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 ± 0.2 and 1.1 ± 0.5 respectively). In contrast, the amino acids exhibited a higher enrichment in the SML with an average EF_{SML} of 2.3 ± 0.4 although they are 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 ($EF_{aer.} = 1.6\text{x}10^5$) compared to the amino acids and carbohydrates ($EF_{aer.} = 1.5\text{x}10^3$ and $1.3\text{x}10^3$ 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 abundance of the individual 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 (≙ 97 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 when 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, specifically 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 aerosol particles here investigated.

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 as they impacts the carbon cycle and radiative properties of aerosol particles (Abbatt et al., 2019; Brooks and Thornton, 2018; Burrows et al., 2013; Gantt and Meskhidze, 2013; Pagnone et al., 2019; Patel and Rastogi, 2020). Furthermore, the function of (marine) aerosol particles as cloud condensation nuclei (CCN) and ice-nucleating particles (INP), i.e. marine aerosol-cloud interaction is still elusive. Important information about marine CCN is still missing (e.g. Bertram et al., 2018). Ocean-derived INPs have been suggested to play a dominant role in determining INP concentrations in near-surface air over remote areas such as the Southern Ocean, but their source strength in other oceanic regions and knowledge of which physicochemical properties determine INP efficiency remain largely unknown (Burrows et al., 2013; McCluskey et al., 2018a; McCluskey et al., 2018b). 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 component to understand the OC on 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 when compared to the low oceanic productivity (O'Dowd et al., 2004; Facchini et al., 2008). 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 (^{14}C) 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 (Bianco 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 some studies, the atmospheric in situ transformation of marine organic compounds and its significance has not yet been extensively studied.

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. Specifically, we followed the concentrations and speciation of OC from the sea to the atmospheric particles, which helps to evaluate the enrichment factors of the various targeted compounds between the compartments. 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 September 2017 – 13 October 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} for the majority 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 on preheated 150 mm quartz fiber filters (Munktell, MK 360) at a flow rate of about 700 L min^{-1} with a high volume PM_1 aerosol sampler (Digitel, Riemer, Germany) installed on the 30 m height tower at the coastline. The sampling times were usually set to 24 h and are listed in Tables S4 and S5, as well as in Triesch et al. (2021b) and in van Pinxteren et al. (2020). Regarding the aerosol sampling system, it needs to be underlined that artefact problems and overestimations due to gas phase absorption and underestimations due to re-volatilisations of the analytes from the filters may represent a certain level of uncertainty. To this end great care was taken to apply field blanks and correct for blank values as pointed out in detail in Sect. 2.2.3.

The seawater samples were taken at Bahia das Gatas, a coastal site that is upwind and about 4 km northwest of the CVAO (Figure S1). Fishing boats were rented to go out on the open ocean and the SML was sampled with a typical glass plate SML sampling strategy (Cunliffe and Wurl, 2014). To this end, a glass plate with a sampling area of 2000 cm^2 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.

After the sampling, all seawater and aerosol samples were stored frozen at -20°C, transported in a reefer at -20 °C to the TROPOS laboratories where they were stored frozen until analysis.

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 GF-F filter of 0.7 µm pore size (Wurl, 2009), however, filter pore sizes between 0.2 and 1.2 µm are often applied e.g. due to requirements of the analytical system (e.g. (Romankevich, 1984; Zäncker et al., 2017). The lipid measurements (from the same samples) were taken from Triesch et al. (2021b), are included in the DOC fraction as well, being filtered via a 0.7 µm pore-sized filter (GF-F, Whatmann) and extracted in an organic solvent, and refer to dissolved lipids (DL).

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

2.2.2. Analytical methods

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

For the DAA analysis, seawater samples (25.5 mL) were desalinated and concentrated to a few mL as described in Triesch et al. (2021a). For the $AA_{aer.}$ from PM_1 particles, an aqueous extract of the amino acids was prepared by shaking a piece of the filter in 2 mL water. After a filtration step (filter pore size: 0.2 µm) 25 µL of ascorbic acid (20 mg mL^{-1}, purity 99 %, Sigma-Aldrich, St. Louis, Missouri, USA) was added to a 200 µL aliquot of the desalted seawater /

aqueous filter extract to avoid the oxidation of the obtained amino acids as suggested in Mandalakis et al. (2010). 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 include 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: the dissolved fraction of seawater samples (obtained after filtration through pre-combusted 0.7 µm GF/F filters) and aerosol filters were extracted with dichloromethane according to specific protocols after adding 2-hexadecanone as an internal standard, as described in more detail in Triesch et al. (2021b). The extract was analysed with thin-layer chromatography (TLC). Lipid classes were separated on Chromarods SIII and calibrated with an external 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. The lipid classes included hydrocarbons (HC), fatty acid methyl esters (ME), free fatty acids (FFA), alcohols (ALC), 1,3-diacylglycerols (1,3 DG), 1,2-diacylglycerols (1,2 DG), monoacylglycerols (MG), wax esters (WE), triacylglycerols (TG), pigments (PIG), 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.

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). The details on sampling and the sample treatment are summarized in Table S1.

Atmospheric concentrations were calculated from the measured analyte concentrations on the filter or in the filer extract. The masses of the analytes on the filter were extrapolated to the total filter and related to the collected air volume that flowed through the filter.

2.2.3 Detection limits and blank handling

Detection limits were 0.5-2.5 µg L^{-1} (DAA) and 0.1-0.2 pg m^{-3} ($AA_{aer.}$) (Triesch et al., 2021a; Triesch et al., 2021c) and 0.13-0.7 µg L^{-1} (DCHO) and 0.5-5 pg m^{-3} ($CHO_{aer.}$) (Zeppenfeld et al., 2021). Regarding the lipids, the method was carefully optimized for seawater analysis (Gašparović et al., 2015, 2017) and adopted for aerosol particle analytics as described in Triesch et al. (2021b). The detection limits were determined as the analyte concentrations corresponding to a signal-to-noise (S/N) ratio of 3 ranged from 0.06 to 0.33 ug as reported previously in Penezić et al. (2022).

For the seawater analysis, field blanks were taken by filling high-purity water in pre-cleaned plastic bottles and handled the same as the seawater samples. The seawater blanks were in general below 10% and for the lipids always below 15% (Triesch et al., 2021b). All data are blank corrected by subtracting the field blank values from the samples.

Field blanks for aerosol particles were prepared using pre-baked quartz fiber filters without an active sampling and treated according to the same procedure as the field samples. The concentrations of the target analytes were calculated by external calibration. Each sample was measured twice with a relative standard deviation of typically < 10 %, and field blanks, which were for most compounds negligible and for the lipid classes always below 20% of the real aerosol particle sample, were subtracted. All presented values are corrected for the field blank.

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):

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

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).

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

To account for the different timescales for ocean and atmospheric processes and to improve robustness, we applied the average concentration values of the respective compound groups in seawater and on aerosol particles as done by Zeppenfeld et al. (2021) and van Pinxteren et al. (2022). It should be noted that EF_{SML} and $EF_{aer.}$ comparisons include samples from the same campaign but not necessarily from the same exact date (details in Table1 and Tables S2 - S5). However, as our focus was not on showing trends within the campaign (this was covered by Triesch et al. 2021a,b) but rather on comparing the three different OC groups with each other, the usage of average values is justified. To investigate the variability of the $EF_{aer.}$, the minimum ratio of $c_{(analyte)aer.}$ /$c_{(Na+)aer.}$ vs. the maximum ratio of $c_{(analyte)seawater}$ /$c_{(Na+)seawater}$ was applied and vice versa. As seawater concentration, the bulk water or the SML concentration can be applied.

Statistical significance was evaluated using the analysis of variance (ANOVA).

3. Results and Discussion

3.1 SML and bulk water: concentration and composition

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, Table 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 to bulk water. However, despite the variability of the DAA in the SML, they are not statistically different to the other two compound groups (DL and DCHO) as well as to the DAA in the bulk water (Anova one way, $p > 0.5$ at the 0.5 level) that is different in the case of free amino acids (FAA). In total, no significant difference is present between the compound groups within the SML and the ULW (Anova one way, $p > 0.5$ at the 0.5 level). Resulting from the higher SML concentrations, the average SML enrichment factors of DAA is 2.3 ± 0.4 (Table 1) and therefore higher compared to the DCHO (EF_{SML} = 1.1 ± 0.5) and DL (EF_{SML} = 1.3 ± 0.2). The high variability of the DAA concentrations agreed well with the FAA that comprise the sum of unbound individual amino acids i.e. not bound in a peptide or protein and were measured at this location during the MarParCloud campaign (Triesch et al., 2021a). However, the FAA in the SML were significantly higher compared to the FAA in the bulk water (Triesch et al., 2021a). Other studies have pointed out highly variable amino acid concentrations as well, 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).

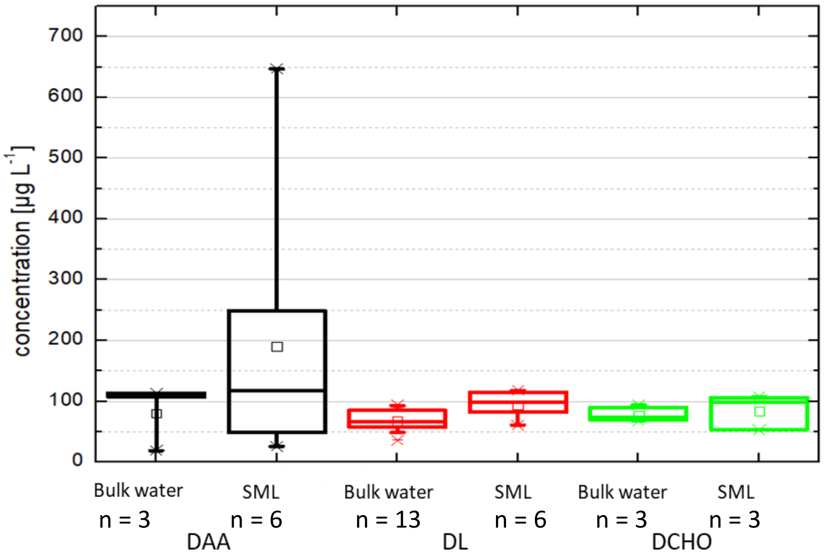

Figure 1

Regarding the composition of the individual DAA measured here, clear differences between the SML and the bulk water characteristics were observed (Figure 2, blue and orange bars, data in Tables S2 - 5). 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 Table S3).

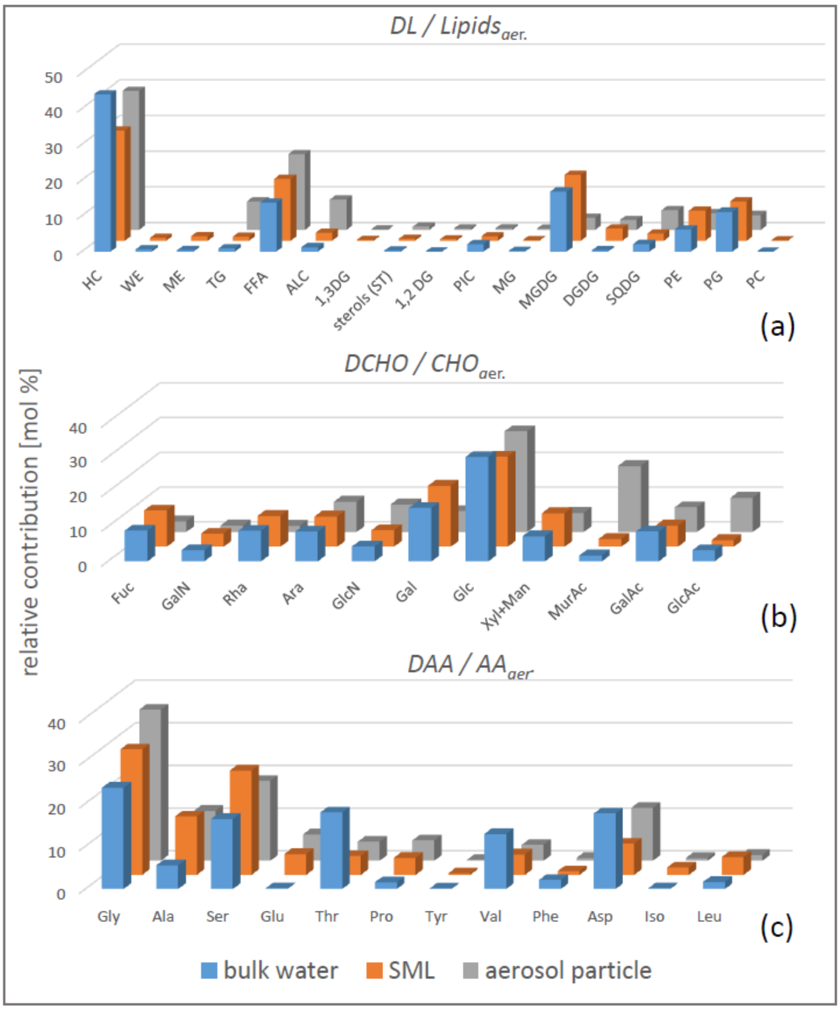

Figure 2

In contrast to the DAA, the DCHO enrichment in the SML was less pronounced with an EF_{SML} of 1.1 ± 0.5 (Table 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 (Figure 2, blue and orange bars).

The enrichment of the DL (EF_{SML} = 1.3 ± 0.2, Table 1) was very similar to the DCHO enrichment and is discussed in Triesch et al. (2021b). 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. However, it is important to mention that the number of samples that have been analysed is different and limited (Table 1 and Figure 1) and samples from partly different dates of the campaign have been analysed and compared.

3.2 Discussion of the SML enrichment

3.2.1 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 groups investigated here, 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. 2021a). Nevertheless, the enrichment of the DL in the SML was significantly lower compared to the carbohydrates and amino acids. This was obvious from a comparison of the averaged values as well as from single samples obtained at the same date (03 October 2017 and 07 October 2017, values in Tables S2, S3, and Triesch et al. 2021b).

One explanation for the finding lies in the sampled SML thickness. With the glass plate technique, an SML thickness of about 100 µm has been sampled and reported for the CVAO area (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 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 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, however, cannot be probed with currently applied 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, particularly when discussing lipid enrichments in the SML. Here, a combination of bulk measurements with dedicated surface probing appears highly desirable.

3.2.2 Details of SML enrichment mechanisms

(i) Co-adsorption

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; Hasenecz 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 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. In incubated cloud water, as another marine compartment, Glu has been shown to be produced via biotic and abiotic mechanisms, e.g. via the oxidation of proline (Jaber et al., 2021 and refs. therein) and such processes may be relevant in the ocean surface as well. Regarding biotic processes, it is well-known that microorganisms have complex and highly interconnected enzymatic networks and can 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 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 is often observed 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 shown 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.

3.3. Aerosol particles: 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 $AA_{aer.}$

and CHO$_{aer.}$ were 2.4 ± 1.1 ng m^{-3} and 1.0 ± 1.1 ng m^{-3}, respectively (Figure 3, Table 1) and not significantly different ULW (Anova one way, p > 0.5 at the 0.5 level).

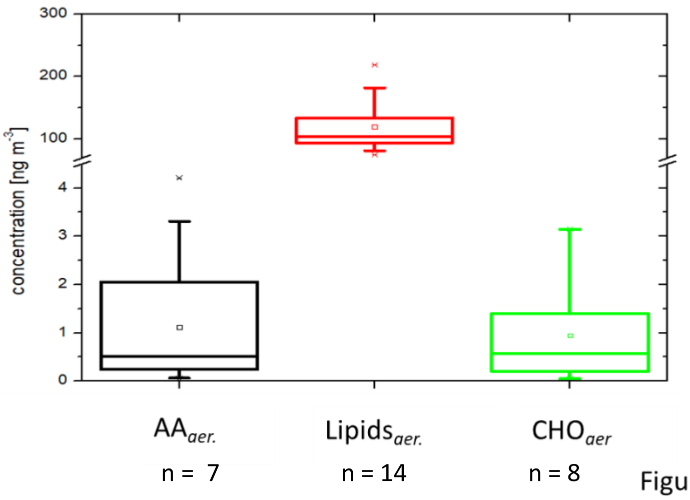

Figure 3

Compared to results from the Polar Regions, the CHO$_{aer.}$ 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. The AA$_{aer.}$ are generally in the same order of magnitude compared to other marine locations (Matos et al., 2016; Matsumoto and Uematsu, 2005; Renard et al., 2022; Wedyan and Preston, 2008). However, concentrations of amino acid and carbohydrates in urban, rural, and forest areas are significantly higher (2-3 orders of magnitudes) compared to the values and the spectrum of compounds is strongly shifted (e.g. Dominutti et al., 2022; Samake et al., 2019; Zhu et al., 2022).

Comparing the data obtained here with those from analytical techniques that use functional group information (FT-IR) has shown that the latter techniques often attribute a large fraction of alcohol (hydroxyl) functional groups on the marine aerosol particles (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$_{aer..}$ 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 AA$_{aer.}$ and CHO$_{aer.}$, the Lipid$_{aer.}$ concentrations were 120 ± 43 ng m^{-3} and therefore two orders of magnitude higher than the other two organic groups (Figure 3, Table 1) The Lipid$_{aer.}$ were significantly higher than the AA$_{aer.}$ ($p = 6.6E-13$) and the CHO$_{aer.}$ ($p = 1.6E-7$) (Anova one way, at the 0.5 level). One possible reason for the higher Lipid$_{aer.}$ concentration could lay in the difference in the extraction procedure (Sect. 2.2) as AA$_{aer.}$ and CHO$_{aer.}$ were extracted in water, while the Lipid$_{aer.}$ were extracted in an organic solvent. Previous lipid analysis on a molecular level revealed concentrations between 0.19 - 23 ng m^{-3} for ALC and between 2.5 - 38 ng m^{-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^{-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^{-3}. Hence, these data are in the same order of magnitude as here measured lipid groups (ALC: 6.3 ng m^{-3}, free fatty acids: 18.5 ng m^{-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.

A recent study using FT-ICR-MS found that among a large number of molecular formulas, large peak numbers were assigned to proteins and lignins (phenolic macromolecules) followed by carbohydrates and lipids in aerosol originating from the Arctic ocean (vs. non-ocean aerosol) (Choi et al., 2019).

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 faction was dominated by lipopolysaccharides, known 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 high Lipid$_{aer.}$ concentrations presented here.

A high Lipid$_{aer.}$ 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$_{aer.}$ 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 Tables S6 and S8). 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.

3.4 Aerosol enrichment

3.4.1 Aerosol enrichment factors

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

Insert Table 1

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

3.4.2 Oceanic transfer and atmospheric in situ formation

The overall high enrichment of OC in the aerosol particles is explained by complex, not yet - resolved interactions at the ocean surface where organic matter is enriched relative to 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 $\text{EF}_{aer.}$ of OC in submicron aerosol particles of 10^2 to 10^3 compared to the SML (Burrows et al., 2014). However, $\text{EF}_{aer.}$ from ambient and laboratory-controlled observations show that for some compounds even higher $\text{EF}_{aer.}$ are obtained. In a controlled tank study, Rastelli et al. (2017) found strong enrichments for lipids (up to $1.4\text{x}10^5$), as well as for proteins (up to 1.2x10^5) and carbohydrates (up to 1.0x10^5, Table 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.

3.5. 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 during the time of the campaign (Figure S2) 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.

3.6 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 (Figure 2, grey bars, and values in Tables S2 - 5). 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 within ocean and atmosphere (Triesch et al., 2021b).

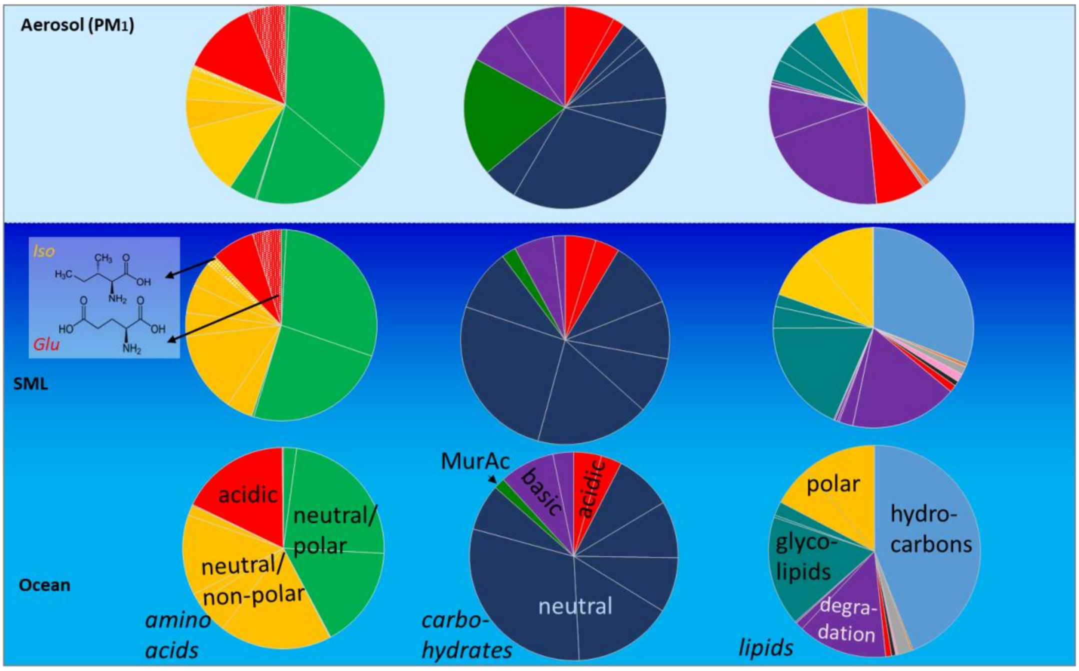

Figure 4

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, Figure 4, individual values in Table S6). 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 measurements performed here, 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 aerosol particles investigated here 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.

3.7 Contribution to aerosol particle OC

3.7.1 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 Table S7). 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 ($\text{Lipids}_{aer.}$, $\text{AA}_{aer.}$, $\text{CHO}_{aer.}$), 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 Figure 5 (values in Table S8). 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 $\text{Lipids}_{aer.}$ 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 $\text{CHO}_{aer.}$ and the $\text{AA}_{aer.}$ made up a minor percentage with 0.3 and 0.4% respectively. Regarding the lipids, it needs to be considered that the analysis performed here 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.

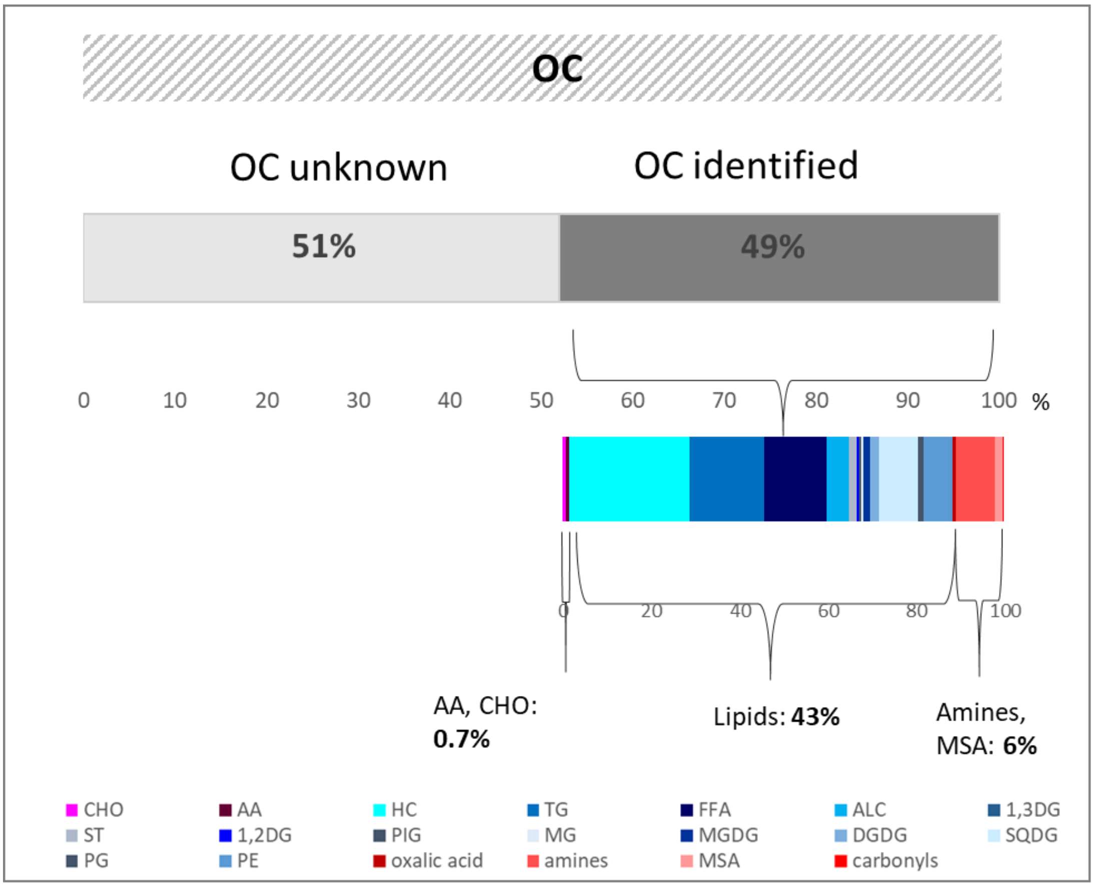

Figure 5

3.7.2 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 methods applied here 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 Beaupre 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 oligotrophic region does not seem to constitute the majority of OC as reported by Kieber et al. (2016).

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

The CVAO is localized in an oligotrophic region and should therefore be reasonably 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, neglects any potential seasonal changes 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 emission fluxes presented here 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 and the sample number is limited, the results suggest 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 with respect to sea salt ($EF_{aer.}$ = 10^3 for the carbohydrates and the amino acids). To this end, the lipids were even more 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 likely 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 $CHO_{aer.}$ 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 reveals 43% of the OC on the aerosol particles, however, the $Lipid_{aer.}$ composition on a molecular level cannot be obtained from the measurements performed here. 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, as (qualitatively) suggested by other studies (Choi et al., 2019; Schmitt-Kopplin et al., 2012). 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 data presented here 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) an 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 $Lipids_{aer.}$ (a), dissolved carbohydrates (DCHO) and $CHO_{aer.}$ (b) and dissolved amino acids (DAA) and AA_{aer}. (c) in the bulk water (blue bars), the SML (orange bars), and the PM_1 aerosol particles (grey bars). Mol% were calculated from the molar masses of the respective analytes. For the lipid groups, the molar masses of the surrogate standard (sec. 2.2.2 and Tab. S8) are applied. The relative mol fractions are relative to the total of each type (DAA, DCHO, and DL) analysed.

Figure 3: Box and whisker plot of the concentrations in the PM_1 aerosol particles (ng m^{-3}); n = 8 for $CHO_{aer.}$, n = 7 for $AA_{aer.}$, n = 14 for $Lipids_{aer}$.
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 / $Lipids_{aer.}$, DCHO / $CHO_{aer.}$ and DAA / AA_{aer}. 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 PM_1 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. To investigate the variability of the $EF_{aer.}$ the minimum ratio of $c_{(analyte)aer.} / c_{(Na+)aer.}$ vs. the maximum ratio of $c_{(analyte)seawater} / c_{(Na+)seawater}$ was applied (and vice versa) and the range of $EF_{aer.}$ is given in brackets.

For comparison, the last column lists the $EF_{aer.}$ for PM_1 from a chamber study (Rastelli et al., 2017).

DCHO / $CHO_{aer.}$

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 (2.33E+02-5.93E+03)	1.35E+03 (1.54E+02-4.56E+03)	1.31E+03	*1.00E+05*
n = 3	n = 3	n = 8					

DAA / $AA_{aer.}$

SML	Bulk water	PM1					
190 ± 238	80 ± 53	2.4 ± 1.1	2.3 ± 0.4	9.23E+02 (1.39E+02-1.62E+04)	2.07E+03 (7.95E+02-2.19E+04)	1.50E+03	*1.20E+05*
n = 6	n = 3	n = 7					

DL / $Lipid_{aer.}$

SML	Bulk water	PM1					
83 ± 24	70 ± 25	120 ± 43	1.3 ± 0.2	1.42E+05 (6.21E+04-3.92E+05)	1.71E+05 (5.83E+04-5.49E+05)	1.57E+05	*1.40E+05*
n = 6	n = 13	n = 14					