto MOUDI stages. As noted earlier,
906 comparison of absolute concentrations between stations cannot be done due to the manner in
907 which the Sea Sweep operates. TEP and CSM concentrations are given for both Sea Sweep and
908 the ambient air samples to demonstrate the capability of our novel method. Concentrations of
909 TEP for Sea Sweep generated SSA ranged from 1.2 to 4.9 $\mu\text{g m}^{-3}$ for PM₁, 1.5 to 7.4 $\mu\text{g m}^{-3}$ for
910 PM_{2.5} and 2.1 to 9.8 $\mu\text{g m}^{-3}$ for PM₁₀. In ambient particles, TEP measured 1.2, 1.4 and 2.1 $\mu\text{g m}^{-3}$
911 for PM₁, PM_{2.5} and PM₁₀, respectively. CSM concentrations for Sea Sweep generated SSA
912 ranged between 0.2 to 9.7 $\mu\text{g m}^{-3}$ for PM₁, 0.32 to 12.2 $\mu\text{g m}^{-3}$ for PM_{2.5} and 1.4 to 16.9 $\mu\text{g m}^{-3}$ for
913 PM₁₀. In ambient particles, CSM measured 0.05, 0.05 and 1.0 $\mu\text{g m}^{-3}$ for PM₁, PM_{2.5} and PM₁₀,
914 respectively.

915 While a large percentage of TEP and CSM particles relative to the total sampled aerosol
916 particle mass were in sizes < 300 nm, relatively large TEP and CSM particles were also collected
917 including some >1,000 nm on MOUDI stage 1 (Figs. 7, and 8). If these large TEP and CSM
918 particles are phytoplankton or bacterial cells or their fragments, they could represent a source of
919 efficient ice nucleating particles (Knopf 2011, Alpert 2011a, b, Pandey et al. 2016). Finally, the
920 ambient particles were collected from an air mass that had been over relatively more productive
921 waters than the waters sampled by the Sea Sweep and presumably carried organic rich particles
922 resulting in enhanced TEP and CMS mass fractions (Fig. 1). Clearly these possibilities suggest
923 the need for additional studies, however, the enrichment of organic rich particles in the finest
924 aerosol sizes is consistent with the findings of Facchini et al. (2008) who showed that microgel
925 organic compounds identified as lipopolysaccharides were preferentially transferred to the
926 submicron aerosol size fraction during bubble bursting over ocean waters of moderate
927 productivity.

928 929 *3.2.3 Summary and Conclusions.*

930
931 The chemical composition and quantity of organic constituents of a given water mass can be
932 expected to directly influence nascent sea spray. In contrast, the characteristics of ambient
933 aerosols will vary regionally, with properties highly dependent on local meteorological
934 conditions and related air mass back trajectories. The HYSPLIT model back trajectories
935 presented in Fig. 1 clearly show that the air masses during the sampling time were from the
936 northeast over open ocean waters and had experienced only minimal continental influence. The
937 altitude dependence of the trajectories shows that all air masses had been in the boundary layer
938 prior to arrival at the sampling location. SeaWIFS images (Fig. 1b) indicate that waters along the
939 trajectory were productive, potentially enhancing the concentration of organic-rich submicron
940 size particles in the ambient air mass sampled at Sta. 2/3.

941 The spatial and temporal variation in numbers and metabolic activities of phytoplankton and
942 bacteria in ocean surface waters may be expected to disproportionately impact the
943 physicochemical and biological properties of the SML, where various components are typically
944 present at higher concentrations than in subsurface waters (Bar-Zeev et al., 2012; Cunliffe et al.,
945 2013). Indeed, in this study we found that both TEP and CSM were enriched in the SML waters
946 of Stas. 1 and 2 with enrichment factor (EF) values of 12.4 ± 3.6 for TEP and 11.1 ± 6.6 for
947 CSM. The similarity in EF values is intriguing given the recent study by Cisternas-Novoa et al.
948 (2015) which demonstrates that at least in subsurface waters exopolymer particles of
949 polysaccharidic composition are a separate particle type and therefore might not be expected to

950 behave the same as particles of proteinaceous composition within the pool of organic matter.
951 Aspects of the behavior of protein-containing gel material in the SML, including the exact
952 association with TEP and the conditions controlling particle formation, are not clear (Engel,
953 2009). However, our data are consistent with previous findings of enhanced CSM, protein, and
954 amino acid concentrations in SML samples (Galgani and Engel, 2013; Kuznetsova et al., 2005;
955 Kuznetsova and Lee, 2001; Mari and Burd, 1998) and Coomassie Stainable Particle (CSP)
956 abundances (Galgani et al., 2016).

957 The enhanced concentrations of both TEP and CSM in the SML and strong enrichment in
958 submicron size of aerosolized particles is highly relevant given recent findings linking marine
959 organic material to ice nucleating particles (INPs) in the atmosphere (e.g. Wilson et al., 2015;
960 Ladino et al., 2015, Knopf et al., 2014). A considerable population of INPs examined by Wilson
961 et al. (2015) from SML material including some collected during the WACS II cruise was
962 smaller than 0.2 μm and therefore likely to consist largely of exudates from phytoplankton and
963 other microorganisms. After heating to 100 $^{\circ}\text{C}$, some of the samples had significantly reduced ice
964 forming activity consistent with the denaturation of proteins and loss of rheological polymer
965 properties and morphological structure of polysaccharides (e.g. Rederstorff et al., 2011)
966 suggesting that the ice nucleating activity was associated with these organic compounds.

967 Predicting aerosol quantity, size distribution, and composition from water quality parameters
968 is currently problematic. The chemical composition as well as relative concentration of
969 individual constituents affects aerosolization of particles from the SML. Surface-active
970 substances stabilize microlayers (e.g. Wurl et al., 2009; Long et al., 2014), impact the size
971 distribution of SSA (e.g. Sellegri et al., 2006; Fuentes et al., 2010;), and can alter the
972 concentration and physicochemical properties of the aerosolized organic material (e.g. O'Dowd
973 et al., 2004; Yoon et al., 2007; Vignati et al., 2010; Russell et al., 2010; Fuentes et al., 2011;
974 Cunliffe et al., 2012; Gantt and Meskhidze, 2013). While phytoplankton community structure
975 and biomass can be related to Chl *a* levels in ocean surface waters, these levels track only a small
976 fraction of the ocean carbon pool and do not necessarily predict levels of DOM in surface waters
977 (e.g. Quinn et al., 2014). Chl *a* also appears to be an imperfect predictor of SSA organic
978 enrichment (e.g. Rinaldi et al., 2013; Quinn et al., 2014) which is confirmed by our results from
979 stations where SSA was Sea Sweep generated. During WACS I, Chl *a* biomass averaged $7.1 \pm$
980 $2.2 \mu\text{g L}^{-1}$ and DOC averaged $89 \pm 3 \mu\text{M}$ ($1.068 \pm 0.036 \text{ mg L}^{-1}$) at a station off Georges Banks
981 in productive waters, whereas Chl *a* averaged $0.03 \pm 0.06 \mu\text{g L}^{-1}$ and DOC averaged $72 \pm 3 \mu\text{M}$
982 at a station in oligotrophic waters off Bermuda. This mismatch was also observed during the
983 WACS II cruise, during which $2.2 \mu\text{g L}^{-1}$ Chl *a* and $63 \mu\text{M}$ DOC were seen at Station 2 surface
984 waters, while $0.1 \mu\text{g L}^{-1}$ Chl *a* and $65 \mu\text{M}$ DOC were seen at Sta. 4. (Table 1). Nevertheless, our
985 findings agree with those of Quinn and colleagues during the WACS I cruise (Quinn et al., 2014)
986 and previously during the CalNEX cruise along the California coast (Bates et al, 2012) in that,
987 that regardless of sampling location, organic enrichment occurs in all particle sizes, with the
988 smallest particles (<180 nm) being most enriched. Additionally, we find that this enrichment is
989 apparent whether SSA are collected as nascent sea spray or as ambient air. Regarding the
990 ambient sample, we do not know how the particles collected were generated (i.e. wave, wind, or
991 combination) and their exact origin. What we do know is that during the previous week air
992 passed over the highly productive continental shelf region of Georges Bank and briefly over
993 Newfoundland, both ideal sources of aerosolized particles including both protein-rich and
994 polysaccharide-rich ones. While the possible contribution to the aerosol mass in the ambient
995 sample by condensing secondary organic material cannot be completely ruled out, the peak

996 absorbance of aged SOA material is at lower wave lengths (Laskin et al., 2015, Chen et al.,
997 2016) than the ones for applied Alcian Blue and Comassie Brilliant Blue dyes. Furthermore, it is
998 not known whether aged SOA material can be stained by either of these dyes. Regardless of the
999 limitations, the size fractionated measurements of polysaccharide and proteinaceous organic
1000 components of SSA collected directly as nascent sea spray and as ambient aerosol presented
1001 here, represent a novel method to infer the relationship between marine biogenic and biological
1002 material and airborne particulate matter.

1003 Although TEP and CSM concentrations can only provide information about a portion of the
1004 particulate organic matter pool in the ambient air together they could make up at least half of the
1005 organic composition and possibly greater depending on conditions in surface waters. Temporal
1006 variability in biological activity is clearly reflected in submicron organic aerosol concentrations.
1007 For example, PM_{2.5} organic aerosol concentrations measured over N.E. Atlantic coastal waters
1008 for a 4 week late summer period varied between 0.36 and 1.0 $\mu\text{g m}^{-3}$ but reached 3.8 $\mu\text{g m}^{-3}$
1009 (Ovadnevaite et al., 2011). Similarly, seasonal organic mass concentrations of SSA PM_{2.5} off
1010 Mace Head reported by Ovadnevaite (et al., 2014) varied from 0.025–0.4 $\mu\text{g m}^{-3}$ but during a
1011 period of high biological activity reached 2.46 $\mu\text{g m}^{-3}$. During WACSII the ambient air sample
1012 PM_{2.5} TEP and CSM concentrations were within this range measuring 1.41 ± 0.35 and $0.054 \pm$
1013 $0.013 \mu\text{g m}^{-3}$, respectively. In more remote open ocean regions of, e.g., the North Atlantic and
1014 Arctic, organic aerosol concentrations can be similar to our data. Although not measured for
1015 PM_{2.5}, for PM₁ the organic component of SSA comprised largely of saccharides and was found
1016 to vary between 0.1 – 0.4 $\mu\text{g m}^{-3}$ with measurements as high as $0.73 \pm 0.37 \mu\text{g m}^{-3}$ (Russell et
1017 al., 2010). In comparison PM₁ TEP at ambient air Sta. 2/3 collected over moderately productive
1018 surface waters averaged $1.23 \pm 0.31 \mu\text{g m}^{-3}$.

1019 Finally, it is well known that primary biological aerosol particles (PBAPs) are an important
1020 subset of atmospheric aerosol (e.g. Jaenicke, 2005; Després et al., 2012) and that the marine
1021 environment acts as an important source. Our novel method of determining the mass fraction of
1022 TEP and CSM in the total aerosol particles mass may be useful for complementary determination
1023 of polysaccharidic and proteinaceous components of airborne organic matter, in general,
1024 including the accumulation and coarse mode for particles up to 18 μm in diameter. In particular,
1025 measurements of CSM would allow comparative studies with fluorescent based detection
1026 techniques to estimate the total biological particulate fraction in environmental aerosol samples
1027 which target tryptophan, the dominant fluorophore in proteins (e.g. Huffman et al., 2010; Pöhlker
1028 et al., 2012; Bianco et al., 2016).

1029

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Highlights:

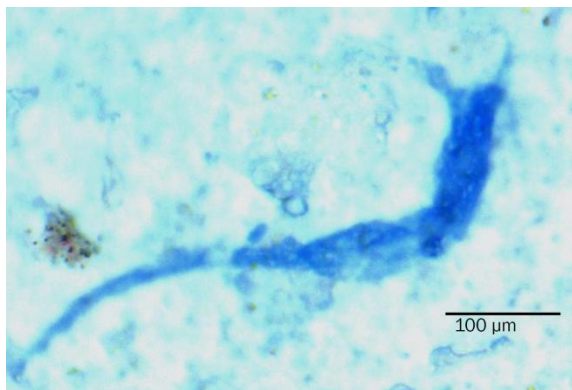
Impaction collected size-fractionated nascent sea spray aerosol over Atlantic Ocean.

Polysaccharidic transparent exopolymer present in sub- and supermicron SSA particles.

Proteinaceous gels present in sub- and supermicron SSA particles.

Marine ambient particles enriched in TEP and proteinaceous material.

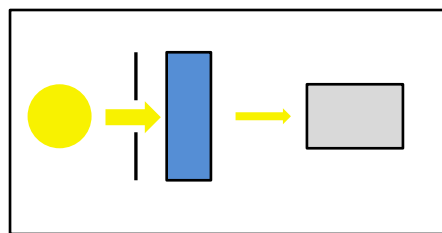
airborne TEP



collection



sea spray aerosol



absorbance



sea spray mass

