Amino acids, carbohydrates and lipids in the tropical oligotrophic Atlantic Ocean: Sea-to-air transfer and atmospheric in situ formation

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Abstract

This study examines carbohydrates, amino acids, and lipids as important contributors to organic carbon (OC) in the tropical Atlantic Ocean at the Cape Verde Atmospheric Observatory (CVAO). The above compounds were measured in both surface seawater and in ambient submicron aerosol particles to investigate their sea-to-air transfer, including their enrichment in the sea surface microlayer (SML), potential atmospheric in situ formation or degradation, and their oceanic contribution to the ambient marine aerosol particles.

In bulk seawater and the SML, similar distributions among species were found for the lipids and carbohydrates with moderate SML enrichments (enrichment factor $EF_{SML} = 1.3\pm0.2$ and $1.1\pm0.5$ respectively). In contrast, the amino acids exhibited a higher enrichment in the SML with an averaging $EF_{SML}$ of $2.4\pm0.3$ although being less surface-active than lipids. The same compounds studied in the seawater were found on the ambient submicron aerosol particles whereas the lipids were more pronounced enriched ($EF_{aer.} = 1.6\times10^5$) compared to the amino acids and carbohydrates ($EF_{aer.} = 1.5\times10^3$ and $1.3\times10^3$ respectively), likely due to their high surface activity and/or the lipophilic character. Detailed molecular analysis of the seawater and aerosol particles revealed changes in the relative composition of the single organic compounds. They were most pronounced for the amino acids and are likely related to an in situ atmospheric processing by biotic and/or abiotic reactions.

On average 49% of the OC on the aerosol particles ($\pm 97 \text{ ng m}^{-3}$) could be attributed to the specific components or component groups investigated in this study. The majority (43%) was composed of lipids. Carbohydrates and amino acids made up less than 1% of the OC. This shows that carbohydrates, at least resolved via molecular measurements of single sugars, do not comprise a very large fraction of OC on marine aerosol particles, in contrast to other studies. However, carbohydrate-like compounds are also present in the high lipid fraction (e.g., as glycolipids), but their chemical composition could not be revealed by the measurements performed here.

Previously determined OC components at the CVAO, in detail amines, oxalic acid, and carbonyls, comprised an OC fraction of around 6%.

Since the identified compounds constituted about 50% of the OC and belong to the rather short-lived biogenic material probably originating from the surface ocean, a pronounced coupling between ocean and atmosphere was indicated for this oligotrophic region. The remaining, non-identified OC fraction might in part contain recalcitrant OC, however, this fraction does not constitute the vast majority of OC in the here investigated aerosol particles.

Keywords: organic carbon, lipids, amino acids, carbohydrates, sea surface microlayer, aerosol particles, Atlantic Ocean, CVAO
1 Introduction

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

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

An important aspect for understanding the OC on the marine aerosol particles is the connection to oceanic bio-productivity. Several studies suggested that the marine aerosol composition is directly coupled to the productivity in the ocean, showing that at elevated chlorophyll-a (chl-a) concentrations in the seawater the OC on the aerosol particles is significantly higher compared to low oceanic productivity (O’Dowd et al., 2004; Facchini et al.,...
A coupling between oceanic bio-productivity and aerosol composition is probably not straightforward. Wang et al., (2015) showed that two successive phytoplankton blooms in the tank seawater resulted in sea spray aerosols (SSA) with vastly different compositions and properties. Other studies, however, propose that the OC transfer from the ocean to aerosol particles is non-correlated to oceanic bio-productivity. Quinn et al., (2014) suggested that the high reservoir of dissolved organic carbon (DOC) in the ocean is responsible for the organic enrichment in freshly emitted sea spray aerosol, thus dominating over any influence of recent local biological activity based on chlorophyll concentrations. Following this, Kieber et al., (2016) proposed that the major component in submicron sea-spray particles is of recalcitrant nature with a stability of months to millennia. They suggested that this persistent form of OC can very efficiently be transferred to the atmosphere via bubble bursting. Although they did not perform a detailed chemical analysis, they concluded that the recalcitrant organic matter exhibits surface-active properties. Applying natural abundance radiocarbon (14C) measurements it was recently suggested that 19 to 40% of the OC associated with freshly produced marine aerosol particles was refractory dissolved organic carbon (rDOC) (Beaupre et al., 2019).

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

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

2. Material and methods

2.1 Aerosol and seawater sampling during the campaign

A field campaign (MarParCloud) was carried out at the Cape Verde Atmospheric Observatory (CVAO, 16°51ˈ49ˈN, 24°52ˈ02ˈE) in autumn 2017 (13.09.2017 – 13.10.2017) and the sampling sites are illustrated and explained in detail in van Pinxteren et al., (2020). The CVAO is a remote marine station in the tropical Atlantic Ocean located on the northeast coast of Sao Vicente island and described in Carpenter et al., (2010) and Fomba et al., (2014). The ocean around the Cape Verde Islands has the lowest surface chlorophyll in the North Atlantic Ocean with values below 0.2 µg L⁻¹ during the major part of each year with periodic events of slightly elevated concentrations up to 0.7 µg L⁻¹ (van Pinxteren et al., 2020 and refs therein).

Submicron aerosol particles were sampled with a high volume PM₁ aerosol sampler (Digitel, Riemer, Germany) installed on the 30 m height tower at the coastline. The seawater samples were taken at Bahia das Gatas, a coastal site that is situated upwind of the CVAO about 4 km northwest in front of the station (Fig. S1). Fishing boats were rented to drive to the open ocean and the SML was sampled with the glass plate technique as one typical SML sampling strategy (Cunliffe and Wurl, 2014). To this end, a glass plate with a sampling area of 2000 cm² was vertically immersed into the water and then slowly drawn upwards with a withdrawal rate between 5 and 10 cm s⁻¹. The surface film adheres to the surface of the glass and is removed using framed Teflon wipers (Stolle et al., 2010;van Pinxteren et al., 2012). Bulk seawater was collected with a specially designed device consisting of a plastic bottle mounted on a telescopic rod. The bottle was opened underwater at depth of 1 m with a specifically conceived seal-opener.

For the sampling of the oceanic water samples, great care was taken that all parts that were in contact with the sample (glass plate, bottles) underwent an intense cleaning with 10% HCl and rinsing with ultrapure water (resistivity = 18.2 MΩ cm) prior to the campaign and in between sampling to avoid contamination and carry over problems.

2.2 Chemical analysis

2.2.1. Seawater and aerosol analysis: general considerations

Within the seawater analysis, we measured the dissolved amino acids (DAA) and dissolved carbohydrates (DCHO) in the DOC fraction, as DOC represents by far the largest pool of organic material in the ocean (Riebesell et al., 2011). DOC is the fraction of OC that passes through a filter of 0.2–0.7 µm pore size (e.g. Zäncker et al., 2017). The lipid measurements (from the same samples) were taken from Triesch et al., (2021b), are included in the DOC
for 20 h. After cooling to room temperature, the hydrolysed filtrate was desalted to a few mL as described in Triesch et al., (2021a). For the DAA analysis, seawater samples (25.5 mL) were desalinated and concentrated to a 250 µL aliquot of the desalted seawater. Aqueous extract of the amino acids was prepared by shaking a piece of the filter in 2 mL water. Following the addition of 250 µL HCl (Supra-quality, ROTIPURAN®Supra 35%, Carl Roth, Karlsruhe, Germany), the hydrolysis was performed at 110 °C for 20 h. After cooling to room temperature, the hydrolysed filtrate was evaporated, resolved in 500 µL milliQ-water (Millipore Elix 3 and Element A10, Merck Millipore, Darmstadt, Germany), filtered, derivatized using AccQ-Tag™ precolumn derivatization method (Waters, Eschborn, Germany), and measured by ultra-high performance liquid chromatography with electrospray ionization and Orbitrap mass spectrometry (UHPLC/ESI-Orbitrap-MS), as described in Triesch et al., (2021a). The analytes comprise the amino acids glycine (Gly), alanine (Ala), serine (Ser), glutamic acid (Glu), threonine (Thr), proline (Pro), tyrosine (Tyr), valine (Val), phenylalanine (Phe), aspartic acid (Asp), isoleucine (Ile), leucine (Leu), methionine (Met), glutamine (Gln) and γ-aminobutyric acid (GABA) (purity ≥ 99 %, Sigma-Aldrich, St. Louis, Missouri, USA).

The DL and Lipids aer. measurements were taken from Triesch et al., (2021b), where the analysis were done with a semi-molecular technique. For a better understanding of the data, a short description is given in the following: Seawater or aerosol filters were extracted with dichloromethane and filtered via GFF (Whatmann, pore size: 0.7 µm) described in more detail in Triesch et al., (2021b). The filtered extract was analysed with thin-layer chromatography (TLC). Lipid classes were separated on Chromarods SIII and calibrated with an external standard.
calibration with a mixture of standard lipids by a chromatograph flame ionisation detector (FID) Iatroscan MKVI (Iatron, Japan). The separation scheme included elution steps in the solvent systems with increasing polarity. More details of the separation technique are given in Frka et al., (2009). This method was carefully optimized for seawater analysis and adopted for aerosol particle analytics as described in Triesch et al., (2021b). The lipid classes included hydrocarbons (HC), fatty acid methyl esters (ME), free fatty acids (ALC), 1,3-diacylglycerols (1,3 DG), 1,2-diacylglycerols (1,2 DG), monoacylglycerols (MG), wax esters (WE), triacylglycerols (TG), phospholipids (PP) including phosphatidylglycerols (PG), phosphatidylethanolamine (PE), phosphatidylcholines (PC), as well as glycolipids (GL) which cover sulfoquinovosyldiacylglycerols (SQDG), monogalactosyl-diacylglycerols (MGDG), digalactosyldiacylglycerols (DGDG) and sterols (ST). It needs to be underlined that, as no single lipid compound but rather lipid groups (based on varying polarity in the TLC system) were measured, the lipid results can be classified as analysis on a semi-molecular level.

Organic carbon (OC) on the aerosol particles (PM$_1$ samples) was measured by means of a thermal-optical method using the Sunset Laboratory Dual-Optical Carbonaceous Analyzer (Sunset Laboratory Inc., U.S.A.) from a filter piece with an area of 1.5 cm$^2$. The EUSAAR 2 temperature protocol was utilized, and a charring correction was applied (Cavalli et al., 2010). The correction value for pyrolytic carbon was determined based on measurements of a sample transmission using a 678 nm laser. Samples were thermally desorbed from the filter medium under an inert He-atmosphere followed by an oxidizing O$_2$/He-atmosphere while applying carefully controlled heating ramps. A flame ionization detector was used to quantify methane following a catalytic methanation of CO$_2$.

Sodium was measured from filtered (0.45 μm syringe filter), aqueous extracts of the PM$_1$ samples using ion chromatography (more details in Zeppenfeld et al., 2021 and van Pinxteren et al., 2022).

2.3 Enrichment factors

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

$$EF_{SML} = \frac{c(\text{analyte})_{SML}}{c(\text{analyte})_{bulk \text{ water}}}$$

An enrichment in the SML is indicated with EF$_{SML}$ > 1 and a depletion in the SML with EF$_{SML} < 1$. The enrichment factor of aerosol (EF$_{aer}$) is a quantitative metric for comparing compounds in the ocean and in the atmosphere. The EF$_{aer}$ concept is mainly applied to closed systems (Quinn et al., 2015 and refs.therein; Rastelli et al., 2017) as degradation and formation pathways on aerosol particles including photochemical and biotic atmospheric reactions and contributions from other (non-marine) sources are excluded from this parameter. Nevertheless, for comparison purposes, it is useful to apply the EF$_{aer}$ to open systems as well, as shown in several studies (Russell et al., 2010; Triesch et al., 2021a; Triesch et al., 2021b; van...
Pinxteren et al., 2017; Zeppenfeld et al., 2021). To this end, the concentration of the analyte of interest in each compartment is related to the respective sodium concentration (equation 2), because sodium is regarded as a conservative sea salt tracer transferred to the atmosphere in the process of bubble bursting (Sander et al., 2003).

\[ EF_{\text{aer.}} = \frac{c(\text{analyte})_{\text{aer}}/c(\text{Na}^+)_{\text{aer}}}{c(\text{analyte})_{\text{seawater}}/c(\text{Na}^+)_{\text{seawater}}} \]  

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

3. Results and Discussion

3.1 SML and Bulk water

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

Figure 1 shows the analyte concentrations in the bulk ocean water (DAA: 80 ± 53 µg L\(^{-1}\), DCHO: 78 ± 15 µg L\(^{-1}\), DL: 70 ± 25 µg L\(^{-1}\)) and in the SML (DAA: 190 ± 238 µg L\(^{-1}\), DCHO: 85 ± 30 µg L\(^{-1}\), DL: 83 ± 24 µg L\(^{-1}\)). Hence, the average concentrations for DCHO and DL are similar in the bulk water and in the SML (detailed values in Sect. 2.2.2, Tab. 1 and DL concentrations can be found in Triesch et al., (2021b)). For the DAA, however, SML concentrations show a larger variability compared to the other compounds and compared to the bulk water. Resulting from the higher SML concentrations, the average SML enrichment factors of DAA is 2.4 ± 0.3 (Tab.1) and therefore higher compared to the DCHO (EF\(_{\text{SML}}\) = 1.1 ± 0.5) and DL (EF\(_{\text{SML}}\) = 1.3 ± 0.2). The high variability of the DAA concentrations agreed well with the free amino acids (FAA) measured at this location during the MarParCloud campaign (Triesch et al., 2021a).

In addition, other studies have pointed out highly variable amino acid concentrations, for example, Zänker et al., (2017) showed FAA concentrations between 32 and 1268 nmol L\(^{-1}\) and DAA varied between 202 and 2007 nmol L\(^{-1}\) (for comparison: the here presented DAA values correspond on average to 1064 nmol L\(^{-1}\) in the bulk water and 2536 nmol L\(^{-1}\) in the SML). High enrichments of FAA in the SML were reported (Kuznetsova and Lee, 2002; Kuznetsova et al., 2004; Reinthaler et al., 2008; van Pinxteren et al., 2012; Engel and Galgani, 2016) with FAA enrichments up to 300 in the SML of the Cape Verde seawaters (Triesch et al., 2021a). A preferential enrichment of FAA over dissolved combined amino acids as a consistent microlayer feature was proposed (Kuznetsova et al., 2004).
Regarding the composition of the individual DAA measured here, clear differences between the SML and the bulk water characteristics were observed (Fig. 2, blue and orange bars, data in Tab. S1 - 4). Besides the higher concentrations in the SML, some DAA were only present in the SML and not in the bulk water (below detection limit). This was most pronounced for Glu, but also evident for Tyr and Iso (detailed values in Tab. S2).
In contrast to the DAA, the DCHO enrichment in the SML was less pronounced with an EF<sub>SML</sub> of 1.1±0.5 (Tab. 1), similar to SML enrichment values obtained for DCHO close to the Peruvian upwelling regime (Zänker et al., 2017) and the Antarctic Peninsula (Zeppenfeld et al., 2021). Regarding the relative composition, the DCHO showed a very homogeneous pattern and were similar in the SML and the bulk water (Fig. 2, blue and orange bars).

The enrichment of the DL (EF<sub>SML</sub> = 1.3±0.2, Tab. 1) was very similar to the DCHO enrichment and is discussed in Triesch et al (2021a). From the individual lipid components and the lipolysis index, it was concluded that the lipids were degraded only to a small extent (Triesch et al., 2021b).

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

### 3.1.2 Discussion of the SML enrichment

#### 3.1.2.1 Surface vs bulk SML

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

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

3.1.2.2 Details of SML enrichment mechanisms

(i) Co-adsorption and complexation

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

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

Further explanations for the accumulation of dissolved compounds require an in situ formation or degradation by SML-specific reactions that might be triggered by distinct environmental conditions in the SML. Biotic pathways and abiotic SML-specific (photo)chemical reactions may strongly impact OC cycling at the sea surface (Liss and Duce, 1997). The high abundance of the amino acid Glu in the SML observed here was also reported in the FAA fraction by Triesch et al. (2021a) and can likely be explained by in situ formation. Glu has shown to be produced via biotic and abiotic mechanisms, e.g. via the oxidation of proline (Jaber et al., 2021 and refs. therein). Regarding biotic processes, it is well-known that microorganisms have complex and highly interconnected enzymatic networks and are able to biodegrade or biosynthesize organic compounds (KEEG pathway). Kuznetsova and Lee (2002) suggested that stressed microorganisms, rich in dissolved and combined amino acids, may be leached and released them, which in turn affects the pools of both these compounds in seawater. Although such formation mechanisms generally happen in the upper ocean, there are indications for SML-specific processes. Along a transect from upwelling regions toward oligotrophic gyres it was found that while in the bulk water a clear trend toward degradation
of amino acids was observed, the production and degradation patterns of amino acids in the SML were much more complex (Reinthaler et al., 2008). This is indicative of the role of the SML in the production of labile DOC driven by coupled microbial and photochemical processes. Similarly, Kuznetsova and Lee (2001) observed that peptide turnover was always faster in the SML than in subsurface waters likely due to the greater concentrations of DOC in the SML. The authors concluded that the accumulation of organic and inorganic compounds in the SML leads to a more nutritious medium for microbial growth and consequently enzymatic hydrolytic activity compared to the bulk water. Connecting this to the results presented here, this might suggest that changes induced by abiotic and biotic processing need to be considered when regarding the SML composition. Although such reactions likely also affect lipids and carbohydrates, they seem to be most pronounced for amino acids.

(iii) Microbial nitrogen fixation at the sea-air interface

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

(iv) Concluding remarks towards the SML enrichment

Although SML enrichment factors for amino acids, carbohydrates, and lipids have been reported in the available literature, they have not previously been shown in such detailed analysis for samples collected from the same site as was the case here. From this study it can be concluded that the amino acids are strongly enriched in the SML compared to carbohydrates and lipids, even under the same environmental conditions. In a recent study we showed a strong enhancement of other nitrogen-containing species (aliphatic amines) in the SML at this location, while the amine concentration in the bulk water was often not detectable (van Pinxteren et al., 2019). This suggests that the pronounced SML enrichment
specifically exists for nitrogen-containing organic species. In addition, the absence of a relation of the SML enrichment to physical compound parameters (e.g. hydrophobicity) suggests that enrichment processes based on physicochemical properties (e.g. surface-activity) alone do not drive SML enrichment. Rather, an SML in situ formation mechanism impacts the abundance of amino acids and likely nitrogen-containing organic species in general.

3.2. Aerosol particles

3.2.1 Concentration and composition

After evaluating the concentrations of the analytes in seawater and the SML, in the next step, their presence in the aerosol particles was investigated. The concentrations of $\text{AA}_{\text{aer}}$ and $\text{CHO}_{\text{aer}}$ were $2.4 \pm 1.1$ ng m$^{-3}$ and $1.0 \pm 1.1$ ng m$^{-3}$, respectively (Fig. 3, Tab. 1).

Compared to results from the Polar Regions, the $\text{CHO}_{\text{aer}}$ concentrations in the tropical Atlantic Ocean analysed here are at the lower end. Leck et al., (2013) determined carbohydrates during the Arctic summer and found 0.7 - 20 ng m$^{-3}$ in submicron particles. Zeppenfeld et al., (2021) found carbohydrate concentrations between 0.2 - 11.3 ng m$^{-3}$ in PM$_{10}$ atmospheric particles, in the Western Antarctic Peninsula, which contributed about 3% to the OC. The same holds true for amino acids, the concentrations found here are slightly lower as reported for other marine regions, e.g. FAA in Antarctic aerosol particles were on average 4.6 ng m$^{-3}$ in Antarctic aerosol (Barbaro et al., 2015). Triesch et al., (2021a) found FAA concentrations between 1.5 and 3.0 ng m$^{-3}$ in the aerosol particles from the Cape Verdes.

Comparing the data obtained here those provided by analytical techniques that use functional group information (FT-IR) showed that the latter techniques often report a large fraction of alcohol (hydroxyl) functional groups on the marine aerosol particles identified and attributed to carbohydrates (Cravigan et al., 2020; Frossard et al., 2014; Russell et al., 2010). According to Russell et al., (2010), the primary marine signal in submicron marine aerosol over the North Atlantic and Arctic Oceans is made on average for 88% of hydroxyl groups corresponding to carbohydrate-like material. Such high fractions of carbohydrates were not
found in the chromatographic analysis of CHO\textsubscript{aer}, presented here, nor in other studies using similar methodologies (e.g. Zeppenfeld et al., 2021). In a recent study, using thermal desorption mass spectrometry, it was suggested that carbohydrates only represented a minor fraction of the FT-IR alcohol group and another thermally stable fraction, different to carbohydrates, was the main contributor to the alcohol group (Lawler et al., 2020). Hence, previous FT-IR measurements might have over-predicted the carbohydrate fraction of marine aerosol particles and further (molecular-based) analysis should be conducted in comparison to resolve existing contradictions.

In contrast to the CAA\textsubscript{aer} and CCHO\textsubscript{aer}, the Lipid\textsubscript{aer} concentrations were 120 ± 43 ng m\textsuperscript{-3} and therefore two orders of magnitude higher than the other two organic groups (Fig. 3, Tab. 1). Previous lipid analysis on a molecular level revealed concentrations between 0.19 - 23 ng m\textsuperscript{-3} for ALC and between 2.5 - 38 ng m\textsuperscript{-3} for free fatty acids on marine aerosol particles from the western North Pacific (Kawamura et al., 2003) and a recent study found marine fatty acid concentrations between 50 and 90 ng m\textsuperscript{-3} in coastal aerosol at Qingdao (Chen et al., 2021).

Mochida et al., (2002) observed saturated fatty acids (C14–C19) on marine aerosol particles over the northern Pacific in atmospheric concentration between 0.8 - 24 ng m\textsuperscript{-3}. Hence, these data are in the same order of magnitude as here measured lipid groups (ALC: 6.3 ng m\textsuperscript{-3}, free fatty acids: 18.5 ng m\textsuperscript{-3}, values in Triesch et al. (2021b)). Cochran et al. (2017) showed that lipid components (long-chain fatty acids) comprised a significant fraction of up to 75% of the identified organic constituents in aerosol particles from a sea spray tank.

High lipid fractions in marine aerosol particles were also reported from NMR measurements. Measurements of nascent aerosol particles produced from North Atlantic seawater showed that the water-soluble organic aerosol fraction was purely aliphatic with hydroxylated moieties of sugars, esters, and polyols, aliphatic groups adjacent to carbonyls, amides, and acids, as well as aliphatic chains with terminal methyl-groups, typical of lipids (Facchini et al., 2008). The water-insoluble organic fraction was dominated by lipopolysaccharides, known as phytoplankton exudate components. A recent study applying NMR analysis to artificially produced aerosol particles after bubbling seawater from offshore areas also showed proof of polyols and lipids (Decesari et al., 2020). NMR measurements of lipids are mainly qualitative, however, the high fraction of lipid-like components from other regions agrees well with the here presented high Lipid\textsubscript{aer} concentrations.

A high Lipid\textsubscript{aer} concentration as observed in the present study agrees well with the modelling results of Burrows et al., (2014), where the ocean-atmosphere transfer was calculated according to the physicochemical properties of the distinct OC groups. Lipids, as the most surface active OC group comprise the largest fraction of the aerosol fraction, although their (modelled) concentration in the seawater is lower compared to carbohydrates and amino acids (Burrows et al., 2014). In a latter model modification, where additional co-adsorption processes were included in the calculations, a more pronounced saccharidic fraction was determined on the aerosol particles from the model results (Burrows et al., 2016), that is different from the findings here, at least regarding the CHO\textsubscript{aer} measured on a molecular level.

However, it needs to be considered that the lipids analysed here include glycolipids (MGDG, DGDG, SQDG) which are components that have the solubility properties of a lipid but also...
contain one or more sugar molecules. The glycolipids comprise a non-negligible portion of the OC on the aerosol particles (values in Table S6). This underlines the complexity of attributing the OC to distinct organic groups and demonstrates that the applied analytical methods must be taken into account when comparing concentrations of substance groups. This is discussed in more detail in 3.4.1. Altogether, there seems to be a discrepancy between the measured concentrations and the modelled results underlining that the transfer of the organic compounds from the ocean to the atmosphere based on their physicochemical properties might not be the only mechanism.

3.2.2 Aerosol enrichment

3.2.2.1 Aerosol enrichment factors

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

\textit{Insert Table 1}

For the amino acids the EF\textsubscript{aer} was between 9.2x10^2 (related to the SML) and 2.1x10^3 (related to the bulk water) and on average 1.5x10^3. For the carbohydrates the EF\textsubscript{aer} was between 1.3x10^3 (related to the SML) and 1.4x10^3 (related to the bulk water) and on average 1.3x10^3 and therefore similar to the EF\textsubscript{aer} of the amino acids. For the lipids, however, the EF\textsubscript{aer} was two orders of magnitude higher (EF\textsubscript{aer} = 1.4x10^5, related to the SML; EF\textsubscript{aer} = 1.7x10^5 related to the bulk water, EF\textsubscript{aer} = 1.6x10^5 on average, Tab. 1).

3.2.2.2 Oceanic transfer and atmospheric in situ formation

The overall high enrichment of OC in the aerosol particles is explained by complex, not yet finally resolved interactions at the ocean surface where organic matter is enriched over sodium during the formation of film and jet droplets. Burrows et al., (2014) applied a conceptual model (“slab” model) where all organics partition to the surface of a “slab” of oceanic water or to both the outer and inner surfaces of a bubble film. The organic enrichment is therefore significantly higher for the thinner bubble films (bubble film thicknesses: 0.01 to 1 μm) than for the thicker SML (typically sampled SML thicknesses: 20 to 400 μm). This mechanism can explain an EF\textsubscript{aer} of OC in submicron aerosol particles of 10^2 to 10^3 compared to the SML (Burrows et al., 2014). However, EF\textsubscript{aer} from ambient and laboratory-controlled observations show that for some compounds even higher EF\textsubscript{aer} are obtained. In a controlled tank study, Rastelli et al., (2017) found strong enrichments for lipids (up to 1.4x10^5), as well as for proteins (up to 1.2x10^5) and carbohydrates (up to 1.0x10^5, Tab. 1). A recent controlled bubble-bursting laboratory study showed that amino acids enrichments can be up to 10^7 in
submicron SSA between 0.029 and 0.060 μm (Triesch et al., 2021c). Similarly, Schmitt-Kopplin et al., (2012) showed that surface-active biomolecules are preferentially transferred from surface water into the atmosphere via bubble bursting. The ambient enrichment factor of the lipids (10^5) shown here and in Triesch et al., (2021b) agreed well with laboratory-derived ones (Rastelli et al., 2017) indicating that the transfer mechanisms simulated in lab experiments agree with here performed observations in the field. Hence, the high surface activity and/or the lipophilic character of the lipid classes might explain their strong (chemo-selective) transfer to the aerosol particles. Even though the lipid composition on the aerosol particles slightly varied from the seawater concentration (Triesch et al., 2021b), their transfer is likely driven by their physicochemical properties (high surface activity and/or the lipophilic character). For the amino acids and carbohydrates, however, more complex mechanisms may determine their transfer to the atmosphere. Rastelli et al., (2017) suggested that diverse biological processes on the ocean drive the properties of proteins and carbohydrates in the ocean surface and in the atmosphere. Moreover, these compounds are known to be involved in marine gel-like particle formation, such as transparent polymer particles (TEP) and coomassie stained particles (CSP), observed in the ocean and more recently in the atmosphere (Aller et al., 2017;Kuznetsova et al., 2005;van Pinxteren et al., 2022) adding more complexity to the system. Hence not only a sea-to-air transfer but also atmospheric in situ formation and degradation might determine the concentration of the OC and notably of the amino acid and carbohydrates. This suggests that atmospheric processing plays an important role besides the physical-driven bubble bursting sea-air transfer of OC.

3.2.3 Limitations of the concept of an aerosol enrichment factor

When comparing OC in the ocean and the atmosphere, it needs to be considered that processes in the ocean and the atmosphere happen on different timescales. In addition, the seawater samples comprise spot samplings in the ocean while the sampling period of PM_1 aerosol particles at the CVAO covers a time span of 24h. These issues make a comparison between the ocean and atmospheric data very challenging. However, the air masses arriving at the CVAO often followed the water current (Pena-Izquierdo et al., 2012;van Pinxteren et al., 2017) and suggest a strong link between the upper ocean and the aerosol particles, as mainly winds drive the ocean currents in the upper 100 m of the ocean. Besides the ocean, Saharan dust is a strong aerosol source at the Cape Verde islands, most pronounced in the months December to February (Fomba et al., 2014). The backward trajectories as well as the mass concentrations of inorganic ions and mineral dust tracers on the aerosol particles measured during the campaign suggested a predominant marine origin with low to medium dust influences (van Pinxteren et al., 2020). Moreover, dust generally influences the supermicron particles to a larger extent than the submicron particles analysed here (Fomba et al., 2013). Hence, although different factors certainly affect the aerosol composition, it is reasonable to assume a strong oceanic contribution.
3.3. Seawater and aerosol particles: Comparison of the relative composition

Regarding the organic components on the aerosol particles, the same compounds that were present in the seawater were generally present on the aerosol particles (Fig. 2, grey bars, and values in Tab. S1 - 4). However, the relative composition of distinct compounds was, at least partly, different. Regarding the carbohydrate composition, the percentages of MurAc, GlcAc, and GlcN in the aerosol particles were higher compared to the seawater. MurAc and GlcN are important constituents in the cell walls of marine microorganisms and notably, MurAc serves as a proxy for bacterial biomass (Mimura and Romano, 1985). Its high concentration might indicate an enrichment of bacteria on the aerosol particles. Zeppenfeld et al., (2021) detected similar (biogenic) carbohydrates in particles sampled in the western Antarctic peninsula and suggested that marine bacteria in atmospheric particles may metabolize a part of the oceanic carbohydrates in a selective enzymatic way analogous to the bacterial processes in seawater. Such processes might explain the changed carbohydrate composition and are likely not restricted to a specific oceanic regime, as they seem to happen in the Southern Ocean (Zeppenfeld et al., 2021) as well as in the tropical Atlantic Ocean, observed here. The elevated relative occurrence of GlcAc found here agrees well with the recent finding of a high abundance of gel-like material in aerosol particles at the CVAO, strongly enriched towards sodium compared to seawater (van Pinxteren et al., 2022) as GlcAc is one main component of marine gelatinous exopolysaccharides (Casillo et al., 2018; Krembs et al., 2002). Regarding the lipids, surfactants such as free fatty acids as well as lipophilic compounds, such as hydrocarbons, had major contributions in the seawater and on the aerosol particles, respectively. However, TG, an energy storage lipid, had a higher contribution to the aerosol particles versus the ocean water. In addition, some other, minor-contributing lipid classes were partly different in the two compartments (Triesch et al., 2021b).
The most remarkable difference in relative composition in seawater and in aerosol particles was found for amino acids, as some DAA were clearly present in the SML and in the aerosol particles but not in the bulk water (e.g. Iso and Glu, Fig. 4, individual values in Tab. S5). The amino acids generally differed a lot regarding their SML and bulk water composition. This was visible in the data set presented here for the DAA, and also reported for the FAA measured from the same campaign (Triesch et al., 2021a). Recently it was reported that the acidic amino acid Glu (in the form of FAA) is transferred to SSA to a large extent (Triesch et al., 2021c) and the results of the present study suggest that Glu might be transferred solely from the SML (and not from the bulk water) to the aerosol particles. However, besides the oceanic transfer, Glu can result from an in situ formation on the aerosol particles. Similarly to the seawater, Glu might form from biotic or abiotic reactions on the aerosol particles. From the here performed measurements it is not possible to differentiate between a selective transfer of Glu from the SML and its biotic and abiotic in situ formation in aerosol particles. Recently, Jaber et al., (2021) and Renard et al., (2022) evaluated the atmospheric aging of the amino acids and considered biotic and abiotic (mainly oxidation) processing. Their calculations revealed different atmospheric lifetimes for the individual amino acids related to oxidation and biological processes, respectively. For example, the amino acids Ser and Ala are degraded quickly by biological processes (lifetime of a few hours) but are more stable towards oxidation (Renard et al., 2022). Such studies can help to understand the patterns of the amino acids as observed here and relate them to sources and atmospheric processing. The presence of Ser and Ala in the here investigated aerosol particles could therefore indicate that biodegradation of these compounds was not pronounced. However, additional studies are needed to better understand atmospheric biotic and abiotic processing. In addition, the transfer of individual DAA exclusively from the SML shall be investigated in further research, preferably within characterized and controlled bubbling systems.

3.4 Contribution to aerosol particle OC

3.4.1 Molecular and semi-molecular analysis

OC concentrations in marine aerosol particles during this campaign varied between 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 with previous OC measurements from the CVAO that were on average 0.27 µg m⁻³ OC (van Pinxteren et al., 2017). To date, only a small percentage of OC on marine aerosol particles is characterised on a molecular level and organic biomarkers often comprise only a few percent of the OC (Chen et al., 2021). Fu et al., (2011) measured more than 140 different single organic species in marine aerosol from different oceanic areas, however the identified species composed less than 5.7% of the OC. Taking together the OC components described here (Lipids_aer, AA_aer, CHO_aer), the contribution of the identified components to the OC was calculated. Furthermore, the OC contribution of recently identified components from previous campaigns within the Cape Verde region, in detail: aliphatic amines, methane-sulfonic acid (MSA), oxalic acid and carbonyls (van Pinxteren et al., 2015) was included. The OC contribution
of the single compounds and compound groups are shown in Fig. 5 (values in Tab. S7).

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

About 50% of the aerosol OC remained uncharacterized on a molecular and semi-molecular level. The non-identified OC part may contain larger macromolecules that might be composed of particulate or non-soluble forms in water (carbohydrates and proteins) or organic solvents (lipids) that were removed in the performed analysis during the sample preparation step. In addition, the unknown part might include component groups that belong to the soluble carbohydrates or amino acids but are either too stable or too labile for the sample preparation procedure (e.g. within the hydrolysis step). Moreover, other complex molecules that cannot be captured with the here applied methods likely add to the unknown fraction including optical active parts summarized as chromophore dissolved organic matter (CDOM), humic-like substances (HULIS), brown carbon and water-soluble pigments. As mentioned above, NMR analysis showed that SSA contains a large fraction of lipopolysaccharides comprising complex, macromolecular groups of sugars, esters, carbonyls as well as acids and lipids (Facchini et al., 2008). However, these components have, not yet been analysed in aerosol particles using chromatographic techniques. The uncharacterized part may also contain particulate OC compounds, such as larger aggregates of marine gels or gel-like particles like transparent exopolymer particles (TEP). High TEP number concentrations
in aerosol particles were recently identified in the Cape Verde region (van Pinxteren et al., 2022) and high mass-concentrations of TEP (e.g. 1.2 µg m\(^{-3}\) for PM\(_1\)) were identified in the western North Atlantic atmosphere (Aller et al., 2017).

Kieber et al., (2016) suggested that the major OC component in submicron sea-spray particles is recalcitrant and recently Beaupré et al., (2019) proposed that 19 to 40% of the OC associated with freshly produced marine aerosol particles was refractory dissolved OC. This percentage agrees with the non-identified OC part from the present study. However, we cannot identify or classify the remaining OC fraction nor attribute it with certainty to the recalcitrant OC. Further studies of the OC, in tropical as well as in other areas of the world, are needed to continue resolving OC and related transfer and formation processes. Nevertheless, the potentially recalcitrant OC fraction in the here investigated oligotrophic region does not seem to constitute the majority of OC as reported by Kieber et al., (2016).

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

The CVAO is localized in an oligotrophic region and should therefore be representative of most of the Earth’s ocean surface. POA emission rates are strongly varying, however modelling studies have estimated global submicron marine POA emission rates of 10±5 Tg yr\(^{-1}\) (Gantt and Meskhidze, 2013). Based on this emission flux and the contribution of the compounds to the OC fraction, we estimated the fluxes of the DAA, DL, and DCHO. Accordingly, the annual rates of emission from the ocean to the atmosphere are 0.03±0.01 Tg 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 includes the potentially recalcitrant components, has a sea-to-air flux of 4.8±2.4 Tg yr\(^{-1}\).

However, this approach only includes the bubble-bursting-mediated transfer of the respective compounds and neglects additional sources and formation processes. Ervens and Amato (2020) investigated the global impact of bacterial processes on carbon mass in cloud water and estimated formation rates of 3.7 Tg C yr\(^{-1}\) of secondary biological aerosol that are in the range of the POA emissions via sea spray (Gantt and Meskhidze, 2013). Hence, the here presented emission fluxes can change once such processes are quantified for these compounds.

4 Summary and Conclusions

A comprehensive chemical investigation of the OC in the tropical Atlantic Ocean and the atmosphere with a focus on its contribution to the OC on the marine aerosol particles in this particular region was performed.

Regarding seawater, a similar distribution of the DL and DCHO was found with a small SML enrichment. However, the DAA, and likely the N-containing compounds in general, exhibit a high and varying enrichment in the SML (although being less surface active than lipids). Although conclusions on the detailed processes that lead to the varying DAA concentrations and the high SML enrichments cannot be resolved here, the results clearly show that processes leading to changes in the organic matter composition within the upper
100 µm oceanic layer are more pronounced for the group of amino acids (and possibly for nitrogen groups in general) compared to other organic compounds groups such as lipids and carbohydrates. The SML is probably a very complex, heterogeneous, seasonality-dependent, and reactive matrix forming a lipid-rich nanolayer. The same compounds studied in the seawater were found on the ambient submicron aerosol particles and strongly enriched towards sea salt (EF_{aer} = 10^3 for the carbohydrates and the amino acids). To this end, the lipids were even stronger enriched in the submicron aerosol particles (EF_{aer} = 10^5) compared to the other groups. This indicates a preferred transfer of the lipids (towards the carbohydrates and the amino acids) from the ocean to the atmosphere that is probably driven by their physicochemical properties (high surface-activity and/or the lipophilic character). Detailed molecular analysis of the seawater and aerosol particles revealed changes in the relative composition of the single compounds. They were most pronounced for the amino acids and are likely related to an in situ atmospheric processing by biotic and/or abiotic reactions that require further investigations. A high saccharide fraction, as described in other studies, could not be found on the aerosol particles, at least when regarding the molecular-resolved carbohydrate analysis. However, saccharidic-like components (e.g. glycolipids) are also included in the lipid fraction analysed here in non-negligible concentrations. This shows that when comparing the concentrations of substance groups, the analytical methods used must be taken into account. Nevertheless, even small concentrations of carbohydrates and amino acids on marine aerosol particles can have a high impact in their microphysical properties, e.g. as ice nucleating particles, and are worth further studying.

Altogether, the marine aerosol particles analysis applied here shows that half of the OC can be attributed to specific components or component groups. However, the molecular-level analysed fraction explains only a small part of the OC, the CH_{aer}O and AA_{aer} made up less than 1%. This shows that the typical representatives of carbohydrates and amino acids within the marine OC measured here can explain only a very small fraction of the organic composition of the aerosol particles on a molecular level. Amines, MSA, oxalic acid carbonyls comprise a fraction of around 6%. Lipid analysis unravel 43% of the OC on the aerosol particles, however, the Lipid_{aer} composition on a molecular level cannot be obtained from the here performed measurements. Altogether, about 50% of the OC remained uncharacterized on a molecular and semi-molecular level. Regarding further marine aerosol analysis, it will be important to resolve the large part of lipid compounds in more detail, as well as getting molecular-level information on the remaining, unidentified OC. This shows the need for further detailed analytical OC studies in the marine environment to resolve formation and transfer mechanisms.

Nevertheless, the results obtained here show that even in such an oligotrophic region, at least half of the OC on the aerosol particles consists of rather short-lived biogenic material, likely from the surface ocean. The non-resolved OC might in part be of recalcitrant nature, as indicated in other studies (Beaupre et al., 2019; Kieber et al., 2016; Lawler et al., 2020). However, the (potentially) recalcitrant OC does not constitute the majority of the OC in the
oligotrophic Atlantic Ocean. Future studies should complement the here achieved data with investigations of the particulate OC fraction. Finally, since large parts of the open oceans are oligotrophic, the findings of this study might be relevant to the majority of the world oceans.

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

Special issue statement.

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Author contributions

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

Competing interest

The authors declare that they have no conflict of interest.
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Caption of Figures:

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

Figure 2: Bar graph showing the average of the relative compositions (mol%) of dissolved lipids (DL) and Lipidsₐer. (a), dissolved carbohydrates (DCHO) and CHOₐer. (b) and dissolved amino acids (DAA) and AAₐer. (c) in the bulk water (blue bars), the SML (orange bars), and the PM₁ aerosol particles (grey bars).

Figure 3: Box and whisker plot of the concentrations in the PM₁ aerosol particles (ng m⁻³); n = 8 for CHOₐer, n = 7 for AAₐer, n = 14 for Lipidsₐer. Each box encloses 50% of the data with the mean value represented as an open square and the median value represented as a line. The bottom of the box marks the 25% limit of the data, while the top marks the 75% limit. The lines extending from the top and bottom of each box are the 5% and 95% percentiles within the data set, while the asterisks indicate the data points lying outside of this range (“outliers”).

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

Figure 5: Graph showing the identified and non-identified OC and the OC contribution of the respective organic compound groups in the PM₁ aerosol particles. The contribution of the measured organic compounds to the total OC fraction was calculated on a carbon basis.
Table 1: Average concentrations of the organic groups and enrichment factor (EF) in the SML (EF$_{SML}$) and in the aerosol particles (EF$_{aer}$) after equations 1 and 2. EF are calculated from the average concentrations of the respective groups (values in Tab. 1). For EF$_{aer}$, the average Na$^+$ concentration in seawater (1.0E+04 mg L$^{-1}$) and the average Na$^+$ concentrations in the PM$_1$ particles from the MarParCloud campaign (100 ng m$^{-3}$, values from Triesch et al., (2021b)) were applied. For comparison, the last column lists the EF$_{aer}$ for PM$_1$ from a chamber study (Rastelli et al., 2017).

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<th>SML (µg L$^{-1}$)</th>
<th>Bulk water (µg L$^{-1}$)</th>
<th>PM$_1$ (ng m$^{-3}$)</th>
<th>EF$_{SML}$ (related to the SML)</th>
<th>EF$_{aer}$ (related to the bulk water)</th>
<th>EF$_{aer}$ (average)</th>
<th>EF$_{aer}$ (Rastelli et al., 2017)</th>
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<td>DCHO</td>
<td>85 ± 30</td>
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<td>DAA</td>
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<td>80 ± 53</td>
<td>2.4 ± 1.1</td>
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<td>2.07E+03</td>
<td>1.50E+03</td>
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<td>DL</td>
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<td>70 ± 25</td>
<td>120 ± 43</td>
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