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1 **Amino acids, carbohydrates and lipids in the tropical oligotrophic Atlantic**

2 **Ocean: Sea-to-air transfer and atmospheric in situ formation**

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37   **Abstract**

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39   This study examines carbohydrates, amino acids, and lipids as important contributors to

40   organic carbon (OC) in the tropical Atlantic Ocean at the Cape Verde Atmospheric Observatory

41   (CVAO). The above compounds were measured in both surface seawater and in ambient

42   submicron aerosol particles to investigate their sea-to-air transfer, including their enrichment

43   in the sea surface microlayer (SML), potential atmospheric in situ formation or degradation,

44   and their oceanic contribution to the ambient marine aerosol particles.

45   In bulk seawater and the SML, similar distributions among species were found for the lipids

46   and carbohydrates with moderate SML enrichments (enrichment factor EF_{SML} = 1.3±0.2 and

47   1.1±0.5 respectively). In contrast, the amino acids exhibited a higher enrichment in the SML

48   with an averaging EF_{SML} of 2.4±0.3 although being less surface-active than lipids. The same

49   compounds studied in the seawater were found on the ambient submicron aerosol particles

50   whereas the lipids were more pronounced enriched ($EF_{aer.}$ = 1.6×10^5) compared to the amino

51   acids and carbohydrates ($EF_{aer.}$ = 1.5×10^3 and 1.3×10^3 respectively), likely due to their high

52   surface activity and/or the lipophilic character. Detailed molecular analysis of the seawater

53   and aerosol particles revealed changes in the relative composition of the single organic

54   compounds. They were most pronounced for the amino acids and are likely related to an in

55   situ atmospheric processing by biotic and/or abiotic reactions.

56   On average 49% of the OC on the aerosol particles (≙ 97 ng m^{-3}) could be attributed to the

57   specific components or component groups investigated in this study. The majority (43%) was

58   composed of lipids. Carbohydrates and amino acids made up less than 1% of the OC. This

59   shows that carbohydrates, at least resolved via molecular measurements of single sugars, do

60   not comprise a very large fraction of OC on marine aerosol particles, in contrast to other

61   studies. However, carbohydrate-like compounds are also present in the high lipid fraction

62   (e.g., as glycolipids), but their chemical composition could not be revealed by the

63   measurements performed here.

64   Previously determined OC components at the CVAO, in detail amines, oxalic acid, and

65   carbonyls, comprised an OC fraction of around 6%.

66   Since the identified compounds constituted about 50% of the OC and belong to the rather

67   short-lived biogenic material probably originating from the surface ocean, a pronounced

68   coupling between ocean and atmosphere was indicated for this oligotrophic region. The

69   remaining, non-identified OC fraction might in part contain recalcitrant OC, however, this

70   fraction does not constitute the vast majority of OC in the here investigated aerosol particles.

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1 Introduction

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79   Marine aerosol particles, their composition, sources and connection to the upper
80 ocean are not yet fully understood, however important to assign, first of all, marine particle
81 composition to the most important contribution of primary sources and involved processes.
82 Marine particle composition then impacts the carbon cycle, radiative properties of aerosol
83 particles, and the function of aerosol particles as cloud condensation nuclei (CCN) and ice-
84 nucleating particles (INP), i.e. marine aerosol-cloud interaction (Abbatt et al., 2019;Brooks and
85 Thornton, 2018;Burrows et al., 2013;Gantt and Meskhidze, 2013;Pagnone et al., 2019;Patel
86 and Rastogi, 2020). Marine aerosol particles, notably in the sub-micrometer range, have been
87 shown to contain a large part of organic carbon (OC) in field experiments as well as in
88 laboratory studies, where nascent aerosol particles are generated by artificial bubble-bursting
89 mechanisms (Facchini et al., 2008;Keene et al., 2007;O'Dowd et al., 2004). Notably, the
90 laboratory experiments, where sources other than the ocean (such as long-range transport)
91 can be excluded, suggest that a certain part of the OC on the aerosol particles is transferred
92 directly from the ocean via bubble bursting (Facchini et al., 2008;Keene et al., 2007). The
93 mechanisms of the OC enrichment finally observed in aerosol particles are not yet fully
94 understood but are likely due to complex interaction at the ocean surface when air bubbles
95 rise and break. Air bubbles collect (organic) matter at their surface (the gas/water interface)
96 when they ascend through the water column and when bursting, they produce film and jet
97 droplets that transfer the OC to the atmosphere and form aerosol particles. At the ocean
98 surface, the air bubbles enter the uppermost layer and the direct interface between the ocean
99 and the atmosphere called the sea surface microlayer (SML) (Engel et al., 2017). The SML is
100 described as a gel-like matrix that accumulates various organic and inorganic material (Cunliffe
101 et al., 2013). The influence of the SML on the bubble bursting and the emission of OC into the
102 atmosphere is difficult to determine and still controversial (Engel et al., 2017).

103   Based on the OC to sodium ratios in the ocean and the atmosphere, the OC in marine
104 aerosol particles has shown to be strongly enriched compared to seawater concentrations. OC
105 aerosol enrichment factors ($EF_{aer.}$) of the order of 10^2 in supermicron aerosol particles and of
106 the orders of 10^3 to 10^5 in submicron aerosol particles have been reported (Quinn et al., 2015
107 and references therein). However, individual chemical groups, such as amino acids, can be
108 even more enriched and $EF_{aer.}$ as high as 10^7 for these particular compounds have been
109 measured in submicron particles resulting from bubble bursting experiments within a tank
110 study (Triesch et al., 2021c). The OC transfer from the ocean to the atmosphere is likely highly
111 chemo-selective and a hydrophobic nature as well as surface-active properties of organic
112 compounds probably favour their transfer from the sea to the air (Rastelli et al., 2017;Schmitt-
113 Kopplin et al., 2012).

114   An important aspect for understanding the OC on the marine aerosol particles is the
115 connection to oceanic bio-productivity. Several studies suggested that the marine aerosol
116 composition is directly coupled to the productivity in the ocean, showing that at elevated
117 chlorophyll-a (chl-a) concentrations in the seawater the OC on the aerosol particles is
118 significantly higher compared to low oceanic productivity (O'Dowd et al., 2004;Facchini et al.,

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119   2008). A coupling between oceanic bio-productivity and aerosol composition is probably not
120   straightforward. Wang et al., (2015) showed that two successive phytoplankton blooms in the
121   tank seawater resulted in sea spray aerosols (SSA) with vastly different compositions and
122   properties. Other studies, however, propose that the OC transfer from the ocean to aerosol
123   particles is non-correlated to oceanic bio-productivity. Quinn et al., (2014) suggested that the
124   high reservoir of dissolved organic carbon (DOC) in the ocean is responsible for the organic
125   enrichment in freshly emitted sea spray aerosol, thus dominating over any influence of recent
126   local biological activity based on chlorophyll concentrations. Following this, Kieber et al.,
127   (2016) proposed that the major component in submicron sea-spray particles is of recalcitrant
128   nature with a stability of months to millennia. They suggested that this persistent form of OC
129   can very efficiently be transferred to the atmosphere via bubble bursting. Although they did
130   not perform a detailed chemical analysis, they concluded that the recalcitrant organic matter
131   exhibits surface-active properties. Applying natural abundance radiocarbon (14C)
132   measurements it was recently suggested that 19 to 40% of the OC associated with freshly
133   produced marine aerosol particles was refractory dissolved organic carbon (rDOC) (Beaupre
134   et al., 2019).

135   In addition to the direct, or primary transfer of organic compounds from the ocean to
136   the atmosphere, atmospheric processing changes the composition. Once released from the
137   ocean to the atmosphere, organic matter can be acidified within seconds due to a pH change
138   in the atmospheric particles or undergo fast photochemical oxidation (Kieber et al., 2016).
139   Moreover, biogenic in situ formation and degradation can change the OC composition in
140   marine aerosol particles and marine cloud water (Bianco et al., 2019;Malfatti et al.,
141   2019;Matulova et al., 2014). Ervens and Amato (2020) provided a framework for estimating
142   the production of secondary biological aerosol mass in clouds through microbial cell growth
143   and multiplication. This pathway could be a significant source of biological aerosol material
144   (Ervens and Amato, 2020;Khaled et al., 2021;Zhang et al., 2021). In other recent studies, the
145   in situ formation of amino acids by biotic and abiotic processes in cloud water was measured
146   and modelled (Jaber et al., 2021) and gel-like, organic particles, originally present in the ocean,
147   were suggested to form in situ in the marine atmosphere via biotic and/or abiotic pathways
148   (Haddrell and Thomas, 2017;Klein et al., 2016;van Pinxteren et al., 2022). Nevertheless,
149   despite a few studies, the atmospheric in situ formation of marine organic compounds and its
150   significance has not been extensively studied so far.

151   To understand the transfer processes of OC from the ocean to the aerosol particles,
152   potential atmospheric OC in situ formation as well as the coupling of the OC on the aerosol
153   particles to processes in the ocean, it is crucial to unravel the chemical composition of the
154   aerosol OC content. In the present study, we investigated samples from the tropical Atlantic
155   Ocean at the CVAO. The focus of this study was on the analysis of amino acids and
156   carbohydrates, as well as of lipid components, as these OC groups are reported as the major
157   marine organic matter groups in the seawater and therefore likely transferred to the aerosol
158   particles via bubble bursting (Burrows et al., 2014). We investigated these compounds on
159   marine aerosol particles and in the ocean SML and bulk water. The results will help to gain a
160   better understanding of the chemical composition of marine aerosol particles in this tropical

161 location, its transfer from the ocean and in situ formation, and finally, help to elucidate the
162 coupling of marine aerosol particles to the surface ocean in an oligotrophic region.
163

164 **2. Material and methods**

165 2.1 Aerosol and seawater sampling during the campaign
166

167 A field campaign (MarParCloud) was carried out at the Cape Verde Atmospheric Observatory
168 (CVAO, 16°51′′49′N, 24°52′02′E) in autumn 2017 (13.09.2017 – 13.10.2017) and the sampling
169 sites are illustrated and explained in detail in van Pinxteren et al., (2020). The CVAO is a remote
170 marine station in the tropical Atlantic Ocean located on the northeast coast of Sao Vicente
171 island and described in Carpenter et al., (2010) and Fomba et al., (2014). The ocean around
172 the Cape Verde Islands has the lowest surface chlorophyll in the North Atlantic Ocean with
173 values below 0.2 µg L^{-1} during the major part of each year with periodic events of slightly
174 elevated concentrations up to 0.7 µg L^{-1} (van Pinxteren et al., 2020 and refs therein).
175 Submicron aerosol particles were sampled with a high volume PM_1 aerosol sampler
176 (Digitel, Riemer, Germany) installed on the 30 m height tower at the coastline. The seawater
177 samples were taken at Bahia das Gatas, a coastal site that is situated upwind of the CVAO
178 about 4 km northwest in front of the station (Fig. S1). Fishing boats were rented to drive to
179 the open ocean and the SML was sampled with the glass plate technique as one typical SML
180 sampling strategy (Cunliffe and Wurl, 2014). To this end, a glass plate with a sampling area of
181 2000 cm^2 was vertically immersed into the water and then slowly drawn upwards with a
182 withdrawal rate between 5 and 10 cm s^{-1}. The surface film adheres to the surface of the glass
183 and is removed using framed Teflon wipers (Stolle et al., 2010;van Pinxteren et al., 2012). Bulk
184 seawater was collected with a specially designed device consisting of a plastic bottle mounted
185 on a telescopic rod. The bottle was opened underwater at depth of 1 m with a specifically
186 conceived seal-opener.
187 For the sampling of the oceanic water samples, great care was taken that all parts that
188 were in contact with the sample (glass plate, bottles) underwent an intense cleaning with 10%
189 HCl and rinsing with ultrapure water (resistivity = 18.2 MΩ cm) prior to the campaign and in
190 between sampling to avoid contamination and carry over problems.
191

192 2.2 Chemical analysis
193

194 2.2.1. Seawater and aerosol analysis: general considerations
195

196 Within the seawater analysis, we measured the dissolved amino acids (DAA) and
197 dissolved carbohydrates (DCHO) in the DOC fraction, as DOC represents by far the largest pool
198 of organic material in the ocean (Riebesell et al., 2011). DOC is the fraction of OC that passes
199 through a filter of 0.2–0.7 µm pore size (e.g. Zäncker et al., 2017). The lipid measurements
200 (from the same samples) were taken from Triesch et al., (2021b), are included in the DOC

201   fraction as well, being filtered via a 0.7 µm pore-sized filter (GF-F, Whatmann) and extracted
202   in an organic solvent, and refer to dissolved lipids (DL).

203   For the aerosol particles (PM_1), we focused on the water-soluble organic (WSOC)
204   fraction of the amino acids ($AA_{aer.}$) and carbohydrates ($CHO_{aer.}$). The lipids, however, were
205   extracted with an organic solvent and filtered (analogues to seawater), hence they comprise
206   the organic-soluble organic fraction of the aerosol particles ($Lipids_{aer.}$).

208   2.2.2. Analytical methods

210   For the analysis of the DCHO and $CHO_{aer.}$ as well as and the DAA and $AA_{aer.}$, molecular-
211   resolved techniques were applied. DCHO in filtered (0.2 µm Millex syringe filters) and
212   desalinated SML and bulk water samples as well as $CHO_{aer.}$, in the filtered PM_1 extracts were
213   quantified using High-Performance Anion-Exchange Chromatography coupled with Pulsed
214   Amperometric Detection (HPAEC-PAD) (Zeppenfeld et al., 2020;Zeppenfeld et al., 2021). After
215   an acid hydrolysis (0.8 M HCl, 100°C, 20 h) the monosaccharides fucose (Fuc), rhamnose (Rha),
216   arabinose (Ara), galactose (Gal), glucose (Glc), xylose (Xyl), mannose (Man), galactosamine
217   (GalN), glucosamine (GlcN), muramic acid (MurAc), galacturonic acid (GalAc) and glucuronic
218   acid (GlcAc) were measured.

219   For the DAA analysis, seawater samples (25.5 mL) were desalinated and concentrated
220   to a few mL as described in Triesch et al., (2021 a). For the $AA_{aer.}$ from PM_1 particles, an
221   aqueous extract of the amino acids was prepared by shaking a piece of the filter in 2 mL water.
222   After a filtration step (filter pore size: 0.2 µm) 25 µL of ascorbic acid (20 mg mL^{-1}, purity 99 %,
223   Sigma-Aldrich, St. Louis, Missouri, USA) was added to a 200 µL aliquot of the desalted seawater
224   / aqueous filter extract to avoid the oxidation of the obtained amino acids as discussed in
225   Mandalakis et al., (2010). Following the addition of 250 µL HCl (Supra-quality,
226   ROTIPURAN®Supra 35%, Carl Roth, Karlsruhe, Germany), the hydrolysis was performed at
227   110 °C for 20 h. After cooling to room temperature, the hydrolysed filtrate was evaporated,
228   resolved in 500 µL milliQ-water (Millipore Elix 3 and Element A10, Merck Millipore, Darmstadt,
229   Germany), filtered, derivatized using AccQ-Tag™ precolumn derivatization method (Waters,
230   Eschborn, Germany), and measured by ultra-high performance liquid chromatography with
231   electrospray ionization and Orbitrap mass spectrometry (UHPLC/ESI-Orbitrap-MS), as
232   described in Triesch et al., (2021a). The analytes comprise the amino acids glycine (Gly),
233   alanine (Ala), serine (Ser), glutamic acid (Glu), threonine (Thr), proline (Pro), tyrosine (Tyr),
234   valine (Val), phenylalanine (Phe), aspartic acid (Asp), isoleucine (Ile), leucine (Leu), methionine
235   (Met), glutamine (Gln) and γ-aminobutyric acid (GABA) (purity ≥ 99 %, Sigma-Aldrich, St. Louis,
236   Missouri, USA).

237   The DL and $Lipids_{aer.}$ measurements were taken from Triesch et al., (2021b), where the
238   analysis were done with a semi-molecular technique. For a better understanding of the data,
239   a short description is given in the following: Seawater or aerosol filters were extracted with
240   dichloromethane and filtered via GFF (Whatmann, pore size: 0.7 µm) described in more detail
241   in Triesch et al., (2021b). The filtered extract was analysed with thin-layer chromatography
242   (TLC). Lipid classes were separated on Chromarods SIII and calibrated with an external

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243 calibration with a mixture of standard lipids by a chromatograph flame ionisation detector
244 (FID) Iatroscan MKVI (Iatron, Japan). The separation scheme included elution steps in the
245 solvent systems with increasing polarity. More details of the separation technique are given
246 in Frka et al., (2009). This method was carefully optimized for seawater analysis and adopted
247 for aerosol particle analytics as described in Triesch et al., (2021b). The lipid classes included
248 hydrocarbons (HC), fatty acid methyl esters (ME), free fatty acids (FFA), alcohols (ALC), 1,3-
249 diacylglycerols (1,3 DG), 1,2-diacylglycerols (1,2 DG), monoacylglycerols (MG), wax esters
250 (WE), triacylglycerols (TG), phospholipids (PP) including phosphatidylglycerols (PG),
251 phosphatidylethanolamine (PE), phosphatidylcholines (PC), as well as glycolipids (GL) which
252 cover sulfoquinovosyldiacylglycerols (SQDG), monogalactosyl-diacylglycerols (MGDG),
253 digalactosyldiacylglycerols (DGDG) and sterols (ST). It needs to be underlined that, as no single
254 lipid compound but rather lipid groups (based on varying polarity in the TLC system) were
255 measured, the lipid results can be classified as analysis on a semi-molecular level.

256 Organic carbon (OC) on the aerosol particles (PM_1 samples) was measured by means
257 of a thermal-optical method using the Sunset Laboratory Dual-Optical Carbonaceous Analyzer
258 (Sunset Laboratory Inc., U.S.A.) from a filter piece with an area of 1.5 cm^2. The EUSAAR 2
259 temperature protocol was utilized, and a charring correction was applied (Cavalli et al., 2010).
260 The correction value for pyrolytic carbon was determined based on measurements of a sample
261 transmission using a 678 nm laser. Samples were thermally desorbed from the filter medium
262 under an inert He-atmosphere followed by an oxidizing O_2/He-atmosphere while applying
263 carefully controlled heating ramps. A flame ionization detector was used to quantify methane
264 following a catalytic methanation of CO_2.

265 Sodium was measured from filtered (0.45 µm syringe filter), aqueous extracts of the
266 PM_1 samples using ion chromatography (more details in Zeppenfeld et al., 2021 and van
267 Pinxteren et al., 2022).

269 2.3 Enrichment factors

271 The SML enrichment factor (EF_{SML}) was calculated by dividing the concentration of the
272 analyte in the SML with the concentration of the analyte in the bulk water after equation (1):

274 $$EF_{SML} = \frac{c\,(analyte)_{SML}}{c(analyte)_{bulk\ water}} \qquad (1)$$

276 An enrichment in the SML is indicated with $EF_{SML} > 1$ and a depletion in the SML with $EF_{SML} < 1$.
277 The enrichment factor of aerosol ($EF_{aer.}$) is a quantitative metric for comparing
278 compounds in the ocean and in the atmosphere. The $EF_{aer.}$ concept is mainly applied to closed
279 systems (Quinn et al., 2015 and refs.therein;Rastelli et al., 2017) as degradation and formation
280 pathways on aerosol particles including photochemical and biotic atmospheric reactions and
281 contributions from other (non-marine) sources are excluded from this parameter.
282 Nevertheless, for comparison purposes, it is useful to apply the $EF_{aer.}$ to open systems as well,
283 as shown in several studies (Russell et al., 2010;Triesch et al., 2021a;Triesch et al., 2021b;van

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284   Pinxteren et al., 2017;Zeppenfeld et al., 2021). To this end, the concentration of the analyte
285   of interest in each compartment is related to the respective sodium concentration (equation
286   2), because sodium is regarded as a conservative sea salt tracer transferred to the atmosphere
287   in the process of bubble bursting (Sander et al., 2003).
288

289    $$EF_{aer.} = \frac{c\ (analyte)_{aer.}/c\ (Na^+)_{aer.}}{c\ (analyte)_{seawater}/c\ (Na^+)_{seawater}}$$ (2)

290

291   As seawater concentration, the bulk water or the SML concentration can be applied.

292

293   **3. Results and Discussion**

294   3.1 SML and Bulk water

295   3.1.1 Concentration and composition of the dissolved amino acids (DAA), dissolved
296   carbohydrates (DCHO) and dissolved lipids (DL)

297   Figure 1 shows the analyte concentrations in the bulk ocean water (DAA: 80 ± 53 µg L^{-1},
298   ^{1}, DCHO: 78 ± 15 µg L^{-1}, DL: 70 ± 25 µg L^{-1}) and in the SML (DAA: 190 ± 238 µg L^{-1}, DCHO: 85 ±
299   30 µg L^{-1}, DL: 83 ± 24 µg L^{-1}). Hence, the average concentrations for DCHO and DL are similar
300   in the bulk water and in the SML (detailed values in Sect. 2.2.2, Tab. 1 and DL concentrations
301   can be found in Triesch et al., (2021b)). For the DAA, however, SML concentrations show a
302   larger variability compared to the other compounds and compared to the bulk water.
303   Resulting from the higher SML concentrations, the average SML enrichment factors of DAA is
304   2.4 ± 0.3 (Tab.1) and therefore higher compared to the DCHO (EF$_{SML}$ = 1.1 ± 0.5) and DL (EF$_{SML}$
305   = 1.3 ± 0.2). The high variability of the DAA concentrations agreed well with the free amino
306   acids (FAA) measured at this location during the MarParCloud campaign (Triesch et al., 2021a).
307   In addition, other studies have pointed out highly variable amino acid concentrations, for
308   example, Zänker et al., (2017) showed FAA concentrations between 32 and 1268 nmol L^{-1} and
309   DAA varied between 202 and 2007 nmol L^{-1} (for comparison: the here presented DAA values
310   correspond on average to 1064 nmol L^{-1} in the bulk water and 2536 nmol L^{-1} in the SML). High
311   enrichments of FAA in the SML were reported (Kuznetsova and Lee, 2002;Kuznetsova et al.,
312   2004;Reinthaler et al., 2008;van Pinxteren et al., 2012;Engel and Galgani, 2016) with FAA
313   enrichments up to 300 in the SML of the Cape Verde seawaters (Triesch et al., 2021a). A
314   preferential enrichment of FAA over dissolved combined amino acids as a consistent
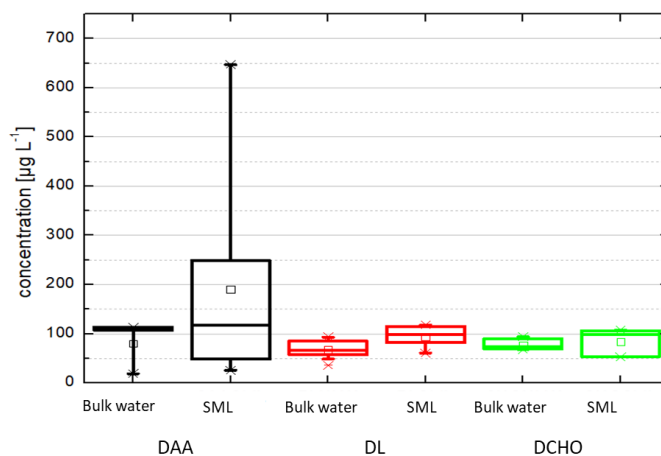315   microlayer feature was proposed (Kuznetsova et al., 2004).
316

Figure 1

317

318   Regarding the composition of the individual DAA measured here, clear differences
319   between the SML and the bulk water characteristics were observed (Fig. 2, blue and orange
320   bars, data in Tab. S1 - 4). Besides the higher concentrations in the SML, some DAA were only
321   present in the SML and not in the bulk water (below detection limit). This was most
322   pronounced for Glu, but also evident for Tyr and Iso (detailed values in Tab. S2).
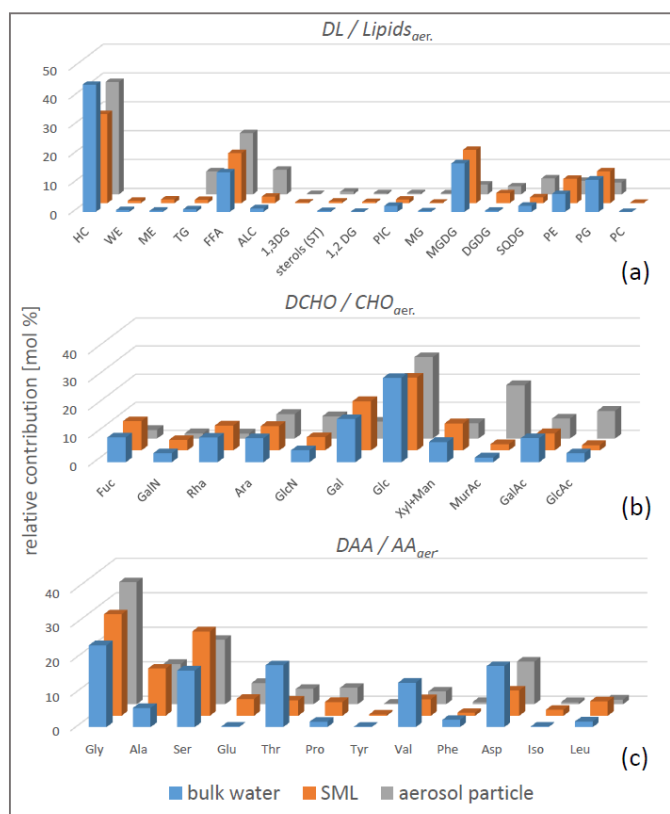

Figure 2

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324   In contrast to the DAA, the DCHO enrichment in the SML was less pronounced with an
325   EF_{SML} of 1.1±0.5 (Tab. 1), similar to SML enrichment values obtained for DCHO close to the
326   Peruvean upwelling regime (Zänker et al., 2017) and the Antarctic Peninsula (Zeppenfeld et
327   al., 2021). Regarding the relative composition, the DCHO showed a very homogeneous pattern
328   and were similar in the SML and the bulk water (Fig. 2, blue and orange bars).

329   The enrichment of the DL (EF_{SML} = 1.3±0.2, Tab. 1) was very similar to the DCHO
330   enrichment and is discussed in Triesch et al (2021a). From the individual lipid components and
331   the lipolysis index, it was concluded that the lipids were degraded only to a small extent
332   (Triesch et al., 2021b).

333   Altogether, the high and varying concentrations and enrichments of DAA in the SML in
334   contrast to the DCHO and DL concentrations underline that significant changes occur for the
335   DAA in the SML that are less pronounced for the other two compound groups.

336

337   3.1.2 Discussion of the SML enrichment

338

339   3.1.2.1 Surface vs bulk SML

340

341   The SML enrichment of DOC components is generally attributed to diffusion, turbulent
342   mixing, as well as scavenging, and transport of surface-active matter from rising gas bubbles
343   in the water column (Liss and Duce, 1997). Within the here investigated groups, the DL are the
344   most hydrophobic compounds and are generally classified as highly surface-active compounds
345   (Burrows et al., 2014). Although the surface-activity parameters (e.g. octanol-water partition
346   coefficient, density, Topological Polar Surface Area) of the individual lipids differ among each
347   other (values in Triesch et al., (2021b)), the lipids are overall more non-polar and surface active
348   compared to the carbohydrates and amino acids (values in Triesch et al., (2021a)).
349   Nevertheless, the enrichment of the DL in the SML was significantly lower compared to the
350   carbohydrates and amino acids.

351   One explanation for the finding lies in the sampled SML thickness. With the glass plate
352   technique, an SML thickness of about 100 µm is typically sampled (van Pinxteren et al., 2017).
353   Hence, the 100 µm-thick SML might be very well-mixed with regards to the soluble amino
354   acids and carbohydrates, however the surface-active compounds, such as the lipids, are
355   potentially located on the very top and form a thin (nm-thick) monolayer. In the literature, the
356   SML is described either as a series of sub-layers of wet and dry surfactants (Hardy, 1982) or as
357   a gelatinous matrix (Sieburth, 1983). Independent of the model, it can well be expected that
358   a gradient along the surface likely forms with surfactants at the very top of the layer. The
359   formation of a lipid-rich nanolayer on the very top agrees with surface-sensitive spectroscopy
360   measurements that are able to tackle the uppermost layer and found strong indications for a
361   nanolayer dominated by soluble surfactants (Lass and Friedrichs, 2011) and hydrophobic low
362   molecular weight lipids (Frka et al., 2012). The nanolayer is, however, not accessible with
363   currently applied bulk SML sampling methods. Therefore, the measured SML concentrations
364   may represent a very diluted (likely highly lipid-enriched) layer. Consequently, the SML

365   structure is even more complex, which needs to be considered, notably when discussing lipid
366   enrichments in the SML. Here, a combination of bulk measurements with dedicated surface
367   probing appears highly desirable.

368

369   3.1.2.2 Details of SML enrichment mechanisms

370

371   (i)   Co-adsorption and complexation

372

373   Regarding the DAA in detail, it is interesting to note that some compounds are
374   exclusively present in the SML, as mentioned above. They belong to hydrophilic (Glu),
375   hydrophobic (Iso) and neutral (Tyr) fractions of amino acids, underlining that their occurrence
376   in the SML might not be related (solely) to their physicochemical properties. Besides an air
377   bubble-driven transfer to the surface, enrichment in the SML can be supported by co-
378   adsorption mechanisms. Less surface-active compounds (e.g. amino acids and carbohydrates)
379   can be attached due to ionic interactions/coulomb interactions to the head groups of the air
380   bubble-attached surfactants (e.g. lipids) that mediate their enrichment in the SML (Burrows
381   et al., 2016;Hasenecz et al., 2019;Link et al., 2019;Schill et al., 2018). Co-adsorption can
382   provide an explanation for the high occurrence of non-surface active, very soluble
383   compounds, such as carbohydrates. A recent laboratory study showed different mechanisms
384   for the co-adsorption of polysaccharides that form a second calcium-bridges sublayer
385   underneath the monolayer whereas monosaccharides intercalate and induce reorganisation
386   within the nanolayer (Vazques de Vasquez et al., 2022). However, in the current study, only a
387   small SML enrichment of the DCHO and, hence, no indication for a strong co-adsorption was
388   observed.

389

390   (ii)   In-situ processing: Abiotic vs. biotic

391

392   Further explanations for the accumulation of dissolved compounds require an in situ
393   formation or degradation by SML-specific reactions that might be triggered by distinct
394   environmental conditions in the SML. Biotic pathways and abiotic SML-specific
395   (photo)chemical reactions may strongly impact OC cycling at the sea surface (Liss and Duce,
396   1997). The high abundance of the amino acid Glu in the SML observed here was also reported
397   in the FAA fraction by Triesch et al. (2021a) and can likely be explained by in situ formation.
398   Glu has shown to be produced via biotic and abiotic mechanisms, e.g. via the oxidation of
399   proline (Jaber et al., 2021 and refs. therein). Regarding biotic processes, it is well-known that
400   microorganisms have complex and highly interconnected enzymatic networks and are able to
401   biodegrade or biosynthesize organic compounds (KEEG pathway). Kuznetsova and Lee (2002)
402   suggested that stressed microorganisms, rich in dissolved and combined amino acids, may be
403   leached and released them, which in turn affects the pools of both these compounds in
404   seawater. Although such formation mechanisms generally happen in the upper ocean, there
405   are indications for SML-specific processes. Along a transect from upwelling regions toward
406   oligotrophic gyres it was found that while in the bulk water a clear trend toward degradation

407 of amino acids was observed, the production and degradation patterns of amino acids in the
408 SML were much more complex (Reinthaler et al., 2008). This is indicative of the role of the
409 SML in the production of labile DOC driven by coupled microbial and photochemical processes.
410 Similarly, Kuznetsova and Lee (2001) observed that peptide turnover was always faster in the
411 SML than in subsurface waters likely due to the greater concentrations of DOC in the SML. The
412 authors concluded that the accumulation of organic and inorganic compounds in the SML
413 leads to a more nutritious medium for microbial growth and consequently enzymatic
414 hydrolytic activity compared to the bulk water. Connecting this to the results presented here,
415 this might suggest that changes induced by abiotic and biotic processing need to be
416 considered when regarding the SML composition. Although such reactions likely also affect
417 lipids and carbohydrates, they seem to be most pronounced for amino acids.

418
419
420 (iii) Microbial nitrogen fixation at the sea-air interface
421
422 A further mechanism contributing to the high and variable SML enrichment of the DAA
423 at the current location might be a microbial nitrogen fixation at the sea-air interface.
424 Measurements showed that cyanobacteria are a very pronounced phytoplankton group in this
425 region (Franklin et al., 2009;Hepach et al., 2014;Zindler et al., 2012), which was dominant
426 during the MarParCloud campaign (van Pinxteren et al., 2020). Cyanobacteria are able to take
427 up nitrogen from the atmosphere (Zehr, 2011). Earlier studies showed that cyanobacteria-
428 fixed nitrogen is incorporated into amino acids (specifically glutamine (Carpenter et al., 1992)).
429 The calculated net amino acids release from cyanobacteria colonies (*Trichodesmium*
430 *thiebautii*) revealed that nitrogen fixation and the biogeochemical turnover of ambient amino
431 acids are an important source of recently fixed ("new") nitrogen within the oceanic surface
432 water (Capone et al., 1994). These considerations are, however, highly speculative and
433 demand further studies to investigate if nitrogen fixation and biosynthesis via cyanobacteria,
434 which occurs broadly in subtropical and tropical oceans (Montoya et al., 2007), might establish
435 a considerable route for amino acid formation and enrichment in the SML from the
436 atmospheric side.

437
438 (iv) Concluding remarks towards the SML enrichment
439
440 Although SML enrichment factors for amino acids, carbohydrates, and lipids have been
441 reported in the available literature, they have not previously been shown in such detailed
442 analysis for samples collected from the same site as was the case here. From this study it can
443 be concluded that the amino acids are strongly enriched in the SML compared to
444 carbohydrates and lipids, even under the same environmental conditions. In a recent study
445 we showed a strong enhancement of other nitrogen-containing species (aliphatic amines) in
446 the SML at this location, while the amine concentration in the bulk water was often not
447 detectable (van Pinxteren et al., 2019). This suggests that the pronounced SML enrichment

448   specifically exists for nitrogen-containing organic species. In addition, the absence of a relation

449   of the SML enrichment to physical compound parameters (e.g. hydrophobicity) suggests that

450   enrichment processes based on physicochemical properties (e.g. surface-activity) alone do not

451   drive SML enrichment. Rather, an SML in situ formation mechanism impacts the abundance

452   of amino acids and likely nitrogen-containing organic species in general.

453

454   3.2. Aerosol particles

455   3.2.1   Concentration and composition

456

457   After evaluating the concentrations of the analytes in seawater and the SML, in the

458   next step, their presence in the aerosol particles was investigated. The concentrations of AA_{aer}

459   and CHO_{aer} were 2.4 ± 1.1 ng m^{-3} and 1.0 ± 1.1 ng m^{-3}, respectively (Fig. 3, Tab. 1).
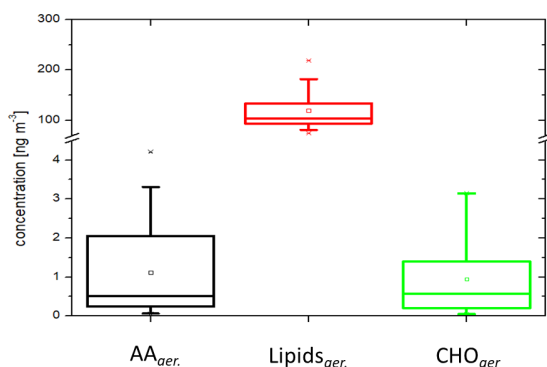

Figure 3

460

461   Compared to results from the Polar Regions, the CHO_{aer} concentrations in the tropical

462   Atlantic Ocean analysed here are at the lower end. Leck et al., (2013) determined

463   carbohydrates during the Arctic summer and found 0.7 - 20 ng m^{-3} in submicron particles.

464   Zeppenfeld et al., (2021) found carbohydrate concentrations between 0.2 - 11.3 ng m^{-3} in PM_{10}

465   atmospheric particles, in the Western Antarctic Peninsula, which contributed about 3% to the

466   OC. The same holds true for amino acids, the concentrations found here are slightly lower as

467   reported for other marine regions, e.g. FAA in Antarctic aerosol particles were on average 4.6

468   ng m^{-3} in Antarctic aerosol (Barbaro et al., 2015). Triesch et al., (2021a) found FAA

469   concentrations between 1.5 and 3.0 ng m^{-3} in the aerosol particles from the Cape Verdes.

470   Comparing the data obtained here those provided by analytical techniques that use

471   functional group information (FT-IR) showed that the latter techniques often report a large

472   fraction of alcohol (hydroxyl) functional groups on the marine aerosol particles identified and

473   attributed to carbohydrates (Cravigan et al., 2020;Frossard et al., 2014;Russell et al., 2010).

474   According to Russell et al., (2010), the primary marine signal in submicron marine aerosol over

475   the North Atlantic and Arctic Oceans is made on average for 88% of hydroxyl groups

476   corresponding to carbohydrate-like material. Such high fractions of carbohydrates were not

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477   found in the chromatographic analysis of $CHO_{aer.}$ presented here, nor in other studies using

478   similar methodologies (e.g. Zeppenfeld et al., 2021). In a recent study, using thermal

479   desorption mass spectrometry, it was suggested that carbohydrates only represented a minor

480   fraction of the FT-IR alcohol group and another thermally stable fraction, different to

481   carbohydrates, was the main contributor to the alcohol group (Lawler et al., (2020)). Hence,

482   previous FT-IR measurements might have over-predicted the carbohydrate fraction of marine

483   aerosol particles and further (molecular-based) analysis should be conducted in comparison

484   to resolve existing contradictions.

485   In contrast to the CAA_{aer} and $CCHO_{aer}$, the $Lipid_{aer}$ concentrations were 120 ± 43 ng m^{-3} and

486   therefore two orders of magnitude higher than the other two organic groups (Fig. 3, Tab. 1).

487   Previous lipid analysis on a molecular level revealed concentrations between 0.19 - 23 ng m^{-3}

488   for ALC and between 2.5 - 38 ng m^{-3} for free fatty acids on marine aerosol particles from the

489   western North Pacific (Kawamura et al., 2003) and a recent study found marine fatty acid

490   concentrations between 50 and 90 ng m^{-3} in coastal aerosol at Qingdao (Chen et al., 2021).

491   Mochida et al., (2002) observed saturated fatty acids (C14–C19) on marine aerosol particles

492   over the northern Pacific in atmospheric concentration between 0.8 - 24 ng m^{-3}. Hence, these

493   data are in the same order of magnitude as here measured lipid groups (ALC: 6.3 ng m^{-3}, free

494   fatty acids: 18.5 ng m^{-3}, values in Triesch et al. (2021b)). Cochran et al. (2017) showed that

495   lipid components (long-chain fatty acids) comprised a significant fraction of up to 75% of the

496   identified organic constituents in aerosol particles from a sea spray tank.

497   High lipid fractions in marine aerosol particles were also reported from NMR

498   measurements. Measurements of nascent aerosol particles produced from North Atlantic

499   seawater showed that the water-soluble organic aerosol fraction was purely aliphatic with

500   hydroxylated moieties of sugars, esters, and polyols, aliphatic groups adjacent to carbonyls,

501   amides, and acids, as well as aliphatic chains with terminal methyl-groups, typical of lipids

502   (Facchini et al., 2008). The water-insoluble organic faction was dominated by

503   lipopolysaccharides, known as phytoplankton exudate components. A recent study applying

504   NMR analysis to artificially produced aerosol particles after bubbling seawater from offshore

505   areas also showed proof of polyols and lipids (Decesari et al., 2020). NMR measurements of

506   lipids are mainly qualitative, however, the high fraction of lipid-like components from other

507   regions agrees well with the here presented high $Lipid_{aer}$ concentrations.

508   A high $Lipid_{aer}$ concentration as observed in the present study agrees well with the modelling

509   results of Burrows et al., (2014), where the ocean-atmosphere transfer was calculated

510   according to the physicochemical properties of the distinct OC groups. Lipids, as the most

511   surface active OC group comprise the largest fraction of the aerosol fraction, although their

512   (modelled) concentration in the seawater is lower compared to carbohydrates and amino

513   acids (Burrows et al., 2014). In a latter model modification, where additional co-adsorption

514   processes were included in the calculations, a more pronounced saccharidic fraction was

515   determined on the aerosol particles from the model results (Burrows et al., 2016), that is

516   different from the findings here, at least regarding the CHO_{aer} measured on a molecular level.

517   However, it needs to be considered that the lipids analysed here include glycolipids (MGDG,

518   DGDG, SQDG) which are components that have the solubility properties of a lipid but also

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519 contain one or more sugar molecules. The glycolipids comprise a non-negligible portion of the
520 OC on the aerosol particles (values in Table S6). This underlines the complexity of attributing
521 the OC to distinct organic groups and demonstrates that the applied analytical methods must
522 be taken into account when comparing concentrations of substance groups. This is discussed
523 in more detail in 3.4.1. Altogether, there seems to be a discrepancy between the measured
524 concentrations and the modelled results underlining that the transfer of the organic
525 compounds from the ocean to the atmosphere based on their physicochemical properties
526 might not be the only mechanism.

527

528 3.2.2   Aerosol enrichment

529

530 3.2.2.1 Aerosol enrichment factors

531   The finding that the Lipids$_{aer}$ were much higher concentrated than the AA$_{aer}$ and the
532 CHO$_{aer}$, resulted in a very different pattern compared to the similar seawater concentrations
533 (Fig. 1 vs. Fig. 3). To quantitatively compare the seawater and the aerosol concentration, the
534 EF$_{aer.}$ was calculated (values in Tab.1).

535

536   *Insert Table 1*

537

538   For the amino acids the EF$_{aer.}$ was between 9.2×10^2 (related to the SML) and 2.1×10^3
539 (related to the bulk water) and on average 1.5×10^3. For the carbohydrates the EF$_{aer.}$ was
540 between 1.3×10^3 (related to the SML) and 1.4×10^3 (related to the bulk water) and on average
541 1.3×10^3 and therefore similar to the EF$_{aer.}$ of the amino acids. For the lipids, however, the EF$_{aer.}$
542 was two orders of magnitude higher (EF$_{aer.}$ = 1.4×10^5, related to the SML; EF$_{aer.}$ = 1.7×10^5
543 related to the bulk water, EF$_{aer.}$ = 1.6×10^5 on average, Tab. 1).

544

545 3.2.2.2 Oceanic transfer and atmospheric in situ formation

546   The overall high enrichment of OC in the aerosol particles is explained by complex, not
547 yet finally resolved interactions at the ocean surface where organic matter is enriched over
548 sodium during the formation of film and jet droplets. Burrows et al., (2014) applied a
549 conceptual model ("slab" model) where all organics partition to the surface of a "slab" of
550 oceanic water or to both the outer and inner surfaces of a bubble film. The organic enrichment
551 is therefore significantly higher for the thinner bubble films (bubble film thicknesses: 0.01 to
552 1 μm) than for the thicker SML (typically sampled SML thicknesses: 20 to 400 μm). This
553 mechanism can explain an EF$_{aer.}$ of OC in submicron aerosol particles of 10^2 to 10^3 compared
554 to the SML (Burrows et al., 2014). However, EF$_{aer.}$ from ambient and laboratory-controlled
555 observations show that for some compounds even higher EF$_{aer.}$ are obtained. In a controlled
556 tank study, Rastelli et al., (2017) found strong enrichments for lipids (up to 1.4×10^5), as well as
557 for proteins (up to 1.2×10^5) and carbohydrates (up to 1.0×10^5, Tab. 1). A recent controlled
558 bubble-bursting laboratory study showed that amino acids enrichments can be up to 10^7 in

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559 submicron SSA between 0.029 and 0.060 µm (Triesch et al., 2021c). Similarly, Schmitt-Kopplin
560 et al., (2012) showed that surface-active biomolecules are preferentially transferred from
561 surface water into the atmosphere via bubble bursting. The ambient enrichment factor of the
562 lipids (10^5) shown here and in Triesch et al., (2021b) agreed well with laboratory-derived ones
563 (Rastelli et al., 2017) indicating that the transfer mechanisms simulated in lab experiments
564 agree with here performed observations in the field. Hence, the high surface activity and/or
565 the lipophilic character of the lipid classes might explain their strong (chemo-selective)
566 transfer to the aerosol particles. Even though the lipid composition on the aerosol particles
567 slightly varied from the seawater concentration (Triesch et al., 2021b), their transfer is likely
568 driven by their physicochemical properties (high surface activity and/or the lipophilic
569 character). For the amino acids and carbohydrates, however, more complex mechanisms may
570 determine their transfer to the atmosphere. Rastelli et al., (2017) suggested that diverse
571 biological processes on the ocean drive the properties of proteins and carbohydrates in the
572 ocean surface and in the atmosphere. Moreover, these compounds are known to be involved
573 in marine gel-like particle formation, such as transparent polymer particles (TEP) and
574 coomassie stained particles (CSP), observed in the ocean and more recently in the atmosphere
575 (Aller et al., 2017;Kuznetsova et al., 2005;van Pinxteren et al., 2022) adding more complexity
576 to the system. Hence not only a sea-to-air transfer but also atmospheric in situ formation and
577 degradation might determine the concentration of the OC and notably of the amino acid and
578 carbohydrates. This suggests that atmospheric processing plays an important role besides the
579 physical-driven bubble bursting sea-air transfer of OC.
580
581 3.2.3 Limitations of the concept of an aerosol enrichment factor
582
583   When comparing OC in the ocean and the atmosphere, it needs to be considered that
584 processes in the ocean and the atmosphere happen on different timescales. In addition, the
585 seawater samples comprise spot samplings in the ocean while the sampling period of PM_1
586 aerosol particles at the CVAO covers a time span of 24h. These issues make a comparison
587 between the ocean and atmospheric data very challenging. However, the air masses arriving
588 at the CVAO often followed the water current (Pena-Izquierdo et al., 2012;van Pinxteren et
589 al., 2017) and suggest a strong link between the upper ocean and the aerosol particles, as
590 mainly winds drive the ocean currents in the upper 100 m of the ocean. Besides the ocean,
591 Saharan dust is a strong aerosol source at the Cape Verde islands, most pronounced in the
592 months December to February (Fomba et al., 2014). The backward trajectories as well as the
593 mass concentrations of inorganic ions and mineral dust tracers on the aerosol particles
594 measured during the campaign suggested a predominant marine origin with low to medium
595 dust influences (van Pinxteren et al., 2020). Moreover, dust generally influences the
596 supermicron particles to a larger extent than the submicron particles analysed here (Fomba
597 et al., 2013). Hence, although different factors certainly affect the aerosol composition, it is
598 reasonable to assume a strong oceanic contribution.
599
600

601   3.3. Seawater and aerosol particles: Comparison of the relative composition

602   Regarding the organic components on the aerosol particles, the same compounds that
603   were present in the seawater were generally present on the aerosol particles (Fig. 2, grey bars,
604   and values in Tab. S1 - 4). However, the relative composition of distinct compounds was, at
605   least partly, different. Regarding the carbohydrate composition, the percentages of MurAc,
606   GlcAc, and GlcN in the aerosol particles were higher compared to the seawater. MurAc and
607   GlcN are important constituents in the cell walls of marine microorganisms and notably,
608   MurAc serves as a proxy for bacterial biomass (Mimura and Romano, 1985). Its high
609   concentration might indicate an enrichment of bacteria on the aerosol particles. Zeppenfeld
610   et al., (2021) detected similar (biogenic) carbohydrates in particles sampled in the western
611   Antarctic peninsula and suggested that marine bacteria in atmospheric particles may
612   metabolize a part of the oceanic carbohydrates in a selective enzymatic way analogous to the
613   bacterial processes in seawater. Such processes might explain the changed carbohydrate
614   composition and are likely not restricted to a specific oceanic regime, as they seem to happen
615   in the Southern Ocean (Zeppenfeld et al., 2021) as well as in the tropical Atlantic Ocean,
616   observed here. The elevated relative occurrence of GlcAc found here agrees well with the
617   recent finding of a high abundance of gel-like material in aerosol particles at the CVAO,
618   strongly enriched towards sodium compared to seawater (van Pinxteren et al., 2022) as GlcAc
619   is one main component of marine gelatinous exopolysaccharides (Casillo et al., 2018;Krembs
620   et al., 2002). Regarding the lipids, surfactants such as free fatty acids as well as lipophilic
621   compounds, such as hydrocarbons, had major contributions in the seawater and on the
622   aerosol particles, respectively. However, TG, an energy storage lipid, had a higher contribution
623   to the aerosol particles versus the ocean water. In addition, some other, minor-contributing
624   lipid classes were partly different in the two compartments (Triesch et al., 2021b).
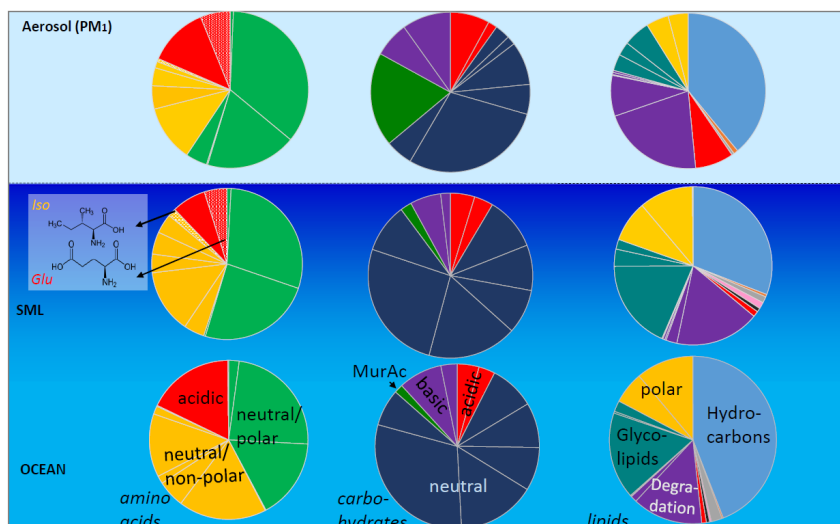
625
626
627   Figure 4

628

629   The most remarkable difference in relative composition in seawater and in aerosol
630   particles was found for amino acids, as some DAA were clearly present in the SML and in the
631   aerosol particles but not in the bulk water (e.g. Iso and Glu, Fig. 4, individual values in Tab. S5).
632   The amino acids generally differed a lot regarding their SML and bulk water composition. This
633   was visible in the data set presented here for the DAA, and also reported for the FAA measured
634   from the same campaign (Triesch et al., 2021a). Recently it was reported that the acidic amino
635   acid Glu (in the form of FAA) is transferred to SSA to a large extent (Triesch et al., 2021c) and
636   the results of the present study suggest that Glu might be transferred solely from the SML
637   (and not from the bulk water) to the aerosol particles. However, besides the oceanic transfer,
638   Glu can result from an in situ formation on the aerosol particles. Similarly to the seawater, Glu
639   might form from biotic or abiotic reactions on the aerosol particles. From the here performed
640   measurements it is not possible to differentiate between a selective transfer of Glu from the
641   SML and its biotic and abiotic in situ formation in aerosol particles. Recently, Jaber et al.,
642   (2021) and Renard et al., (2022) evaluated the atmospheric aging of the amino acids and
643   considered biotic and abiotic (mainly oxidation) processing. Their calculations revealed
644   different atmospheric lifetimes for the individual amino acids related to oxidation and
645   biological processes, respectively. For example, the amino acids Ser and Ala are degraded
646   quickly by biological processes (lifetime of a few hours) but are more stable towards oxidation
647   (Renard et al., 2022). Such studies can help to understand the patterns of the amino acids as
648   observed here and relate them to sources and atmospheric processing. The presence of Ser
649   and Ala in the here investigated aerosol particles could therefore indicate that biodegradation
650   of these compounds was not pronounced. However, additional studies are needed to better
651   understand atmospheric biotic and abiotic processing. In addition, the transfer of individual
652   DAA exclusively from the SML shall be investigated in further research, preferably within
653   characterized and controlled bubbling systems.

654

655   3.4 Contribution to aerosol particle OC

656

657   3.4.1 Molecular and semi-molecular analysis

658   OC concentrations in marine aerosol particles during this campaign varied between
659   0.13 and 0.31 µg m^{-3} with an average value of 0.20 µg m^{-3} (values in Tab. S6). This agreed well
660   with previous OC measurements from the CVAO that were on average 0.27 µg m^{-3} OC (van
661   Pinxteren et al., 2017). To date, only a small percentage of OC on marine aerosol particles is
662   characterised on a molecular level and organic biomarkers often comprise only a few percent
663   of the OC (Chen et al., 2021). Fu et al., (2011) measured more than 140 different single organic
664   species in marine aerosol from different oceanic areas, however the identified species
665   composed less than 5.7% of the OC. Taking together the OC components described here
666   (Lipids$_{aer.}$, AA$_{aer.}$, CHO$_{aer.}$), the contribution of the identified components to the OC was
667   calculated. Furthermore, the OC contribution of recently identified components from previous
668   campaigns within the Cape Verde region, in detail: aliphatic amines, methane-sulfonic acid
669   (MSA), oxalic acid and carbonyls (van Pinxteren et al., 2015) was included. The OC contribution

670   of the single compounds and compound groups are shown in Fig. 5 (values in Tab. S7).
671   Altogether, about 48% of the average OC could be explained by the identified components.
672   Regarding the maximum (0.31 µg m^{-3}) and minimum (0.13 µg m^{-3}) OC concentrations within
673   the campaign, the OC contributions of the respective compounds are between 31% (lower
674   limit) and 74% (upper limit). The major identified OC fraction (related to the average OC) were
675   the Lipids$_{aer}$ with 43%. They were followed by the aliphatic amines (4%) that is in good
676   agreement with a recent CVAO study, where they contributed on average with 5% to the
677   (water-soluble) OC (van Pinxteren et al., 2019). MSA (0.9%) and oxalic acid (0.3%) were minor
678   OC contributors. Similarly, the CHO$_{aer}$ and the AA$_{aer}$ made up a minor percentage with 0.3 and
679   0.4% respectively. Regarding the lipids, it needs to be taken into account that the here
680   performed analysis was not based on the detection of individual analytes but on an organic
681   solvent extraction of the particle constituents and extract separation by solvents with
682   different polarities applied in the TLC. The analytical method has been optimized for seawater
683   analysis. Within atmospheric processing, additional organic compounds can form, which
684   might contain a hydrophobic part and are potentially included in the lipid analysis performed
685   here. However, the large similarity of the lipid groups within the seawater and the aerosol
686   particles, as well as the agreeing concentrations of the single lipid groups (FFA, ALC) to
687   measurements from other marine stations with molecular techniques (GC-MS) suggests that
688   the same compound classes were present in the particles. Future analysis of the lipid fraction
689   with mass spectrometric techniques will help to better resolve this issue.
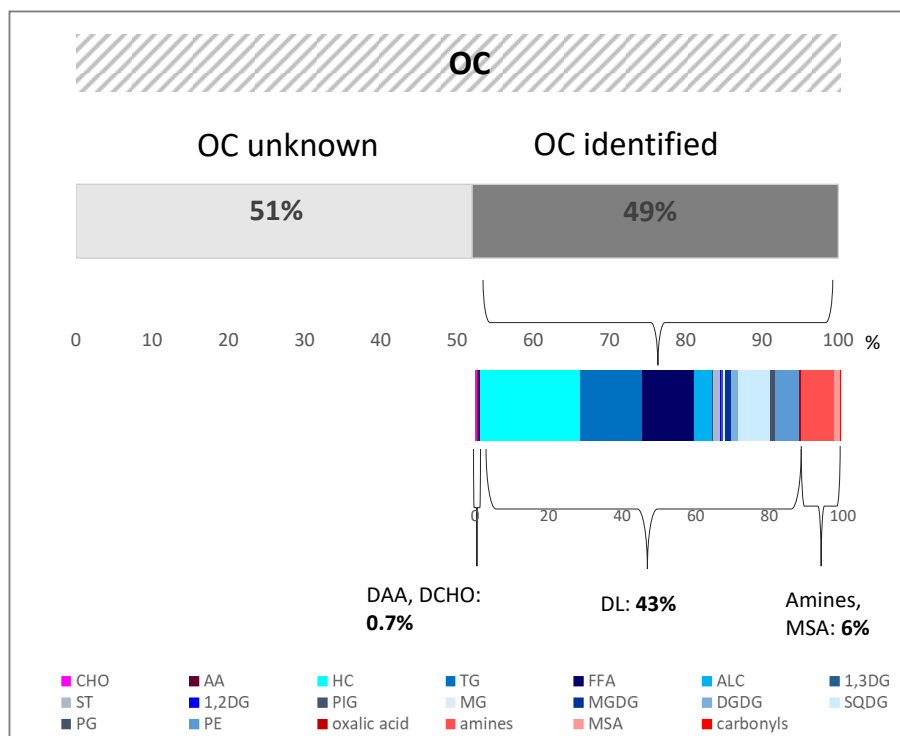690
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Figure 5

692
693
694 3.4.2 Non-identified, recalcitrant OC in aerosol particles
695

696   About 50% of the aerosol OC remained uncharacterized on a molecular and semi-
697 molecular level. The non-identified OC part may contain larger macromolecules that might be
698 composed of particulate or non-soluble forms in water (carbohydrates and proteins) or
699 organic solvents (lipids) that were removed in the performed analysis during the sample
700 preparation step. In addition, the unknown part might include component groups that belong
701 to the soluble carbohydrates or amino acids but are either too stable or too labile for the
702 sample preparation procedure (e.g. within the hydrolysis step). Moreover, other complex
703 molecules that cannot be captured with the here applied methods likely add to the unknown
704 fraction including optical active parts summarized as chromophore dissolved organic matter
705 (CDOM), humic-like substances (HULIS), brown carbon and water-soluble pigments. As
706 mentioned above, NMR analysis showed that SSA contains a large fraction of
707 lipopolysaccharides comprising complex, macromolecular groups of sugars, esters, carbonyls
708 as well as acids and lipids (Facchini et al., 2008). However, these components have, not yet
709 been analysed in aerosol particles using chromatographic techniques. The uncharacterized
710 part may also contain particulate OC compounds, such as larger aggregates of marine gels or
711 gel-like particles like transparent exopolymer particles (TEP). High TEP number concentrations

712   in aerosol particles were recently identified in the Cape Verde region (van Pinxteren et al.,

713   2022) and high mass-concentrations of TEP (e.g. 1.2 µg m^{-3} for PM$_1$) were identified in the

714   western North Atlantic atmosphere (Aller et al., 2017).

715   Kieber et al., (2016) suggested that the major OC component in submicron sea-spray

716   particles is recalcitrant and recently Beaupre et al., (2019) proposed that 19 to 40% of the OC

717   associated with freshly produced marine aerosol particles was refractory dissolved OC. This

718   percentage agrees with the non-identified OC part from the present study. However, we

719   cannot identify or classify the remaining OC fraction nor attribute it with certainty to the

720   recalcitrant OC. Further studies of the OC, in tropical as well as in other areas of the world, are

721   needed to continue resolving OC and related transfer and formation processes. Nevertheless,

722   the potentially recalcitrant OC fraction in the here investigated oligotrophic region does not

723   seem to constitute the majority of OC as reported by Kieber et al., (2016).

724

725   3.5 Sea-to-air fluxes of the individual OC groups

726

727   The CVAO is localized in an oligotrophic region and should therefore be representative

728   of most of the Earth's ocean surface. POA emission rates are strongly varying, however

729   modelling studies have estimated global submicron marine POA emission rates of 10±5 Tg yr^{-1}

730   (Gantt and Meskhidze, 2013). Based on this emission flux and the contribution of the

731   compounds to the OC fraction, we estimated the fluxes of the DAA, DL, and DCHO.

732   Accordingly, the annual rates of emission from the ocean to the atmosphere are 0.03±0.01 Tg

733   yr^{-1} for DCHO, 0.04±0.02 Tg yr^{-1} for DAA, and 4.2±2.1 Tg yr^{-1} for DL. The unknown OC that

734   includes the potentially recalcitrant components, has a sea-to-air flux of 4.8±2.4 Tg yr^{-1}.

735   However, this approach only includes the bubble-bursting-mediated transfer of the respective

736   compounds and neglects additional sources and formation processes. Ervens and Amato

737   (2020) investigated the global impact of bacterial processes on carbon mass in cloud water

738   and estimated formation rates of 3.7 Tg C yr^{-1} of secondary biological aerosol that are in the

739   range of the POA emissions via sea spray (Gantt and Meskhidze, 2013). Hence, the here

740   presented emission fluxes can change once such processes are quantified for these

741   compounds.

742

743   **4   Summary and Conclusions**

744

745   A comprehensive chemical investigation of the OC in the tropical Atlantic Ocean and

746   the atmosphere with a focus on its contribution to the OC on the marine aerosol particles in

747   this particular region was performed.

748   Regarding seawater, a similar distribution of the DL and DCHO was found with a small

749   SML enrichment. However, the DAA, and likely the N-containing compounds in general,

750   exhibit a high and varying enrichment in the SML (although being less surface active than

751   lipids). Although conclusions on the detailed processes that lead to the varying DAA

752   concentrations and the high SML enrichments cannot be resolved here, the results clearly

753   show that processes leading to changes in the organic matter composition within the upper

754   100 µm oceanic layer are more pronounced for the group of amino acids (and possibly for
755   nitrogen groups in general) compared to other organic compounds groups such as lipids and
756   carbohydrates. The SML is probably a very complex, heterogeneous, seasonality-dependent,
757   and reactive matrix forming a lipid-rich nanolayer.
758   The same compounds studied in the seawater were found on the ambient submicron aerosol
759   particles and strongly enriched towards sea salt ($EF_{aer.}$ = 10^3 for the carbohydrates and the
760   amino acids). To this end, the lipids were even stronger enriched in the submicron aerosol
761   particles ($EF_{aer.}$ = 10^5) compared to the other groups. This indicates a preferred transfer of the
762   lipids (towards the carbohydrates and the amino acids) from the ocean to the atmosphere
763   that is probably driven by their physicochemical properties (high surface-activity and/or the
764   lipophilic character). Detailed molecular analysis of the seawater and aerosol particles
765   revealed changes in the relative composition of the single compounds. They were most
766   pronounced for the amino acids and are likely related to an in situ atmospheric processing by
767   biotic and/or abiotic reactions that require further investigations. A high saccharide fraction,
768   as described in other studies, could not be found on the aerosol particles, at least when
769   regarding the molecular-resolved carbohydrate analysis. However, saccharidic-like
770   components (e.g. glycolipids) are also included in the lipid fraction analysed here in non-
771   negligible concentrations. This shows that when comparing the concentrations of substance
772   groups, the analytical methods used must be taken into account. Nevertheless, even small
773   concentrations of carbohydrates and amino acids on marine aerosol particles can have a high
774   impact in their microphysical properties, e.g. as ice nucleating particles, and are worth further
775   studying.
776   Altogether, the marine aerosol particles analysis applied here shows that half of the
777   OC can be attributed to specific components or component groups. However, the molecular-
778   level analysed fraction explains only a small part of the OC, the CHO_{aer} and AA_{aer} made up less
779   than 1%. This shows that the typical representatives of carbohydrates and amino acids within
780   the marine OC measured here can explain only a very small fraction of the organic composition
781   of the aerosol particles on a molecular level. Amines, MSA, oxalic acid carbonyls comprise a
782   fraction of around 6%. Lipid analysis unravel 43% of the OC on the aerosol particles, however,
783   the $Lipid_{aer}$ composition on a molecular level cannot be obtained from the here performed
784   measurements. Altogether, about 50% of the OC remained uncharacterized on a molecular
785   and semi-molecular level. Regarding further marine aerosol analysis, it will be important to
786   resolve the large part of lipid compounds in more detail, as well as getting molecular-level
787   information on the remaining, unidentified OC. This shows the need for further detailed
788   analytical OC studies in the marine environment to resolve formation and transfer
789   mechanisms.
790   Nevertheless, the results obtained here show that even in such an oligotrophic region,
791   at least half of the OC on the aerosol particles consists of rather short-lived biogenic material,
792   likely from the surface ocean. The non-resolved OC might in part be of recalcitrant nature, as
793   indicated in other studies (Beaupre et al., 2019;Kieber et al., 2016;Lawler et al., 2020).
794   However, the (potentially) recalcitrant OC does not constitute the majority of the OC in the

795 oligotrophic Atlantic Ocean. Future studies should complement the here achieved data with
796 investigations of the particulate OC fraction.
797   Finally, since large parts of the open oceans are oligotrophic, the findings of this study
798 might be relevant to the majority of the world oceans.

799

800 Data availability. The amino acid and carbohydrate data are listed in the SI. The lipid data are
801 available through the World Data Centre PANGAEA under the following link:
802 https://doi.org/10.1594/PANGAEA.921832 (Triesch et al., 2020). Further data can be made
803 available by the authors upon request.

804

805 Special issue statement.

806

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820
821 Author contributions
822 MvP led the MarParCloud campaign with support from KWF and HH. SZ performed the
823 analytical measurements of the carbohydrates and supported the data analysis. SF was in
824 charge of the lipid measurements. NT performed the measurements of the amino acids. MvP
825 performed the data interpretation and wrote the manuscript with contributions from all
826 authors.

827
828 Competing interest
829 The authors declare that they have no conflict of interest.

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833   References:

834   Abbatt, J. P. D., Leaitch, W. R., Aliabadi, A. A., Bertram, A. K., Blanchet, J. P., Boivin-Rioux, A.,
835   Bozem, H., Burkart, J., Chang, R. Y. W., Charette, J., Chaubey, J. P., Christensen, R. J., Cirisan, A.,
836   Collins, D. B., Croft, B., Dionne, J., Evans, G. J., Fletcher, C. G., Gali, M., Ghahremaninezhad, R., Girard,
837   E., Gong, W. M., Gosselin, M., Gourdal, M., Hanna, S. J., Hayashida, H., Herber, A. B., Hesaraki, S.,
838   Hoor, P., Huang, L., Hussherr, R., Irish, V. E., Keita, S. A., Kodros, J. K., Kollner, F., Kolonjari, F., Kunkel,
839   D., Ladino, L. A., Law, K., Levasseur, M., Libois, Q., Liggio, J., Lizotte, M., Macdonald, K. M., Mahmood,
840   R., Martin, R. V., Mason, R. H., Miller, L. A., Moravek, A., Mortenson, E., Mungall, E. L., Murphy, J. G.,
841   Namazi, M., Norman, A. L., O'Neill, N. T., Pierce, J. R., Russell, L. M., Schneider, J., Schulz, H., Sharma,
842   S., Si, M., Staebler, R. M., Steiner, N. S., Thomas, J. L., von Salzen, K., Wentzell, J. J. B., Willis, M. D.,
843   Wentworth, G. R., Xu, J. W., and Yakobi-Hancock, J. D.: Overview paper: New insights into aerosol
844   and climate in the Arctic, Atmospheric Chemistry and Physics, 19, 2527-2560, 10.5194/acp-19-2527-
845   2019, 2019.

846   Aller, J. Y., Radway, J. C., Kilthau, W. P., Bothe, D. W., Wilson, T. W., Vaillancourt, R. D., Quinn,
847   P. K., Coffman, D. J., Murray, B. J., and Knopf, D. A.: Size-resolved characterization of the
848   polysaccharidic and proteinaceous components of sea spray aerosol, Atmos. Environ., 154, 331-347,
849   10.1016/j.atmosenv.2017.01.053, 2017.

850   Barbaro, E., Zangrando, R., Vecchiato, M., Piazza, R., Cairns, W. R. L., Capodaglio, G., Barbante,
851   C., and Gambaro, A.: Free amino acids in Antarctic aerosol: potential markers for the evolution and
852   fate of marine aerosol, Atmospheric Chemistry and Physics, 15, 5457-5469, 10.5194/acp-15-5457-
853   2015, 2015.

854   Beaupre, S. R., Kieber, D. J., Keene, W. C., Long, M. S., Maben, J. R., Lu, X., Zhu, Y. T., Frossard,
855   A. A., Section, J. D. K., Duplessis, P., Chang, R. Y. W., and Bisgrove, J.: Oceanic efflux of ancient marine
856   dissolved organic carbon in primary marine aerosol, Science Advances, 5, 10.1126/sciadv.aax6535,
857   2019.

858   Bianco, A., Deguillaume, L., Chaumerliac, N., Vaïtilingom, M., Wang, M., Delort, A.-M., and
859   Bridoux, M. C.: Effect of endogenous microbiota on the molecular composition of cloud water: a
860   study by Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS), Scientific
861   Reports, 9, 7663, 10.1038/s41598-019-44149-8, 2019.

862   Brooks, S. D., and Thornton, D. C. O.: Marine Aerosols and Clouds, in: Annual Review of Marine
863   Science, Vol 10, edited by: Carlson, C. A., and Giovannoni, S. J., Annual Review of Marine Science,
864   Annual Reviews, Palo Alto, 289-313, 2018.

865   Burrows, S. M., Hoose, C., Poschl, U., and Lawrence, M. G.: Ice nuclei in marine air: biogenic
866   particles or dust?, Atmospheric Chemistry and Physics, 13, 245-267, 10.5194/acp-13-245-2013, 2013.

867   Burrows, S. M., Ogunro, O., Frossard, A. A., Russell, L. M., Rasch, P. J., and Elliott, S. M.: A
868   physically based framework for modeling the organic fractionation of sea spray aerosol from bubble
869   film Langmuir equilibria, Atmospheric Chemistry and Physics, 14, 13601-13629, 10.5194/acp-14-
870   13601-2014, 2014.

871   Burrows, S. M., Gobrogge, E., Fu, L., Link, K., Elliott, S. M., Wang, H. F., and Walker, R.:
872   OCEANFILMS-2: Representing coadsorption of saccharides in marine films and potential impacts on
873   modeled marine aerosol chemistry, Geophysical Research Letters, 43, 8306-8313,
874   10.1002/2016gl069070, 2016.

875   Capone, D. G., Ferrier, M. D., and Carpenter, E. J.: Amino Acid Cycling in Colonies of the
876 Planktonic Marine Cyanobacterium TRICHODESMIUM-THIEBAUTII, Applied and Environmental
877 Microbiology, 60, 3989-3995, 10.1128/aem.60.11.3989-3995.1994, 1994.

878   Carpenter, E. J., Bergman, B., Dawson, R., Siddiqui, P. J. A., Soderback, E., and Capone, D. G.:
879 Glutamine Synthetase and Nitrogen Cycling in Colinies of the Marine Diazotrophic Cyanobacteria
880 TRICHODESMIUM SPP, Applied and Environmental Microbiology, 58, 3122-3129,
881 10.1128/aem.58.9.3122-3129.1992, 1992.

882   Carpenter, L. J., Fleming, Z. L., Read, K. A., Lee, J. D., Moller, S. J., Hopkins, J. R., Purvis, R. M.,
883 Lewis, A. C., Müller, K., Heinold, B., Herrmann, H., Fomba, K. W., van Pinxteren, D., Müller, C., Tegen,
884 I., Wiedensohler, A., Müller, T., Niedermeier, N., Achterberg, E. P., Patey, M. D., Kozlova, E. A.,
885 Heimann, M., Heard, D. E., Plane, J. M. C., Mahajan, A., Oetjen, H., Ingham, T., Stone, D., Whalley, L.
886 K., Evans, M. J., Pilling, M. J., Leigh, R. J., Monks, P. S., Karunaharan, A., Vaughan, S., Arnold, S. R.,
887 Tschritter, J., Pohler, D., Friess, U., Holla, R., Mendes, L. M., Lopez, H., Faria, B., Manning, A. J., and
888 Wallace, D. W. R.: Seasonal characteristics of tropical marine boundary layer air measured at the
889 Cape Verde Atmospheric Observatory, Journal of Atmospheric Chemistry, 67, 87-140,
890 10.1007/s10874-011-9206-1, 2010.

891   Casillo, A., Lanzetta, R., Parrilli, M., and Corsaro, M. M.: Exopolysaccharides from Marine and
892 Marine Extremophilic Bacteria: Structures, Properties, Ecological Roles and Applications, Marine
893 Drugs, 16, 10.3390/md16020069, 2018.

894   Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J. P.: Toward a standardised thermal-
895 optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol,
896 Atmospheric Measurement Techniques, 3, 79-89, 2010.

897   Chen, Q., Guo, Z. G., Yu, M., Sachs, J. P., Hou, P. F., Li, L., Jin, G. E., Liu, Y. Y., and Zhao, M. X.:
898 Lipid biomarker estimates of seasonal variations of aerosol organic carbon sources in coastal
899 Qingdao, China, Organic Geochemistry, 151, 10.1016/j.orggeochem.2020.104148, 2021.

900   Cochran, R. E., Ryder, O. S., Grassian, V. H., and Prather, K. A.: Sea Spray Aerosol: The Chemical
901 Link between the Oceans, Atmosphere, and Climate, Accounts Chem. Res., 50, 599-604,
902 10.1021/acs.accounts.6b00603, 2017.

903   Cravigan, L. T., Mallet, M. D., Vaattovaara, P., Harvey, M. J., Law, C. S., Modini, R. L., Russell, L.
904 M., Stelcer, E., Cohen, D. D., Olsen, G., Safi, K., Burrell, T. J., and Ristovski, Z.: Sea spray aerosol
905 organic enrichment, water uptake and surface tension effects, Atmos. Chem. Phys., 20, 7955-7977,
906 10.5194/acp-20-7955-2020, 2020.

907   Cunliffe, M., Engel, A., Frka, S., Gasparovic, B., Guitart, C., Murrell, J. C., Salter, M., Stolle, C.,
908 Upstill-Goddard, R., and Wurl, O.: Sea surface microlayers: A unified physicochemical and biological
909 perspective of the air-ocean interface, Progress in Oceanography, 109, 104-116,
910 10.1016/j.pocean.2012.08.004, 2013.

911   Cunliffe, M., and Wurl, O.: "Guide to best practices to study the ocean's surface", Occasional
912 Publications of the Marine Biological Association of the United Kingdom (Plymouth, UK), 118 pp. ,
913 (http://www.mba.ac.uk/NMBL/). 2014.

914   Decesari, S., Paglione, M., Rinaldi, M., Dall'Osto, M., Simó, R., Zanca, N., Volpi, F., Facchini, M.
915 C., Hoffmann, T., Götz, S., Kampf, C. J., O'Dowd, C., Ceburnis, D., Ovadnevaite, J., and Tagliavini, E.:
916 Shipborne measurements of Antarctic submicron organic aerosols: an NMR perspective linking

917   multiple sources and bioregions, Atmos. Chem. Phys., 20, 4193-4207, 10.5194/acp-20-4193-2020,
918   2020.

919   Engel, A., and Galgani, L.: The organic sea-surface microlayer in the upwelling region off the
920   coast of Peru and potential implications for air-sea exchange processes, Biogeosciences, 13, 989-
921   1007, 10.5194/bg-13-989-2016, 2016.

922   Engel, A., Bange, H., Cunliffe, M., Burrows, S., Friedrichs, G., Galgani, L., Herrmann, H.,
923   Hertkorn, N., Johnson, M., Liss, P., Quinn, P., Schartau, M., Soloviev, A., Stolle, C., Upstill-Goddard, R.,
924   van Pinxteren, M., and Zäncker, B.: The Ocean's Vital Skin: Toward an Integrated Understanding of
925   the Sea Surface Microlayer, Front. Mar. Sci., 4, doi: 10.3389/fmars.2017.00165, 2017.

926   Ervens, B., and Amato, P.: The global impact of bacterial processes on carbon mass,
927   Atmospheric Chemistry and Physics, 20, 1777-1794, 10.5194/acp-20-1777-2020, 2020.

928   Facchini, M. C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis,
929   D., Flanagan, R., Nilsson, E. D., de Leeuw, G., Martino, M., Woeltjen, J., and O'Dowd, C. D.: Primary
930   submicron marine aerosol dominated by insoluble organic colloids and aggregates, Geophysical
931   Research Letters, 35, 10.1029/2008gl034210, 2008.

932   Fomba, K. W., Müller, K., van Pinxteren, D., and Herrmann, H.: Aerosol size-resolved trace
933   metal composition in remote northern tropical Atlantic marine environment: case study Cape Verde
934   islands, Atmos. Chem. Phys., 13, 4801-4814, 10.5194/acp-13-4801-2013, 2013.

935   Fomba, K. W., Müller, K., van Pinxteren, D., Poulain, L., van Pinxteren, M., and Herrmann, H.:
936   Long-term chemical characterization of tropical and marine aerosols at the Cape Verde Atmospheric
937   Observatory (CVAO) from 2007 to 2011, Atmospheric Chemistry and Physics, 14, 8883-8904,
938   10.5194/acp-14-8883-2014, 2014.

939   Franklin, D., Poulton, J. A., Steinke, M., Young, J., Peeken, I., and Malin, G.: Dimethylsulphide,
940   DMSP-lyase activity and microplankton community structure inside and outside of the Mauritanian
941   upwelling, Progress in Oceanography, 83, 134–142, 2009.

942   Frka, S., Kozarac, Z., and Ćosović, B.: Characterization and seasonal variations of surface active
943   substances in the natural sea surface micro-layers of the coastal Middle Adriatic stations, Estuarine
944   Coastal and Shelf Science, 85, 555-564, 10.1016/j.ecss.2009.09.023, 2009.

945   Frka, S., Pogorzelski, S., Kozarac, Z., and Ćosović, B.: Physicochemical Signatures of Natural Sea
946   Films from Middle Adriatic Stations, The Journal of Physical Chemistry A, 116, 6552-6559,
947   10.1021/jp212430a, 2012.

948   Frossard, A. A., Russell, L. M., Burrows, S. M., Elliott, S. M., Bates, T. S., and Quinn, P. K.:
949   Sources and composition of submicron organic mass in marine aerosol particles, Journal of
950   Geophysical Research-Atmospheres, 119, 12977-13003, 10.1002/2014jd021913, 2014.

951   Fu, P., Kawamura, K., and Miura, K.: Molecular characterization of marine organic aerosols
952   collected during a round-the-world cruise, Journal of Geophysical Research-Atmospheres, 116,
953   10.1029/2011jd015604, 2011.

954   Gantt, B., and Meskhidze, N.: The physical and chemical characteristics of marine primary
955   organic aerosol: a review, Atmospheric Chemistry and Physics, 13, 3979-3996, 10.5194/acp-13-3979-
956   2013, 2013.

957   Haddrell, A. E., and Thomas, R. J.: Aerobiology: Experimental Considerations, Observations, and
958 Future Tools, Applied and Environmental Microbiology, 83, 10.1128/aem.00809-17, 2017.

959   Hardy, J. T.: The Sea-Surface Microlayer - Biology, Chemistry and Antrophogenic Enrichment,
960 Progress in Oceanography, 11, 307-328, 10.1016/0079-6611(82)90001-5, 1982.

961   Hasenecz, E. S., Kaluarachchi, C. P., Lee, H. D., Tivanski, A. V., and Stone, E. A.: Saccharide
962 Transfer to Sea Spray Aerosol Enhanced by Surface Activity, Calcium, and Protein Interactions, ACS
963 Earth Space Chem., 3, 2539-2548, 10.1021/acsearthspacechem.9b00197, 2019.

964   Hepach, H., Quack, B., Ziska, F., Fuhlbrügge, S., Atlas, E., Peeken, I., Krüger, K., and Wallace, D.
965 W. R.: Drivers of diel and regional variations of halocarbon emissions from the tropical North East
966 Atlantic, Atmospheric Chemistry and Physics, 14, 1255–1275, 10.5194/acp-14-1255-2014, 2014.

967   Jaber, S., Joly, M., Brissy, M., Leremboure, M., Khaled, A., Ervens, B., and Delort, A. M.: Biotic
968 and abiotic transformation of amino acids in cloud water: experimental studies and atmospheric
969 implications, Biogeosciences, 18, 1067-1080, 10.5194/bg-18-1067-2021, 2021.

970   Kawamura, K., Ishimura, Y., and Yamazaki, K.: Four years' observations of terrestrial lipid class
971 compounds in marine aerosols from the western North Pacific, Global Biogeochemical Cycles, 17,
972 10.1029/2001gb001810, 2003.

973   Keene, W. C., Maring, H., Maben, J. R., Kieber, D. J., Pszenny, A. A. P., Dahl, E. E., Izaguirre, M.
974 A., Davis, A. J., Long, M. S., Zhou, X., Smoydzin, L., and Sander, R.: Chemical and physical
975 characteristics of nascent aerosols produced by bursting bubbles at a model air-sea interface, Journal
976 of Geophysical Research-Atmospheres, 112, 10.1029/2007jd008464, 2007.

977   Khaled, A., Zhang, M. H., Amato, P., Delort, A. M., and Ervens, B.: Biodegradation by bacteria in
978 clouds: an underestimated sink for some organics in the atmospheric multiphase system,
979 Atmospheric Chemistry and Physics, 21, 3123-3141, 10.5194/acp-21-3123-2021, 2021.

980   Kieber, D. J., Keene, W. C., Frossard, A. A., Long, M. S., Maben, J. R., Russell, L. M., Kinsey, J. D.,
981 Tyssebotn, I. M. B., Quinn, P. K., and Bates, T. S.: Coupled ocean-atmosphere loss of marine
982 refractory dissolved organic carbon, Geophysical Research Letters, 43, 2765-2772,
983 10.1002/2016gl068273, 2016.

984   Klein, A. M., Bohannan, B. J. M., Jaffe, D. A., Levin, D. A., and Green, J. L.: Molecular Evidence
985 for Metabolically Active Bacteria in the Atmosphere, Frontiers in Microbiology, 7,
986 10.3389/fmicb.2016.00772, 2016.

987   Krembs, C., Eicken, H., Junge, K., and Deming, J. W.: High concentrations of exopolymeric
988 substances in Arctic winter sea ice: implications for the polar ocean carbon cycle and cryoprotection
989 of diatoms, Deep-Sea Research Part I-Oceanographic Research Papers, 49, 2163-2181,
990 10.1016/s0967-0637(02)00122-x, 2002.

991   Kuznetsova, M., and Lee, C.: Enhanced extracellular enzymatic peptide hydrolysis in the sea-
992 surface microlayer, Marine Chemistry, 73, 319-332, 10.1016/s0304-4203(00)00116-x, 2001.

993   Kuznetsova, M., and Lee, C.: Dissolved free and combined amino acids in nearshore seawater,
994 sea surface microlayers and foams: Influence of extracellular hydrolysis, Aquat. Sci., 64, 252-268,
995 10.1007/s00027-002-8070-0, 2002.

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996   Kuznetsova, M., Lee, C., Aller, J., and Frew, N.: Enrichment of amino acids in the sea surface
997 microlayer at coastal and open ocean sites in the North Atlantic Ocean, Limnol. Oceanogr., 49, 1605-
998 1619, 10.4319/lo.2004.49.5.1605, 2004.

999   Kuznetsova, M., Lee, C., and Aller, J.: Characterization of the proteinaceous matter in marine
1000 aerosols, Marine Chemistry, 96, 359-377, 10.1016/j.marchem.2005.03.007, 2005.

1001   Lass, K., and Friedrichs, G.: Revealing structural properties of the marine nanolayer from
1002 vibrational sum frequency generation spectra, J. Geophys. Res.-Oceans, 116, 10.1029/2010jc006609,
1003 2011.

1004   Lawler, M. J., Lewis, S. L., Russell, L. M., Quinn, P. K., Bates, T. S., Coffman, D. J., Upchurch, L.
1005 M., and Saltzman, E. S.: North Atlantic marine organic aerosol characterized by novel offline thermal
1006 desorption mass spectrometry: polysaccharides, recalcitrant material, and secondary organics,
1007 Atmospheric Chemistry and Physics, 20, 16007-16022, 10.5194/acp-20-16007-2020, 2020.

1008   Leck, C., Gao, Q., Rad, F. M., and Nilsson, U.: Size-resolved atmospheric particulate
1009 polysaccharides in the high summer Arctic, Atmospheric Chemistry and Physics, 13, 12573-12588,
1010 10.5194/acp-13-12573-2013, 2013.

1011   Link, K. A., Spurzem, G. N., Tuladhar, A., Chase, Z., Wang, Z. M., Wang, H. F., and Walker, R. A.:
1012 Organic Enrichment at Aqueous Interfaces: Cooperative Adsorption of Glucuronic Acid to DPPC
1013 Monolayers Studied with Vibrational Sum Frequency Generation, Journal of Physical Chemistry A,
1014 123, 5621-5632, 10.1021/acs.jpca.9b02255, 2019.

1015   Liss, P. S., and Duce, R. A.: The Sea Surface and Global Change, edited by: Cambrigde University
1016 Press, C., 1997.

1017   Malfatti, F., Lee, C., Tinta, T., Pendergraft, M. A., Celussi, M., Zhou, Y. Y., Sultana, C. M., Rotter,
1018 A., Axson, J. L., Collins, D. B., Santander, M. V., Morales, A. L. A., Aluwihare, L. I., Riemer, N., Grassian,
1019 V. H., Azam, F., and Prather, K. A.: Detection of Active Microbial Enzymes in Nascent Sea Spray
1020 Aerosol: Implications for Atmospheric Chemistry and Climate, Environmental Science & Technology
1021 Letters, 6, 171-177, 10.1021/acs.estlett.8b00699, 2019.

1022   Mandalakis, M., Apostolaki, M., and Stephanou, E. G.: Trace analysis of free and combined
1023 amino acids in atmospheric aerosols by gas chromatography-mass spectrometry, J. Chromatogr. A,
1024 1217, 143-150, 10.1016/j.chroma.2009.11.021, 2010.

1025   Matulova, M., Husarova, S., Capek, P., Sancelme, M., and Delort, A. M.: Biotransformation of
1026 Various Saccharides and Production of Exopolymeric Substances by Cloud-Borne Bacillus sp 3B6,
1027 Environmental Science & Technology, 48, 14238-14247, 10.1021/es501350s, 2014.

1028   Mimura, T., and Romano, J. C.: Muramin acid measurements for bacterial investigations in
1029 marine environments by high-pressure-liquid-chromatography, Applied and Environmental
1030 Microbiology, 50, 229-237, 10.1128/aem.50.2.229-237.1985, 1985.

1031   Mochida, M., Kitamori, Y., Kawamura, K., Nojiri, Y., and Suzuki, K.: Fatty acids in the marine
1032 atmosphere: Factors governing their concentrations and evaluation of organic films on sea-salt
1033 particles, Journal of Geophysical Research-Atmospheres, 107, 10.1029/2001jd001278, 2002.

1034   Montoya, J. P., Voss, M., and Capone, D. G.: Spatial variation in N_2-fixation rate
1035 and diazotroph activity in the Tropical Atlantic, Biogeosciences, 4, 369-376, 10.5194/bg-4-369-2007,
1036 2007.

1037   O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon,
1038   Y. J., and Putaud, J. P.: Biogenically driven organic contribution to marine aerosol, Nature, 431, 676-
1039   680, Doi 10.1038/Nature02959, 2004.

1040   Pagnone, A., Volker, C., and Ye, Y.: Processes affecting dissolved iron across the Subtropical
1041   North Atlantic: a model study, Ocean Dyn., 69, 989-1007, 10.1007/s10236-019-01288-w, 2019.

1042   Patel, A., and Rastogi, N.: Chemical Composition and Oxidative Potential of Atmospheric PM10
1043   over the Arabian Sea, ACS Earth Space Chem., 4, 112-121, 10.1021/acsearthspacechem.9b00285,
1044   2020.

1045   Pena-Izquierdo, J., Pelegri, J. L., Pastor, M. V., Castellanos, P., Emelianov, M., Gasser, M.,
1046   Salvador, J., and Vazquez-Dominguez, E.: The continental slope current system between Cape Verde
1047   and the Canary Islands, Scientia Marina, 76, 65-78, 10.3989/scimar.03607.18C, 2012.

1048   Quinn, P. K., Bates, T. S., Schulz, K. S., Coffman, D. J., Frossard, A. A., Russell, L. M., Keene, W.
1049   C., and Kieber, D. J.: Contribution of sea surface carbon pool to organic matter enrichment in sea
1050   spray aerosol, Nature Geoscience, 7, 228-232, 10.1038/ngeo2092, 2014.

1051   Quinn, P. K., Collins, D. B., Grassian, V. H., Prather, K. A., and Bates, T. S.: Chemistry and
1052   Related Properties of Freshly Emitted Sea Spray Aerosol, Chemical Reviews, 115, 4383-4399,
1053   10.1021/cr5007139, 2015.

1054   Rastelli, E., Corinaldesi, C., Dell'Anno, A., Lo Martire, M., Greco, S., Facchini, M. C., Rinaldi, M.,
1055   O'Dowd, C., Ceburnis, D., and Danovaro, R.: Transfer of labile organic matter and microbes from the
1056   ocean surface to the marine aerosol: an experimental approach, Scientific Reports, 7,
1057   10.1038/s41598-017-10563-z, 2017.

1058   Reinthaler, T., Sintes, E., and Herndl, G. J.: Dissolved organic matter and bacterial production
1059   and respiration in the sea-surface microlayer of the open Atlantic and the western Mediterranean
1060   Sea, Limnology and Oceanography, 53, 122-136, 10.4319/lo.2008.53.1.0122, 2008.

1061   Renard, P., Brissy, M., Rossi, F., Leremboure, M., Jaber, S., Baray, J. L., Bianco, A., Delort, A. M.,
1062   and Deguillaume, L.: Free amino acid quantification in cloud water at the Puy de Dome station
1063   (France), Atmospheric Chemistry and Physics, 22, 2467-2486, 10.5194/acp-22-2467-2022, 2022.

1064   Riebesell U., F. V. J., Hansson L. & Gattuso J.-P. (eds) (2011) Guide to best practices for ocean
1065   acidification research and data reporting. [reprinted edition including erratum]. Luxembourg,
1066   Publications Office of the European Union, 258pp. (EUR 24872 EN). DOI 10.2777/66906, 2011.

1067   Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K., and Bates, T. S.: Carbohydrate-like
1068   composition of submicron atmospheric particles and their production from ocean bubble bursting,
1069   Proceedings of the National Academy of Sciences of the United States of America, 107, 6652-6657,
1070   10.1073/pnas.0908905107, 2010.

1071   Sander, R., Keene, W. C., Pszenny, A. A. P., Arimoto, R., Ayers, G. P., Baboukas, E., Cainey, J. M.,
1072   Crutzen, P. J., Duce, R. A., Honninger, G., Huebert, B. J., Maenhaut, W., Mihalopoulos, N., Turekian, V.
1073   C., and Van Dingenen, R.: Inorganic bromine in the marine boundary layer: a critical review,
1074   Atmospheric Chemistry and Physics, 3, 1301-1336, 2003.

1075   Schill, S. R., Burrows, S. M., Hasenecz, E. S., Stone, E. A., and Bertram, T. H.: The Impact of
1076   Divalent Cations on the Enrichment of Soluble Saccharides in Primary Sea Spray Aerosol,
1077   Atmosphere, 9, 10.3390/atmos9120476, 2018.

1078   Schmitt-Kopplin, P., Liger-Belair, G., Koch, B. P., Flerus, R., Kattner, G., Harir, M., Kanawati, B.,
1079   Lucio, M., Tziotis, D., Hertkorn, N., and Gebefuegi, I.: Dissolved organic matter in sea spray: a transfer
1080   study from marine surface water to aerosols, Biogeosciences, 9, 1571-1582, 10.5194/bg-9-1571-
1081   2012, 2012.

1082   Sieburth, J. M.: Microbiological and organic-chemical processes in the surface and mixed
1083   layers, in: Air-Sea Exchange of Gases and Particles, edited by: Liss, P. S., Slinn, W.G.N., Reidel
1084   Publishers Co, Hingham, MA, 121-172, 1983.

1085   Stolle, C., Nagel, K., Labrenz, M., and Jürgens, K.: Succession of the sea-surface microlayer in
1086   the coastal Baltic Sea under natural and experimentally induced low-wind conditions,
1087   Biogeosciences, 7, 2975-2988, 2010.

1088   Triesch, N., van Pinxteren, M., Engel, A., and Herrmann, H.: Concerted measurements of free
1089   amino acids at the Cape Verde Islands: High enrichments in submicron sea spray aerosol particles
1090   and cloud droplets, Atmos. Chem. Phys., 21, 163–181, 2021a.

1091   Triesch, N., van Pinxteren, M., Frka, S., Stolle, C., Spranger, T., Hoffmann, E. H., Gong, X., Wex,
1092   H., Schulz-Bull, D., Gašparović, B., and Herrmann, H.: Concerted measurements of lipids in seawater
1093   and on submicrometer aerosol particles at the Cabo Verde islands: biogenic sources, selective
1094   transfer and high enrichments, Atmos. Chem. Phys., 21, 4267-4283, 10.5194/acp-21-4267-2021,
1095   2021b.

1096   Triesch, N., van Pinxteren, M., Salter, M., Stolle, C., Pereira, R., Zieger, P., and Herrmann, H.:
1097   Sea Spray Aerosol Chamber Study on Selective Transfer and Enrichment of Free and Combined
1098   Amino Acids, ACS Earth Space Chem., 5, 1564-1574, 10.1021/acsearthspacechem.1c00080, 2021c.

1099   van Pinxteren, M., Müller, C., Iinuma, Y., Stolle, C., and Herrmann, H.: Chemical
1100   Characterization of Dissolved Organic Compounds from Coastal Sea Surface Micro layers (Baltic Sea,
1101   Germany), Environmental Science & Technology, 46, 10455-10462, 10.1021/es204492b, 2012.

1102   van Pinxteren, M., Fiedler, B., van Pinxteren, D., Iinuma, Y., Koertzinger, A., and Herrmann, H.:
1103   Chemical characterization of sub-micrometer aerosol particles in the tropical Atlantic Ocean: marine
1104   and biomass burning influences, Journal of Atmospheric Chemistry, 72, 105-125, 10.1007/s10874-
1105   015-9307-3, 2015.

1106   van Pinxteren, M., Barthel, S., Fomba, K., Müller, K., von Tümpling, W., and Herrmann, H.: The
1107   influence of environmental drivers on the enrichment of organic carbon in the sea surface microlayer
1108   and in submicron aerosol particles – measurements from the Atlantic Ocean, Elem Sci Anth, 5,
1109   https://doi.org/10.1525/elementa.225, 2017.

1110   van Pinxteren, M., Fomba, K. W., van Pinxteren, D., Triesch, N., Hoffmann, E. H., Cree, C. H. L.,
1111   Fitzsimons, M. F., von Tumpling, W., and Herrmann, H.: Aliphatic amines at the Cape Verde
1112   Atmospheric Observatory: Abundance, origins and sea-air fluxes, Atmos. Environ., 203, 183-195,
1113   10.1016/j.atmosenv.2019.02.011, 2019.

1114   van Pinxteren, M., Fomba, K. W., Triesch, N., Stolle, C., Wurl, O., Bahlmann, E., Gong, X. D.,
1115   Voigtlander, J., Wex, H., Robinson, T. B., Barthel, S., Zeppenfeld, S., Hoffmann, E. H., Roveretto, M., Li,
1116   C. L., Grosselin, B., Daele, V., Senf, F., van Pinxteren, D., Manzi, M., Zabalegui, N., Frka, S., Gasparovic,
1117   B., Pereira, R., Li, T., Wen, L., Li, J. R., Zhu, C., Chen, H., Chen, J. M., Fiedler, B., Von Tumpling, W.,
1118   Read, K. A., Punjabi, S., Lewis, A. C., Hopkins, J. R., Carpenter, L. J., Peeken, I., Rixen, T., Schulz-Bull,
1119   D., Monge, M. E., Mellouki, A., George, C., Stratmann, F., and Herrmann, H.: Marine organic matter in
1120   the remote environment of the Cape Verde islands - an introduction and overview to the

Atmospheric
Chemistry
and Physics
Discussions

1121   MarParCloud campaign, Atmospheric Chemistry and Physics, 20, 6921-6951, 10.5194/acp-20-6921-
1122   2020, 2020.

1123   van Pinxteren, M., Robinson, T. B., Zeppenfeld, S., Gong, X. D., Bahlmann, E., Fomba, K. W.,
1124   Triesch, N., Stratmann, F., Wurl, O., Engel, A., Wex, H., and Herrmann, H.: High number
1125   concentrations of transparent exopolymer particles in ambient aerosol particles and cloud water - a
1126   case study at the tropical Atlantic Ocean, Atmospheric Chemistry and Physics, 22, 5725-5742,
1127   10.5194/acp-22-5725-2022, 2022.

1128   Vazques de Vasquez, M. G., Rogers, M. M., Carter-Fenk, K. A., and Allen, H. C.: Discerning Poly-
1129   and Monosaccharide Enrichment Mechanisms: Alginate and Glucuronate Adsorption to a Stearic Acid
1130   Sea Surface Microlayer, ACS Earth Space Chem., 6, 1581-1595, 10.1021/acsearthspacechem.2c00066,
1131   2022.

1132   Wang, X., Sultana, C. M., Trueblood, J., Hill, T. C. J., Malfatti, F., Lee, C., Laskina, O., Moore, K.
1133   A., Beall, C. M., McCluskey, C. S., Cornwell, G. C., Zhou, Y., Cox, J. L., Pendergraft, M. A., Santander, M.
1134   V., Bertram, T. H., Cappa, C. D., Azam, F., DeMott, P. J., Grassian, V. H., and Prather, K. A.: Microbial
1135   Control of Sea Spray Aerosol Composition: A Tale of Two Blooms, ACS Central Science, 1, 124-131,
1136   10.1021/acscentsci.5b00148, 2015.

1137   Zäncker, B., Bracher, A., Röttgers, R., and Engel, A.: Variations of the Organic Matter
1138   Composition in the Sea Surface Microlayer: A Comparison between Open Ocean, Coastal, and
1139   Upwelling Sites Off the Peruvian Coast, Frontiers in Microbiology, 8, 10.3389/fmicb.2017.02369,
1140   2017.

1141   Zehr, J. P.: Nitrogen fixation by marine cyanobacteria, Trends in Microbiology, 19, 162-173,
1142   https://doi.org/10.1016/j.tim.2010.12.004, 2011.

1143   Zeppenfeld, S., van Pinxteren, M., Engel, A., and Herrmann, H.: A protocol for quantifying
1144   mono- and polysaccharides in seawater and related saline matrices by electro-dialysis (ED) -
1145   combined with HPAEC-PAD, Ocean Science, 16, 817-830, 10.5194/os-16-817-2020, 2020.

1146   Zeppenfeld, S., van Pinxteren, M., van Pinxteren, D., Wex, H., Berdalet, E., Vaqué, D., Dall'Osto,
1147   M., and Herrmann, H.: Aerosol Marine Primary Carbohydrates and Atmospheric Transformation in
1148   the Western Antarctic Peninsula, ACS Earth Space Chem., 10.1021/acsearthspacechem.0c00351,
1149   2021.

1150   Zhang, M. H., Khaled, A., Amato, P., Delort, A. M., and Ervens, B.: Sensitivities to biological
1151   aerosol particle properties and ageing processes: potential implications for aerosol-cloud interactions
1152   and optical properties, Atmospheric Chemistry and Physics, 21, 3699-3724, 10.5194/acp-21-3699-
1153   2021, 2021.

1154   Zindler, C., Peeken, I., Marandino, C. A., and Bange, H. W.: Environmental control on the
1155   variability of DMS and DMSP in the Mauritanian upwelling region, Biogeosciences, 9, 1041-1051,
1156   10.5194/bg-9-1041-2012, 2012.

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1162 **Caption of Figures:**

1163 Figure 1: Box and whisker plot of the concentrations in seawater (µg L^{-1}), distinguished into
1164 SML and bulk water for the dissolved amino acids (DAA) in the SML (n = 6) and in bulk water
1165 (n = 6), the dissolved carbohydrates (DCHO) in the SML (n = 3) and in bulk water (n = 3) an for
1166 the dissolved lipids (DL) in the SML (n = 6) and in bulk water (n = 13).
1167 Each box encloses 50% of the data with the mean value represented as an open square and
1168 the median value represented as a line. The bottom of the box marks the 25% limit of the
1169 data, while the top marks the 75% limit. The lines extending from the top and bottom of each
1170 box are the 5% and 95% percentiles within the data set, while the asterisks indicate the data
1171 points lying outside of this range ("outliers").

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1173 Figure 2: Bar graph showing the average of the relative compositions (mol%) of dissolved lipids
1174 (DL) and *Lipids$_{aer.}$* (a), dissolved carbohydrates (DCHO) and CHO$_{aer.}$ (b) and dissolved amino
1175 acids (DAA) and AA$_{aer}$. (c) in the bulk water (blue bars), the SML (orange bars), and the PM$_1$
1176 aerosol particles (grey bars).

1177

1178 Figure 3: Box and whisker plot of the concentrations in the PM$_1$ aerosol particles (ng m^{-3}); n =
1179 8 for CHO$_{aer}$, n = 7 for AA$_{aer}$, n = 14 for Lipids$_{aer}$.
1180 Each box encloses 50% of the data with the mean value represented as an open square and
1181 the median value represented as a line. The bottom of the box marks the 25% limit of the
1182 data, while the top marks the 75% limit. The lines extending from the top and bottom of each
1183 box are the 5% and 95% percentiles within the data set, while the asterisks indicate the data
1184 points lying outside of this range ("outliers").

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1186 Figure 4: Scheme underlining the seawater (SML and bulk water) as well as the PM1 relative
1187 compositions of DL / *Lipids$_{aer.}$*, DCHO / CHO$_{aer.}$ and DAA / AA$_{aer}$. Assignment: amino acids:
1188 neutral/polar: Phe, Gly, Ser,Tyr, neutral/non-polar: Thr, Ala, Pro, Val, Leu, Iso, acidic: Aps, Glu;
1189 carbohydrates: basic: GlcN, GalN, neutral: Fuc, Rha, Ara, Gal, GlC, Xyl, Man, acidic: MurAc,
1190 GasAc, GlAc; lipids: hydrocarbons (HC), sterols (ST), pigments (PIC), fatty acid methyl ester
1191 (MW), membrane component: WE, metabolic reserve: TC, degradation lipids: FFA, ALC, 1,3
1192 DG, 1,2 DG, MG, glycolipids: MGDG, DGDG, SQDG, polar lipids: PE, PG, PC.

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1194 Figure 5: Graph showing the identified and non-identified OC and the OC contribution of the
1195 respective organic compound groups in the PM$_1$ aerosol particles. The contribution of the
1196 measured organic compounds to the total OC fraction was calculated on a carbon basis.

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1202 Table 1: Average concentrations of the organic groups and enrichment factor (EF) in the SML
1203 (EF$_{SML}$) and in the aerosol particles (EF$_{aer}$) after equations 1 and 2. EF are calculated from the
1204 average concentrations of the respective groups (values in Tab. 1). For EF$_{aer.}$ the average Na$^+$
1205 concentration in seawater (1.0E+04 mg L^{-1}) and the average Na$^+$ concentrations in the PM$_1$
1206 particles from the MarParCloud campaign (100 ng m^{-3}, values from Triesch et al., (2021b))
1207 were applied. For comparison, the last column lists the EF$_{aer}$ for PM$_1$ from a chamber study
1208 (Rastelli et al., 2017).

1209

			DCHO				
SML (µg L^{-1})	Bulk water (µg L^{-1})	PM$_1$ (ng m^{-3})	EF$_{SML}$	EF$_{aer}$ (related to the SML)	EF$_{aer}$ (related to the bulk water)	EF$_{aer}$ (average)	EF$_{aer}$ (Rastelli et al., 2017)
85 ± 30	78 ± 15	1.0 ± 1.1	1.1±0.5	1.26E+03	1.35E+03	1.31E+03	1.00E+05
n = 3	n = 3	n = 8					
			DAA				
SML	Bulk water	PM1					
190 ± 238	80 ± 53	2.4 ± 1.1	2.4±0.3	9.23E+02	2.07E+03	1.50E+03	1.20E+05
n = 6	n = 3	n = 7					
			DL				
SML	Bulk water	PM1					
83 ± 24	70 ± 25	120 ± 43	1.3±0.2	1.42E+05	1.71E+05	1.57E+05	1.40E+05
n = 6	n = 13	n = 14					

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