Concerted measurements of free amino acids at the Cape Verde Islands: High enrichments in submicron sea spray aerosol particles and cloud droplets

5   Nadja Triesch[1], Manuela van Pinxteren[1], Anja Engel[2] and Hartmut Herrmann[1]

[1]Leibniz-Institute for Tropospheric Research (TROPOS), Atmospheric Chemistry Department (ACD), Leipzig 04318, Germany
[2]GEOMAR Helmholtz Centre for Ocean Research, Kiel 24105, Germany

10   *Correspondence to*: Hartmut Herrmann (herrmann@tropos.de)

Abstract.

This study presents measurements of free amino acids (FAA) in the marine environment to elucidate their transfer from the ocean into the atmosphere to marine aerosol particles and to clouds. FAA were investigated in seawater (underlying water (ULW), sea surface microlayer (SML)), in ambient marine size-segregated aerosol particle samples at two heights (ground

15   based at the Cape Verde Atmospheric Observatory (CVAO) and at the Mt. Verde, 744 m height) and in cloud water using concerted measurements. The ∑FAA concentration in the SML varied between 0.13-3.64 µmol L^{-1}, in the ULW between 0.01-1.10 µmol L^{-1} and a strong enrichment of ∑FAA in the SML (EF$_{SML}$: 1.1-298.4, average of 57.2) was observed. In the submicron (0.05-1.2 µm) aerosol particles at the CVAO, the composition of FAA was more complex and higher atmospheric concentration of ∑FAA (up to 6.3 ng m^{-3}) compared to the supermicron (1.2-10 µm) aerosol particles (maxima of 0.5 ng m^{-3})

20   were observed. The total ∑FAA concentration (PM$_{10}$) was between 1.8-6.8 ng m^{-3} and tended to increase during the campaign. Averaged ∑FAA concentrations on the aerosol particles at the Mt. Verde were lower (submicron: 1.5 ng m^{-3}, supermicron: 1.2 ng m^{-3}) compared to the CVAO. A similar percentage contribution of ∑FAA to dissolved organic carbon (DOC) in the seawater (up to 7.6 %) and to water-soluble organic carbon (WSOC) on the submicron aerosol particles (up to 5.3 %) indicated a related transfer process of FAA and DOC in the marine environment. The FAA were strongly enriched in the submicron

25   aerosol particles (EF$_{aer(∑FAA)}$ 4·10^2-3·10^4, EF$_{aer(WSOC)}$ 2·10^3-1·10^4), possibly resulting from film droplet formation. The enrichment in supermicron aerosol particles was several orders of magnitude lower compared to submicron size range with EF$_{aer(∑FAA)}$ 1·10^1-2·10^1, EF$_{aer(WSOC)}$ 3·10^2-4·10^2. A case study showed that several amino acids were transported from the ocean up to cloud level (e.g. aspartic acid, glutamic acid, proline) while other amino acids might not be transferred or quickly degraded (e.g. phenylalanine, tyrosine) or produced (e.g. GABA). The cloud water samples exhibited a similar composition of FAA compared to the SML but a strong variation of the atmospheric concentration of ∑FAA during the campaign (11.2-

30   489.9 ng m^{-3}). FAA in cloud water samples showed a strong enrichment by a factor of 4·10^3 compared to the SML. The presence of high concentrations of FAA in general and of biologically produced FAA (aspartic acid) in particular together with

the presence of inorganic marine tracers (sodium, methane sulfonic acid) demonstrates the influence of oceanic sources on marine clouds.

Keywords

5   amino acids, organic matter, seawater, sea surface microlayer, size-segregated aerosol particles, cloud water, transfer, enrichment factor, Cape Verde Atmospheric Observatory (CVAO)

1.   Introduction

Most of the standing stock of fixed nitrogen in the surface global ocean (upper 200 m) exists in the form of dissolved organic nitrogen (DON) (Bronk, 2002;Aluwihare et al., 2005). In the euphotic zone (<100 m) the bulk DON pool can become

10   bioavailable to the resident microbial community. The remineralized nitrogen can then provide a potential source of new nitrogen to support primary production in oligotrophic systems (Letscher et al., 2013) and can serve as nutrients for marine biological systems. One important DON group are proteinaceous compounds that include amino acids either free (FAA) or in combined form (CAA). The proteinaceous compounds are often analysed as a sum parameter 'proteins' using an analytical staining method with Coomassie blue developed by Bradford (1976) and often applied in previous studies (Gutiérrez-Castillo

15   et al., 2005;Mandalakis et al., 2011;Rastelli et al., 2017). Besides determining the sum parameter 'proteins', it is important to investigate FAA, because these compounds are more utilizable sources of nitrogen than proteins for aquatic organism such as phytoplankton and bacteria (Antia et al., 1991;McGregor and Anastasio, 2001). It was shown in previous studies that amino acids in aerosol particles can have both natural and anthropogenic sources. Amino acids were detected in volcanic emissions (Scalabrin et al., 2012), during biomass burning events (Chan et al., 2005;Feltracco et al., 2019) and can be produced by plants,

20   pollens, fungi, bacterial spores and algae (Milne and Zika, 1993;Zhang and Anastasio, 2003;Matos et al., 2016). Because of their hygroscopic properties, some amino acids can act as ice-forming particles (INP) (Szyrmer and Zawadzki, 1997) and cloud condensation nuclei (CCN) (Chan et al., 2005;Kristensson et al., 2010) in the atmosphere.

Amino acids are also present and have been described in the marine environment. They contribute to global nitrogen and carbon cycles and to the atmosphere-biosphere nutrient cycling (Zhang and Anastasio, 2003;Wedyan and Preston, 2008).

25   Moreover, amino acids are produced in the ocean and reported in the upper layer of the ocean, the sea surface microlayer (SML) (Kuznetsova et al., 2004;Reinthaler et al., 2008;van Pinxteren et al., 2012;Engel and Galgani, 2016). The SML, as the direct interface between the ocean and the atmosphere, may play an important role as a source of organic matter (OM) in aerosols in the marine environment (Engel et al., 2017). Specific organic groups of compounds, among them nitrogen containing OM (Engel and Galgani, 2016) can be strongly enriched in the compounds from the SML. It was shown that

30   especially FAA exhibit a high enrichment in the SML (EF_{SML}), e.g. in the subtropical Atlantic ($EF_{SML(\sum FAA)}$: 7.6-229.4, average of 59.3±68.8) and in the western Mediterranean Sea ($EF_{SML(\sum FAA)}$: 6.2-26.1, average of 16.5±9.1) (Reinthaler et al., 2008). Moreover, correlations between individual amino acids and (micro)biological lifeforms in the marine environment were

observed. Hammer and Kattner (1986) reported correlations between aspartic acid and diatoms and zooplankton in seawater. GABA (γ-aminobutyric acid) is an indicator of microbiological decomposition of organic matter (Dauwe et al., 1999;Engel et al., 2018) and used as a microbiological proxy in aerosol particles. From the ocean, amino acids as part of proteinaceous compounds can be transferred to the atmosphere via bubble bursting (Kuznetsova et al., 2005;Rastelli et al., 2017).

5 In most parameterisations regarding the transfer of organic matter (OM) from the ocean into the atmosphere, OM is described via chlorophyll-*a* (chl-*a*) concentrations as chl-*a* is a broad indicator for biological productivity (Gantt et al., 2011;Rinaldi et al., 2013). However, chl-*a* concentration solely does not adequately describe the complete spectrum of biological activity (Quinn et al., 2014) and especially in oligotrophic regions additional parameters besides wind speed and chl-*a* must be taken into consideration for accurately prediction of organic matter on aerosol particles (van Pinxteren et al., 2017). Moreover,

10 different groups of OM, such as lipids, carbohydrates and proteins show different characteristics in terms of their sea-air transfer (Burrows et al., 2014). In a new approach, Burrows et al. (2014) included important compound classes of OM instead of chl-*a* only and developed a parameterization based on the compounds' molecular weight, physical and chemical characteristics and the surface adsorption behaviour. To apply and further develop such parameterizations, distinct measurements of these organic compound groups, such as amino acids in different oceanic regions are urgently needed.

15 Although the study and characterization of amino acids is on the agenda of atmospheric scientist, the true role and the fate of amino acids in the atmosphere still are poorly understood (Matos et al., 2016). Several studies of FAA also in the marine regime exist to date. However, there is a lack of measurements that regard the abundance and molecular composition of amino acids simultaneously in marine compartments - in the seawater and especially in size-segregated aerosol particles. Matsumoto and Uematsu (2005) investigated FAA in marine aerosol particles over the western North Pacific Ocean with the differentiation

20 between $PM_{2.5}$ and $>PM_{2.5}$ aerosol particles. Mace et al. (2003) studied the presence of FAA and their contribution to organic nitrogen in size-separated aerosol particles, differentiated between coarse mode (>1 µm) and fine mode aerosol (<1 µm), collected at the Cap Grim sampling station in Tasmania (Australia). Using a five-stage cascade impactor, Barbaro et al. (2015) investigated FAA in size-segregated Antarctic aerosol particles to gain information about FAA as possible tracers of primary biological production in Antarctic aerosol particles. Although there are several studies in different marine regions, there is a

25 lack of ambient measurements of FAA simultaneously in seawater and in size-segregated aerosol particles in the tropical Atlantic Ocean.

The aim of the present study is to investigate the occurrence of FAA in the marine environment in the remote tropical North Atlantic Ocean at the Cape Verde Atmospheric Observatory (CVAO). Their abundance, origins and the possible transfer from the seawater and their transport within the atmosphere is investigated. Especially the similarities and differences between the

30 amino acid composition in the submicron (0.05-1.2 µm) and the supermicron (1.2-10 µm) aerosol particles will be elucidated. To this end, concerted measurements, comprising measurements of FAA in the underline seawater (ULW), in the SML and in size-segregated aerosol particle samples from a remote station, the Cape Verde Atmospheric Observatory (CVAO), were performed during a campaign from 13 September to 13 October 2017. Additionally, the concentrations of FAA in size-segregated aerosol particles and in cloud water samples, collected at the mountain station on the top of 'Monte Verde' (MV)

will be discussed. This data set of different marine compartments – seawater including the SML, aerosol particles at two different heights and cloud water samples – will be applied to characterize amino acids more detailed regarding their complexity, sources, potential transfer and their transport within the marine atmosphere. Finally, the potential of individual FAA as proxies or tracer for specific sources of aerosol particles and cloud water shall be elucidated.

2. Experimental

2.1 Study area

In the framework of the MarParCloud (Marine biological production, organic aerosol particles and marine clouds: a Process chain) project with contribution of MARSU (MARine atmospheric Science Unravelled: Analytical and mass spectrometric techniques development and application), a field campaign at the Cape Verde Atmospheric Observatory (CVAO) from 13 September to 13 October 2017 was performed. The CVAO, a remote marine station, is located at the northeast coast of São Vicente island, directly at the ocean (16°51'49'N, 24°52'02''W) and is described more detailed in Fomba et al. (2014);Carpenter et al. (2010). During this campaign, concerted measurements were performed including sampling of size-segregated aerosol particles at the CVAO and seawater sampling at the ocean site (~16°53'30'N, ~24°54'00''W). The location was carefully chosen with minimal influence of the island and located in wind direction to the CVAO. Additionally, aerosol sampler and cloud water sampler were installed at the mountain station on the top of the mountain 'Monte Verde' (MV). Further details on the MarParCloud campaign with contribution of MARSU will be provided by van Pinxteren et al. (2019a).

2.1.1   Seawater sampling: SML and ULW

The seawater samples were taken with a fishing boat, starting from Bahia das Gatas, São Vicente. A glass plate with a sampling area of 2000 cm² was vertically immersed into the seawater and then slowly drawn upwards to sample the SML. The surface films adhered to the surface of the glass plate and were removed with Teflon wipers directly in a pre-cleaned bottle. This glass plate approach is described in detail by Cunliffe (2014). The ULW was sampled in a depth of 1 m into a pre-cleaned plastic bottle fitted on a telescopic rod. To avoid influences from the SML, the bottles were opened underwater at the intended sampling depth. All seawater samples were stored in pre-cleaned plastic bottles at -20 °C until the time of analysis. All materials for seawater sampling were pre-cleaned using a 10 % HCl solution and high purity water.

2.1.2   Aerosol particles sampling

The sampling of the size-segregated aerosol particle samples was performed at the top of a 30 m sampling tower at the CVAO and on the top of the mountain 'Monte Verde' (744 m a.s.l.) using five stage Berner-type impactors (Hauke, Gmunden, Austria). The Berner impactors were operated with a flow rate of 75 L min^{-1} for 24 h and pre-baked aluminium foils (350°C for two hours) were used for substrate material. The five stage Berner impactor includes stage 1 (B1): 0.05-0.14 µm, stage 2 (B2): 0.14-0.42 µm, stage 3 (B3): 0.42-1.2µm, stage 4 (B4): 1.2-3.5 µm and stage 5 (B5): 3.5-10 µm. In our study, the size-segregated aerosol particle samples were distinguished in the submicron size range (B1, B2, B3), the supermicron size range

(B4, B5) and in PM_{10} (B1-5) aerosol particle samples. After sampling, the aluminium foils were stored in aluminium boxes and stored at -20 °C until the time of analysis.

2.1.3   Cloud water sampling

For the sampling of cloud water, an Acrylic glass Caltech Active Strand Cloud water Collector version 2 (CASCC2) according to Demoz et al. (1996) was used at the mountain station 'Monte Verde' (MV). During a 'cloud event' the bottles were changed every 2-3 h, on the other days the sampling time was e.g. overnight (12 h). For each sampling, the used Teflon rods were pre-cleaned using a 10 % HCl solution followed by high purity water. The liquid water content (LWC) of the cloud were measured continuously by a particle volume monitor (PVM-100, Gerber Scientific, USA). The collected cloud water was sampled in pre-cleaned plastic bottles and stored at -20 °C until the time of analysis.

2.2   Analytics

2.2.1   Seawater samples analytics

For the DOC/TDN content and the analysis of inorganic ions, the seawater samples were filtered first (0.45 µm syringe filter) and then quantified using a TOC-VCPH analyser (Shimadzu, Japan) or ion chromatography (ICS3000, Dionex, Sunnyvale, CA, USA) as described in van Pinxteren et al. (2017). For amino acid analysis, the seawater samples need to undergo a desalination step first. To achieve this, 32 mL (SML samples) or 48 mL (ULW samples) were desalinated using Dionex™ OnGuard™II Ag/H cartridges (Thermo Fisher Scientific™, Waltham, Massachusetts, USA). The volume of desalinated samples was reduced to several µL using a vacuum concentrator at T=30 °C (miVac sample Duo, GeneVac Ltd., Ipswich, United Kingdom) with a recovery rate of >86 %. The enriched samples were filtered using 0.2 µm syringe filters (Acrodisc-GHP; 25 mm, Pall Corporation, New York, USA) and a derivatization was performed using AccQ-Tag™ precolumn derivatization method (Waters, Eschborn, Germany). The amino acid analysis includes glycine (Gly), L-alanine (Ala), L-serine (Ser), L-glutamic acid (Glu), L-threonine (Thr), L-proline (Pro), L-tyrosine (Tyr), L-valine (Val), L-phenylalanine (Phe), L-aspartic acid (Asp), L-isoleucine (Ile), L-leucine (Leu), L-methionine (Met), L-glutamine (Gln) and γ-aminobutyric acid (GABA) (purity ≥ 99 %, Sigma-Aldrich, St. Louis, Missouri, USA). The analytical measurements of the derivatized FAA were performed with ultra high performance liquid chromatography with electrospray ionization and Orbitrap mass spectrometry (UHPLC/ESI-Orbtitrap-MS). The UHPLC system (Vanquish Horizon UHPLC system, Thermo Fisher Scientific™, Waltham, Massachusetts, USA) was coupled to an ESI-Orbitrap mass spectrometer (Q Exactive™ plus, Thermo Fisher Scientific™, Waltham, Massachusetts, USA). The samples were separated using an ACQUITY UPLC® HSS T3 column (Waters, Eschborn, Germany) with the dimensions 1.8 µm, 2.1 x 100 mm at constant temperature of 30 °C and a detection in positive mode. The eluent composition was (A) 0.2 vol % acetic acid in high purity water (Millipore Elix 3 and Element A10, Merck Millipore, Darmstadt, Germany) and (B) acetonitrile (Optima® LC/MS Grade, Fisher Scientific, Hampton, New Hampshire, USA). The flow rate of the eluent was 0.3 mL min^{-1} and the eluent gradient program was 5 % B for 1 min, 5 % B to 100 % B in 16 min, 100 % B for 2 min constant, in 0.1 min back to 5 % B and held constant for 3.9 min. This analytical can be used for amines,

too, as described in van Pinxteren et al. (2019b). The amino acid concentrations were determined via external calibration. Since no chiral column was used in the UHPLC separation, it is possible that not only L-amino acids, which were used as the standard, were quantified, but that the here presented concentrations were possibly quantified as the sum of the L- and D-amino acids. Each seawater sample was measured as a duplicate with relative standard deviation <10 % and under consideration of the blank samples for seawater. The blank samples for seawater consist of high purity water, which was filled in pre-cleaned plastic bottles and handled the same as the seawater samples. The LOQ of the individual FAA in seawater samples is in good agreement with FAA analysis in seawater samples (e.g. Kuznetsova et al. (2004)) and is listed in Table S1.

2.2.2 Aerosol particle filter analytics

For analysing the size-segregated aerosol particle samples, the substrate material of each stage was extracted in 3 mL high purity water (Millipore Elix 3 and Element A10, Merck Millipore, Darmstadt, Germany). The aqueous particle extracts were divided into aliquots for the analysis of water-soluble organic carbon (WSOC)/ total dissolved nitrogen (TDN), inorganic ions and amino acids. The aliquots for WSOC/ TDN were filtered using a 0.45 µm syringe filter and then determined by a TOC-VCPH analyser (Shimadzu, Japan) as described in van Pinxteren et al. (2012). For the analysis of inorganic ions, the aliquots (250 µL) were filtered (0.45 µm syringe filter) and investigated using ion chromatography (ICS3000, Dionex, Sunnyvale,CA, USA), as described in Mueller et al. (2010). The aliquot (1.5 mL) of the aqueous particle extracts was reduced to several µL using a vacuum concentrator at T=30 °C (miVac sample Duo, GeneVac Ltd., Ipswich, United Kingdom), derivatized and analysed using the UHPLC/ESI-Orbtitrap-MS method as described in section 2.2.1 for seawater samples. Amino acid concentrations were calculated via external calibration, measured each sample in duplicate with a relative standard deviation <10 % and under consideration of field blanks. For generating field blanks, pre-baked aluminium foils without active sampling, were cut and prepared the same as field samples, including extraction and measurements for WSOC/ TDN, inorganic ions and amino acids analysis. Because field blank samples (n=9) were available for all investigated compounds, the mean value of the blank results were taken into account during evaluations. All here presented values for aerosol samples are blank corrected. The limit of quantification (LOQ) of the individual FAA in aerosol particle samples is listed in Table S1 and is in good agreement with the sensitivity of other analytical methods for FAA in aerosol particles (e.g. Matsumoto and Uematsu (2005)). The analysis of mineral dust tracers of the individual Berner stages was performed as described in Fomba et al. (2013).

2.2.3 Cloud water samples analytics

The cloud water samples were operated the same as seawater samples for the analysis of DOC/TDN and inorganic ions (section 2.2.1). For amino acid analysis, the volume of cloud water samples (44 mL) was reduced to several mL using a vacuum concentrator at T=30 °C (miVac sample Duo, GeneVac Ltd., Ipswich, United Kingdom). After the filtration using 0.2 µm syringe filters filters (Acrodisc-GHP; 25 mm, Pall Corporation, New York, USA), an aliquot of the prepared cloud water was derivatized using AccQ-Tag™ precolumn derivatization method (Waters, Eschborn, Germany). The analytical measurements of the derivatized (FAA) were performed with UHPLC/ESI-Orbtitrap-MS (section 2.2.1). The cloud water samples were

measured as duplicates with relative standard deviation <10 %. Via external calibration the amino acid concentrations under consideration of the cloud water blanks were calculated. The blank samples of cloud water were generated by rinsing the pre-cleaned Teflon rods with high purity water after its installation in the cloud water sampler. The blank samples were handled the same as the field cloud water samples including derivatization and analytical separation as described in section 2.2.1. The

5   LOQ of the individual FAA in cloud water samples is in good agreement with the reported sensitivity of FAA analysis in cloud water (Bianco et al., 2016) and listed in Table S1. To calculate the atmospheric concentration of FAA in cloud water, the measured concentration were multiplied with the measured liquid water content (LWC) of the clouds as described in Fomba et al. (2015).

10   **2.2.4   Enrichment factors**

The enrichment factor in SML (EF$_{SML}$) was calculated by dividing the concentration of the analyte in the SML with the concentration of the analyte in the underlying seawater (ULW) using the following equation (1):

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

Accordingly, an enrichment in the SML is indicated by EF$_{SML}$ > 1, a depletion in the SML with EF$_{SML}$ < 1.

To calculate the enrichment factor of the individual analytes in different matrices (M), the concentration of the analyte in matrix 1 (M$_1$) related to the sodium (Na$^+$) concentration in M$_1$ was divided by the analyte concentration in matrix 2 (M$_2$)

20   relation to the Na$^+$ concentration in M$_2$ using equation (2):

$$EF_{M1} = \frac{c\,(analyte)_{M1)}/c\,(Na^+)_{M1}}{c\,(analyte)_{M2}/c\,(Na^+)_{M2}} \qquad (2)$$

Therefore, it was possible to calculate the enrichment factor in aerosol particles (EF$_{aer}$) with the concentration of the analyte

25   and Na$^+$ of the five stages of the Berner impactor (B$_x$ with x = 1 - 5) as M$_1$ and of the SML as M$_2$. For this purpose, aerosol particle concentrations, typically sampled at a 24-hour interval, were combined with SML concentrations, which have been collected during the aerosol sampling period. The analyte concentration in each size class of size-segregated aerosol particle samples (B1-5) was combined with the analyte concentration in SML. The calculation of the enrichment factor aerosol EF$_{aer}$ was limited to the availability of data in both matrices – size-segregated aerosol particles and SML samples. The EF$_{aer}$ could

30   only be calculated if the concentration of the analyte as well as the sodium concentration in the size-segregated aerosol particles and in the corresponding SML samples could be quantified. To calculate the enrichment factor in cloud water (EF$_{CW}$) the concentration of the analyte and Na$^+$ of the cloud water as M$_1$ and of the SML as M$_2$ were considered. The determination of

the EF_{aer} was possible for n=3 samples and the determination of EF_{CW} was possible for n=1 and will be discussed in more detail in section 3.4.

3. Results and Discussion

3.1 Seawater samples

Free amino acids in seawater samples

FAA were measured in the seawater as a source region of FAA on primary marine aerosol particles. In Fig. 1, the measured $\sum FAA$ concentration in the SML and the ULW samples together with their enrichment factor EF_{SML} (Eq. 1) are shown.

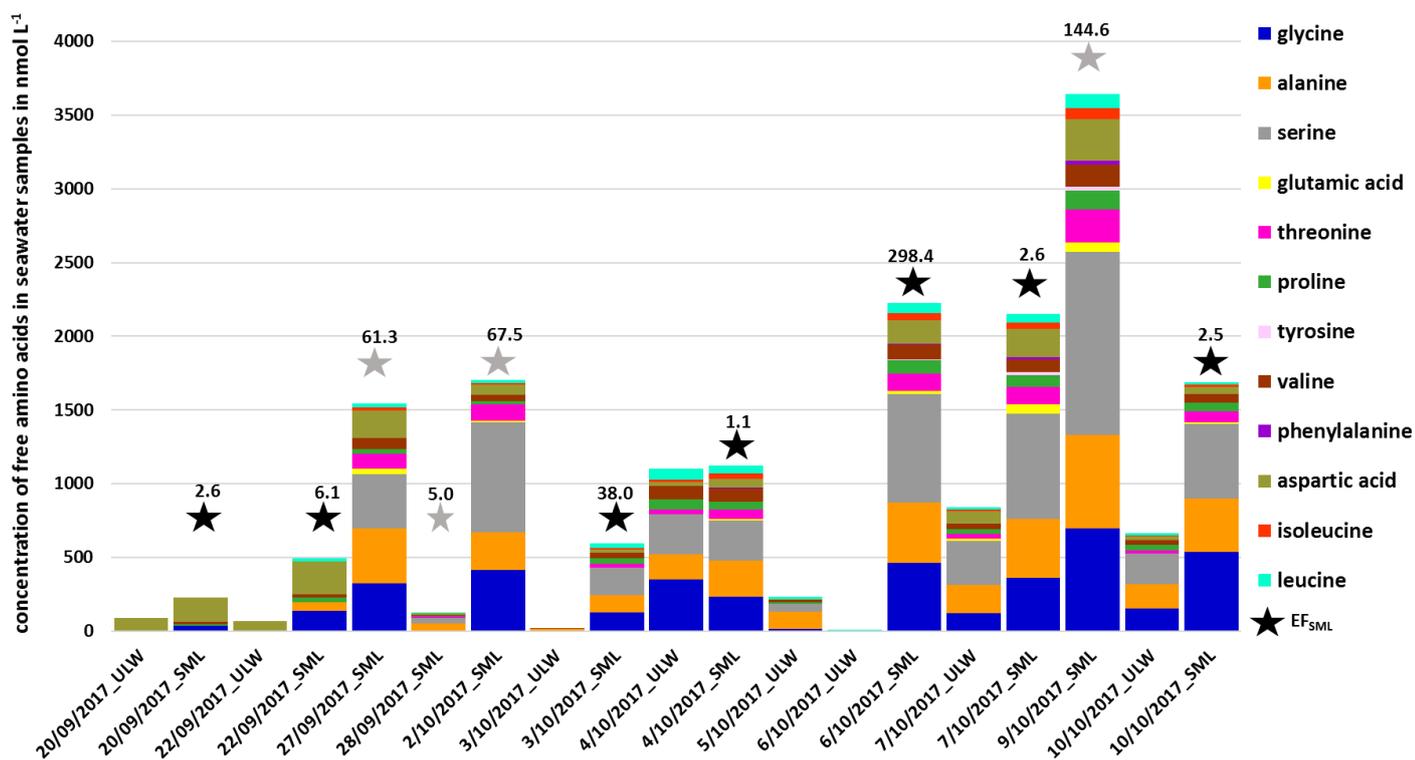



Figure 1: Individual FAA concentration in the seawater samples (ULW, SML) in nmol L^{-1}, and the enrichment factor EF_{SML} of $\sum FAA$; EF_{SML} based on measurements (black stars), EF_{SML} based on LOQ/2 estimation (grey stars)

$\sum FAA$ included all investigated amino acids (listed in 2.2.1) with the exception of methionine, glutamine and GABA. These analytes were not detected in the seawater samples (ULW and SML). The concentration of $\sum FAA$ varied between 0.01-1.10 µmol L^{-1} in the ULW and between 0.13-3.64 µmol L^{-1} in the SML. In the second half of the campaign, the $\sum FAA$ concentration was higher than in the first part. A general strong variability of $\sum FAA$ concentration, especially in the SML, were reported in different oceanic areas in previous studies (Kuznetsova and Lee, 2002;Kuznetsova et al., 2004;Reinthaler et al., 2008;van Pinxteren et al., 2012;Engel and Galgani, 2016). Reinthaler et al. (2008) reported concentrations of dissolved

FAA in subtropical Atlantic Ocean of 0.02-0.13 µmol L^{-1} (ULW) and 0.43-11.58 µmol L^{-1} (SML) and in the western Mediterranean Sea 0.07-0.60 µmol L^{-1} (ULW) and 0.77-3.76 µmol L^{-1} (SML). Reinthaler et al. (2008) concluded that the SML in the open ocean is a highly variable environment with high concentrations of dissolved FAA and their strong enrichment in the SML, however, without clear diel variations in their concentrations. The wind speed (Table S2) could not explain the

5 variability of the FAA in the SML or in the ULW and no correlation between wind speed and concentration or enrichment of FAA was observed. This is consistent with other publications, which observed that amino acid concentration in seawater is unrelated to environmental parameters such as wind, humidity and light (Kuznetsova et al., 2004;van Pinxteren et al., 2012). The results of the individual FAA concentration in seawater (ULW, SML) and their EF$_{SML,}$ listed in Table S3, showing clear differences between the single amino acids. Ser was the highest concentrated amino acids in the SML and clearly lower

10 concentrated in the ULW, resulting in the highest value and variance of EF$_{SML}$ (1.1-515.6) of the observed individual FAA. However, other amino acids as e.g. Tyr showed smaller EF$_{SML}$ (2.1-18.7) caused by significantly smaller concentration in ULW and SML samples (Table S3). Our study confirmed previous observations that the SML is often non-uniformly enriched with FAA (Kuznetsova and Lee, 2002;Reinthaler et al., 2008;van Pinxteren et al., 2012;Engel and Galgani, 2016). Different factors, such as the transport of FAA from the ULW to the SML, an in situ production via extracellular hydrolysis of CAA or

15 a direct release of FAA by cell lysis can cause the observed enrichment of FAA in the SML. Kuznetsova and Lee (2002) showed that the fast extracellular hydrolysis of CAA in the SML is not a cause of the non-uniformly enrichment in SML. Moreover, Kuznetsova and Lee (2002) suggested that the intracellular pools of organisms, which are rich in DFAA and DCAA compared to seawater, can be leaching out by stressed microorganisms resulting in an release of DFAA and DFAA with an effect on DFAA and DCAA pools in seawater. On the basis of previous studies, the transportation and the releasing

20 mechanisms seems to be most likely for the observed enrichment of FAA. However, further experiments are required to finally elucidate the most important drivers causing the enrichment. Altogether, it can be concluded that there is a certain variability within the concentration of the FAA in the SML and in the ULW with a clear trend of their strong enrichment in the SML. Nevertheless, the concentration are in the same order of magnitude as reported for these oceanic areas in the literature (Kuznetsova et al., 2004;Reinthaler et al., 2008) and for the here investigated region (Table S4). It can be concluded that the

25 here observed FAA concentrations are representative for the tropical North Atlantic Ocean.

Contribution of FAA to DOC and TDN content in seawater

The DOC and TDN concentrations and their enrichment in the SML (EF$_{SML}$) are listed in Table S5. The contribution of ∑FAA to DOC or to TDN in the seawater was calculated (considering the carbon and nitrogen content of the amino acids, Table S6)

30 and are also listed in Table S5. The carbon content of ∑FAA contributed to DOC between 0.1-7.6 %. in the seawater samples with a median of 2.4 % (n=17), differentiated in SML with 2.8 % (n=11) and in ULW samples with 1.8 % (n=6). Considering the nitrogen content of ∑FAA to TDN in the seawater samples, 0.1-42.4 % of TDN consisted of ∑FAA with a median of 8.3 % (n=18). In the SML, ∑FAA contributed on average with 11.9 % (n=11) and in the ULW with 3.2 % (n=7) to TDN. The observed daily variations of the contribution of ∑FAA to DOC/ TDN, result from daily variations of the concentration of

∑FAA in seawater (Fig. 1) and of DOC/ TDN (Table S5). In the study of Reinthaler et al. (2008) DFAA contributed with ~12 % to DOC and with ~ 30 % to dissolved organic nitrogen (DON) in the SML of the Atlantic ocean and the western Mediterranean Sea. The results concerning contribution to DOC were in the same order of magnitude but slightly lower compared to Reinthaler et al. (2008).

3.2 Size-segregated aerosol particles

3.2.1 Size-segregated aerosol particles at the CVAO

Free amino acids in size-segregated aerosol particles

The atmospheric concentration of ∑FAA in each Berner stage at the CVAO is shown in Fig. 2 lower panel and in the submicron

10 (B1-3), the supermicron (B4-5) and PM_{10} (B1-5) aerosol size range in the upper panel. In the submicron aerosol particles, the concentration of ∑FAA was between 1.3 ng m^{-3} (1/10/2017) and 6.3 ng m^{-3} (7/10/2017). In the supermicron size range, the concentration of ∑FAA varied between 0.2 ng m^{-3} (6/10/2017) and 1.4 ng m^{-3} (22/09/2017). It is obvious that the highest atmospheric concentrations of ∑FAA were found in the submicron aerosol particles (mean of 3.2 ng m^{-3}) compared to the supermicron aerosol particles (mean of 0.6 ng m^{-3}). ∑FAA included all investigated amino acids (listed in 2.2.1) with the

15 exception of methionine and glutamine, both analytes were not detected in the size-segregated aerosol particle samples.

The observed total atmospheric concentration of dissolved FAA (sum of B1-5) was between 1.76-6.82 ng m^{-3} (averaged 3.82 ng m^{-3}) and in good agreement with previous studies focussing on marine aerosols in remote areas. Matsumoto and Uematsu (2005) reported averaged total concentrations of dissolved FAA with 4.5 ng m^{-3} in the western North Pacific Ocean. Wedyan and Preston (2008) observed during a transect ship cruise in the Atlantic Ocean a mean concentration of dissolved

20 FAA of 2.5 ng m^{-3} on total suspended particles (TSP). In Antarctic aerosol particles, the observed mean FAA total concentration at Mario Zucchelli Station was 4.6 ng m^{-3} (Barbaro et al., 2015).

Especially towards the end of the campaign (4/10/2017-7/10/2017), a high contribution of GABA and Asp were detected (Fig. 2 upper panel). The higher complexity in the composition of the submicron amino acids and especially the presence of GABA can often only be recognized when higher overall FAA concentrations (above 3 ng m^{-3}) occur. Lower concentration of amino

25 acids generally contained mainly Gly and in smaller concentrations Ala and Ser. However, on 10/10/2017, the ∑FAA concentration was high (3.8 ng m^{-3}) but contained fewer single amino acids and no GABA. The presence of the individual amino acids on the size-segregated aerosol particles will be discussed more detail in section 3.4.

To facilitate the comparison of amino acids in between different studies, one possibility is to summarize amino acids into a hydrophilic (Glu, Asp, GABA), neutral (Ser, Gly, Thr, Pro, Tyr) and hydrophobic amino acid class (Ala, Val, Phe, Ile, Leu) -

30 as shown in Table S7. This classification is based on the physicochemical properties of amino acids ('hydropathy' index (Kyte and Doolittle, 1982)) as suggested by Pommié et al. (2004). Following this classification, the submicron aerosol particles consisted on average of 5 % hydrophobic, 15 % hydrophilic and 80 % neutral amino acids and the supermicron aerosol particles contained on average only 7 % hydrophobic and 93 % neutral amino acids.

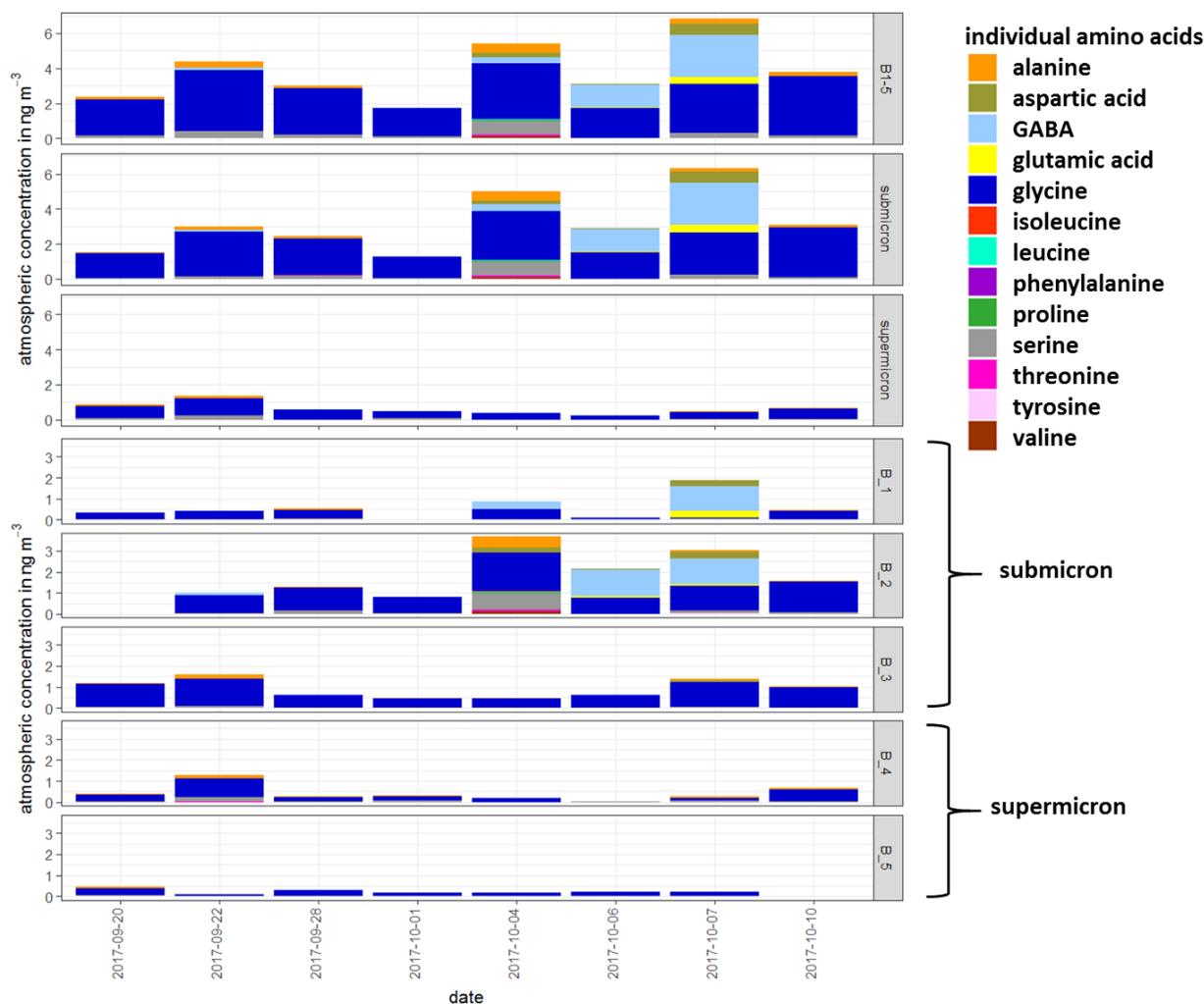



Figure 2: Atmospheric concentration of individual amino acids contributing to the ∑FAA in different aerosol particle size classes: the sum of all Berner stages (B1 - 5), in the submicron (B1-3) and the supermicron (B4-5) size range (upper panel); the atmospheric concentration of FAA in all individual Berner stages (lower panel) during the campaign at the CVAO

5   During the campaign, an increase in the contribution of hydrophilic amino acids was observed with a maximum of 55 % on 7/10/2017. Mandalakis et al. (2011) observed 6 % hydrophobic, 23 % hydrophilic and 71 % neutral amino acids contributing to FAA in TSP collected over the Eastern Mediterranean, which agrees well to the data presented here. Barbaro et al. (2015) reported that the hydrophilic components were predominant (60 %) in the locally produced marine Antarctic aerosols and hydrophobic compounds were dominant in aerosols collected at the continental station (23 % and 27 %). The observed

10 percentage of hydrophilic amino acids (average of 15 % and range of 4-55 %) at the CVAO was smaller as in Barbaro et al. (2015) for Antarctic aerosol particles. However, the presence of Glu, Asp and GABA as part of the hydrophilic species in the submicron aerosol particles (on 22/09/2017, 4/10/2017, 6/10/2017, 7/10/2017) strongly indicated a local oceanic origin. Moreover, the comparatively low averaged presence of hydrophobic species (5 % in the submicron, 7 % in the supermicron)

in the size-segregated aerosol particle samples at the CVAO was in agreement with the results of Barbaro et al. (2015) for locally marine produced Antarctic aerosol particles (5 % hydrophobic species). Considering the amino acid classifications from Barbaro et al. (2015)), it can be concluded that the submicron aerosol particles with low averaged percentage of hydrophobic species (5 %) and higher percentages of hydrophilic species (4-55 %, mean of 15 %) could have local oceanic origin. This is supported by a predominant marine origin of the aerosol particles according to the air masses history, particulate MSA concentrations and MSA/sulfate ratios and particulate concentrations of dust tracers (Table S8).

The higher complexity in the FAA composition on the submicron aerosol particles could only be determined because the analytical method applied here is able to quantify the individual molecular FAA species. With methods that determine the proteins as a sum parameter (e.g the often applied Bradford method) such a differentiation would not be possible. The composition of FAA on the size-segregated aerosol particle samples with focus on the comparison of the submicron with the supermicron aerosol particles as well as the comparison of aerosol composition with the seawater composition will be discussed more detailed in section 3.4.

Contribution of FAA to WSOC and WSON

In consideration of the carbon or nitrogen content of the amino acids (Table S6), the contribution of ∑FAA to WSOC and water-soluble organic nitrogen (WSON) in the size-segregated aerosol particles was calculated (Table S9). In the submicron size range, ∑FAA contributed up to 5.3 % (average 1.1 %) to WSOC, whereas ∑FAA in the supermicron contributed only up to 0.04 % to WSOC. Considering the total contribution of ∑FAA to WSOC (PM$_{10}$), 0.7 % of WSOC consist of ∑FAA, which was in good agreement with the study of Mandalakis et al. (2011). Considering the nitrogen content of the amino acids, ∑FAA contributed to the estimated WSON (WSON = 25 % of measured TDN concentrations according to Lesworth et al. (2010)) with an average of 0.4 % in the submicron and 0.05 % in the supermicron size range. The observed daily variations of the contribution of ∑FAA to WSOC/WSON, resulted from the daily variation of the atmospheric concentration of ∑FAA (Fig. 2) and of WSOC/ WSON (Table S9). In summary, ∑FAA contributed up to 5.3 % to WSOC or up to 1.8 % to WSON on the submicron aerosol particles (7/10/2017) and up until 0.15 % to WSOC or up until 0.1 % to WSON on the supermicron aerosol particles. These percentages were in the same order of magnitude as of other organic compound groups, e.g. amines. van Pinxteren et al. (2019b) showed that amines contributed on average with 5 % to the submicron WSOC content on marine aerosol particles. Especially, the percentage of ∑FAA to WSOC (up to 5.3 %) in the submicron aerosol particles demonstrated that FAA comprised a substantial fraction of submicron WSOC in marine aerosol particles.

3.2.2 Size-segregated aerosol particles at the mountain station (MV)

In order to investigate the aerosol particle composition not only at the ground-based level CVAO, but also at cloud level, size-segregated aerosol particles were also collected at the mountain station 'MV' (744 m a.s.l.). From these samples, FAA and additional parameters such as particulate matter (PM), WSOC, sodium and MSA were investigated. The results are listed in Table S10. The submicron aerosol particles at the MV had an averaged ∑FAA concentration of 1.5 ng m^{-3} (0.8-1.9 ng m^{-3}),

similar to the $\sum$FAA concentration in the supermicron aerosol particles (1.2 ng m^{-3}; 0.2-2.9 ng m^{-3}). The averaged PM for the submicron (2517 ng m^{-3}) and the supermicron (13669 ng m^{-3}) aerosol samples at the CVAO were 3-4 times higher compared to the MV (submicron: 735 ng m^{-3}, supermicron: 3668 ng m^{-3}). Moreover, the averaged WSOC content on the submicron aerosol particles (2.6 ng m^{-3}) was similar to the supermicron aerosol particles (5.9 ng m^{-3}) at the MV station and considerably

5   smaller as at the CVAO (submicron: 22.1 ng m^{-3}, supermicron: 50.6 ng m^{-3}). $\sum$FAA contributed on average with 0.2 % to WSOC content on the submicron and on the supermicron aerosol particles. To obtain information on the origin of the size-segregated aerosol samples at the MV station, the Na$^+$ and MSA concentration were compared with the corresponding data at the CVAO. With concentration of Na$^+$ (averaged 17.0 ng m^{-3}) and of MSA (0.04-4.2 ng m^{-3}) in the submicron aerosol particles and in the supermicron aerosol particles (averaged Na$^+$: 111.3 ng m^{-3}, MSA: 1.1-3.7 ng m^{-3}), the MV aerosol particle samples

10   were lower concentrated in marine inorganic tracers as the corresponding CVAO samples (Table S10). The lower concentrations of marine compounds (e.g. MSA, Na$^+$) at the MV compared to the CVAO (maybe due to atmospheric reactions), these marine tracers were still present and indicated an oceanic contribution to the aerosol particles at cloud level. The FAA composition at both sampling stations (CVAO and MV) will be discussed in detail in section 3.4.

15   ## 3.3 Cloud water samples

To the best of our knowledge, this study was the first time that the analysis of FAA in cloud water in the marine environment was performed. The cloud water samples were collected at the MV station with various sampling times and the individual atmospheric concentration of FAA in cloud water was calculated (section 2.2.3) based on the measured liquid water content (LWC) (Table S11). The $\sum$FAA in cloud water had a strong variation during the investigated campaign days (11.2-489.9 ng m^{-3})

20   as shown in Fig. 3. Our observed carbon concentration of FAA in cloud water at the MV station showed a higher variance (17-757 µg C L^{-1}) but was in the same order of magnitude as in a previous study of cloud water sampled on top of puy de Dôme mountain, inland of France. At puy de Dôme, Bianco et al. (2016) detected amino acids in cloud water samples with 211±19 µg C L^{-1}. Additionally to the concentration, the composition of FAA in cloud water in the here presented study showed a high variability. In cloud water samples with $\sum$FAA <65 ng m^{-3}, usually Gly was dominant followed by Ser. Cloud water

25   samples with $\sum$FAA >290 ng m^{-3} showed a higher complexity in the FAA composition, especially towards the end of the campaign, including the appearance of Asp. Other abundant FAA were e.g. Thr, Leu, Ile. During the campaign, there may be different types of clouds, which we cannot distinguish in this paper.

To gain information about the origin of the cloud water, inorganic ions as sodium, sulfate and MSA were considered (Table S11). The averaged measured atmospheric concentration of sodium was 5.0 µg m^{-3} (1.6-7.2 µg m^{-3}), of sulfate 2.9 µg m^{-3} (1.8-

30   3.6 µg m^{-3}) and of MSA 26.1 ng m^{-3} (11.0-39.0 ng m^{-3}) in the cloud water samples. No clear trend for the inorganic ions was observed. In comparison to other studies, it can be shown that the concentrations of sulfate and sodium were higher than in Gioda et al. (2009).

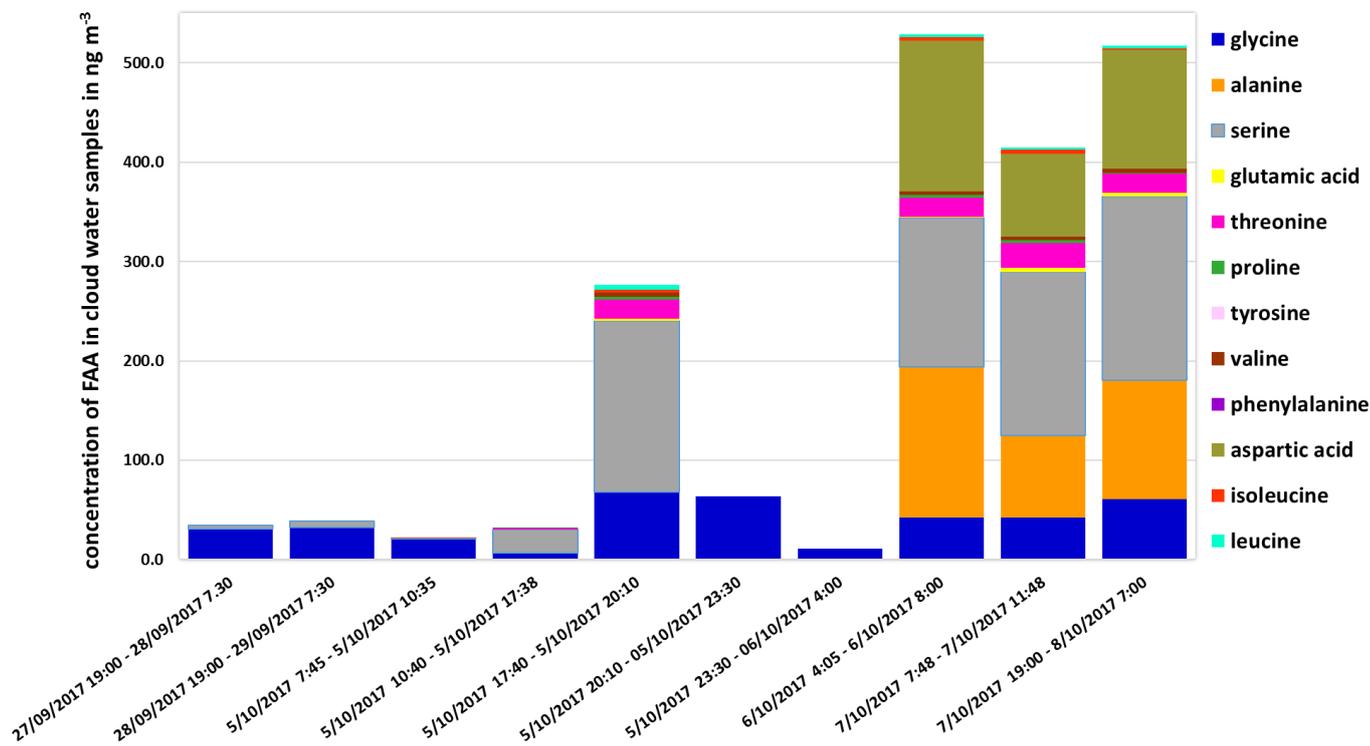



Figure 3: Concentration of individual FAA in cloud water samples at the MV station in ng m⁻³. The time represents the local start and end time of the cloud water sampling

Because of the limited number of studies dealing with cloud water in the marine environment and its comparison with aerosol
5   particles (Sorooshian et al. (2009); M. Coggon et al. (2012) and references therein), it was challenging to identify the origin of
the cloud water. However, the presence of marine tracers (sodium, MSA) suggests that the cloud water was strongly influenced
by marine sources. A more detailed comparison of the composition of cloud water and aerosol particles and seawater samples
will be given in section 3.4.

10   **3.4   Concerted measurements of FAA in the marine compartments (seawater, aerosol particles and cloud water)**

Only a few studies concerning the simultaneous investigation of FAA in the marine compartments – seawater, aerosol particles
and cloud water - using concerted measurements are present to date and most of them measured artificially generated aerosol
particles. Kuznetsova et al. (2005) characterized proteinaceous compounds in marine ambient aerosol particles, in the
generated aerosol particles and in the corresponding SML samples. Rastelli et al. (2017) investigated the transfer of organic
15   matter (sum parameter for lipids, carbohydrates and proteins) from the ocean surface into the marine aerosol using a bubble-
bursting experimental system under controlled conditions.

Within the here presented study, simultaneous sampling of all marine matrices - seawater (ULW, SML), size-segregated
aerosol particles (CVAO, MV) and cloud water samples - could be obtained for a period between 4/10/2017 and 7/10/2017

comprising 6 blocks of size-segregated aerosol particles (3 at the CVAO, 3 at the MV), 3 seawater samples (3 SML and 3 ULW) and one cloud water sample (7/10/2017; 7:48-11:48). For these sampling intervals, the fractional residence time of the air masses was mainly over water and trace metal and inorganic marine tracer (sodium, MSA) concentration (Table S8) strongly suggest a dominant marine origin of the air masses and therefore no significant contributions from dust or continental

5   sources. The averaged values of these sampling days represent a case study to combine and compare the FAA in all matrices to investigate a possible transfer of FAA from the ocean into the atmosphere and a transport of FAA inside the atmosphere. The comparability of the different matrices (e.g. seawater samples as a spot sample, aerosol particles samples covering a 24 h period) is discussed in the Fig. S1.

The averaged FAA composition of this case study in all marine compartments is presented in Fig. 4. For a better comparison
10 of the individual amino acids, the reactivity/ mean life time τ of the amino acids in the CVAO ('remote aerosol case') and in the MV ('remote cloud case') aerosol particle samples were considered as described in Table S12. Representatives of the hydrophilic, neutral and hydrophobic and aromatic amino acids are discussed below with respect to their distribution within the different marine matrices and with regard to a potential transfer.

3.4.1. Hydrophlic amino acids

The hydrophilic amino acids (Asp, Glu, GABA) were found in the seawater (Asp, Glu), in the submicron aerosol particles at the CVAO (Asp, Glu, GABA), in 1.2-3.5 µm (B4) aerosol particles at the MV (Asp, Glu) and in the cloud water sample (Asp, Glu) (Fig. 4a-d). Glutamic acid was present in the seawater and in the submicron aerosol particles at the CVAO indicating that Glu might preferibly be transferred from the ocean into the atmosphere possibly via bubble bursting. In addition, the presence
20 of Glu in aerosol particle samples (1.2-3.5 µm) at the MV and in cloud water samples suggests that Glu was not only transferred from the ocean, but also transported (upwards) in the marine environment. The mean lifetime τ of Glu (remote aerosol case: 0.02 d, remote cloud case: 3.3 d, Table S12), showed a comparatively low atmospheric reactivity indicating that a transfer process from the ocean into the atmosphere and a vertical transport without transformation reactions of Glu is likely. Similar to Glu, the amino acid aspartic acid could be detected in all investigated compartments (Fig. 4a-d). Since correlations
25 have been found in the marine environment between Asp with diatoms and zooplankton (Hammer and Kattner, 1986), the presence of Asp in the marine environment can be traced back to a biogenic origin. It is noticeable that high concentrations of Asp were also present in cloud water (Fig. 3 & 4d). The third hydrophilic amino acid GABA was exclusively detected in the submicron aerosol particle samples at the CVAO (Fig. 4b). GABA is a metabolic product of the decarboxylation of Glu produced by microorganisms (Dhakal et al., 2012) and an indicator of microbiological decomposition of organic matter
30 (Dauwe et al., 1999;Engel et al., 2018). The presence of GABA on the submicron aerosol particles pointed out that (marine) microorganisms were present on the aerosol particles and produced GABA via microbiological decarboxylation of Glu.

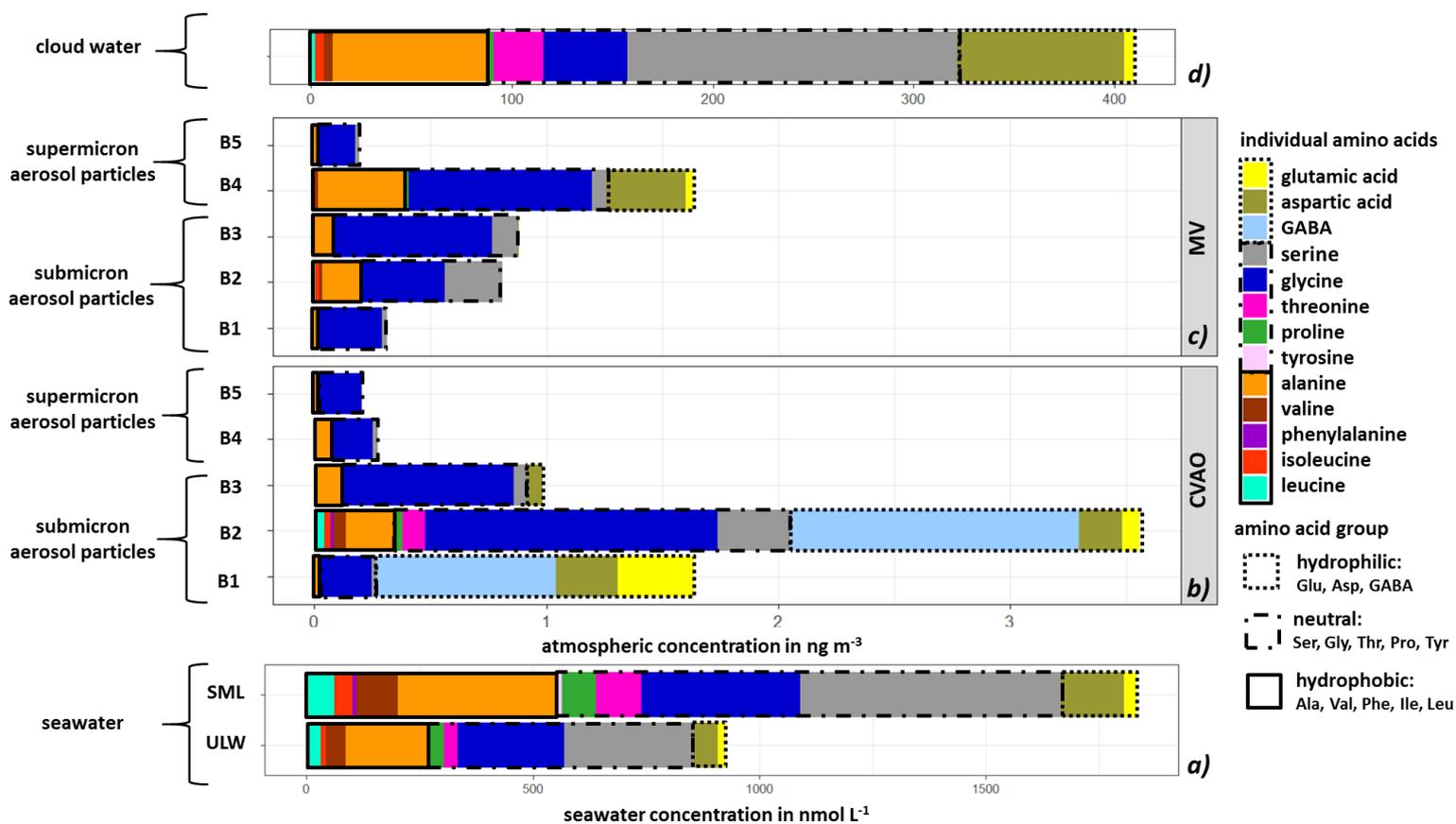



Figure 4: Case study: individual FAA concentration in a) seawater samples (ULW, SML) nmol L⁻¹, in b) size-segregated aerosol particle samples at the CVAO and c) at the MV station (size range : 0-4 ng m⁻³) and in d) cloud water sample (size range: 0-400 ng m⁻³)

GABA was not detected in cloud water samples, although bacteria were found in cloud water during the MarParCloud campaign (van Pinxteren et al., 2019a) and the presence of bacteria in cloud waters has been reported in the literature (Jiaxian et al., 2019). Whether GABA was degraded in cloud water despite its rather long lifetime (remote cloud case: 1.2 d, Table S12) or whether GABA was not produced by the bacteria in cloud water remains speculative.

3.4.2 Neutral and hydrophobic amino acids

Neutral amino acis were generally the amino acid group with highest concentration in all investigated marine comparments (Fig. 4a-d), especially Ser and Gly were the dominant representatives of this group. The presence of Gly in the seawater (Fig. 4a) and in aerosol particles at the CVAO (Fig. 4b) pointed to a potential transfer of Gly from the ocean into the atmosphere

10 via bubble bursting. A further explanation approach for the appereance of Gly in large quantities on aerosol particles (Fig. 4b/c) and in cloud water (Fig. 4d) could be that Gly was the result of transport or production processes. Chemical transformations like photochemical reactions of amino acids can lead to the formation of Gly as a main compound. Compared to other amino acids, Gly is more stable (Barbaro et al., 2015) and had very low atmospheric reactivity (McGregor and Anastasio, 2001). Gly and Ser have a higher mean lifetime τ (Gly: 0.02 d, Ser: 0.01 d; remote aerosol case, Table S12)

15 compared to other investigated amino acids (usually $\tau \leq 0.01$ d, Table S12). The neutral amino acid proline has been reported to be of biogenic origin in the marine environment and was detected in seawater (Fig. 4a), on submicron aerosol particles at the CVAO (Fig. 4b) and in cloud water (Fig. 4d).

Fischer et al. (2004) demonstrated that Pro can be used to identify the presence of algal spores on aerosol particles. The presence of Pro in the compartments suggested that Pro was transferred from the ocean into the atmosphere up to cloud level.

20 The comparatively low atmospheric reactivity of Pro (remote aerosol case: 0.01 d, Table S12) supports its presence in the different compartments. One representative of the hydrophobic amino acids, which was also present in all marine compartments (Fig. 4a-d) was Alanine. Ala shows a similar mean lifetime at remote aerosol case (0.05 d) as Gly and Ser. Maria et al. (2004) suggested a longer hydrophobic aerosol lifetime as a result of the slower oxidation rates and Barbaro et al. (2015) explained the presence of Ala in Antarctic 'remote aerosols' because of missing degradation processes during transport.

25 Because of this lower atmospheric reactivity, it is possible that FAA were transformed to Gly, Ser and Ala resulting in the observed high percentage in aerosol samples. Hence for the non hydrophilic amino acids (Gly, Ser, Ala), both, transfer from the ocean via bubble bursting and transport from long distances together with atmospheric reactions might explain their abundance on the aerosol particles.

30 ### 3.4.3 Aromatic amino acids

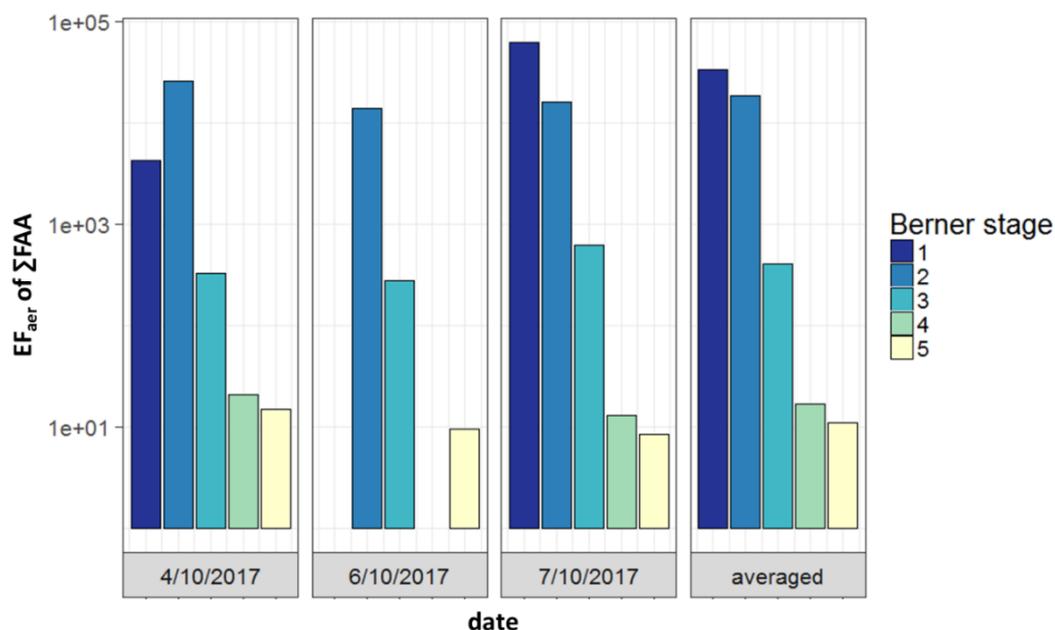
Aromatic FAA as phenylalanine and tyrosine were present in seawater, but not on the aerosol particles and in cloud water samples. It could be assumed that these aromatic FAA were either not transferred from the ocean into the atmosphere, or they already reacted after their transfer because of chemical transformation reactions or they were not detected because of their low atmospheric concentration. The mean lifetime τ of Phe (0.0006 d) and Tyr (0.0003 d) (Table S12) showed that both FAA had

a comparatively high atmospheric reactivity ($\tau < 1$ min) at remote aerosol case conditions. Hence, a fast chemical reaction of these compounds is most likely. Moreover, previous studies reported low atmospheric concentration of Tyr and Phe on aerosol particles. Barbaro et al. (2011) found Phe (0.5 ng m^{-3}) and Tyr (0.3 ng m^{-3}) with a contribution < 1 % to $\sum$FAA ($\sum$FAA: 42.5 ng m^{-3}) on TSP samples in urban background (Venice, Italy). In our study at the CVAO, the mean value of $\sum$FAA in

5   PM$_{10}$ aerosol particles was 3.8 ng m^{-3} (section 3.2). Assuming that Phe and Tyr were contributing to $\sum$FAA in a very small fraction as reported in Barbaro et al. (2011), their concentrations were below detection limit. It can therefore concluded that the aromatic FAA are either not transferred from the ocean into the aerosol particles or react very fast in the atmosphere.

3.4.4 Transfer of amino acids in size-segregated aerosol particles

10   The EF$_{aer}$, calculated using Eq. (2), is often included in ocean-atmosphere transfer considerations as a quantitative metric (e.g. Russell et al. (2010), van Pinxteren et al. (2017)). For the calculated EFaer, it should be noted that no further FAA formation or degradation pathways on the aerosol particles are considered, including biological or photochemical atmospheric reactions, or a possible transport from other than marine sources is included in this parameter. The EF$_{aer}$ of $\sum$FAA in the individual Berner stages for the single days of the case study at the CVAO (4/10/2017, 6/10/2017, 7/10/2017) and as an average are

15   presented in Fig. 5. The EF$_{aer}$ of $\sum$FAA in the supermicron size range ($1 \cdot 10^1$ (B5), $7 \cdot 10^1$ (B4)) were several orders of magnitude smaller than in the submicron ($7 \cdot 10^2$ (B3), $2 \cdot 10^4$ (B2), $3 \cdot 10^4$ (B1)). Regarding the transfer of OM from the ocean into ambient aerosol particles, solely organic carbon as a sum parameter has been regarded to date and no distinction of single organic matter classes for ambient measurements has been performed.

20   **Figure 5: Enrichment factor aerosol (EF$_{aer}$) of $\sum$FAA in the size-segregated aerosol particle samples (Berner stage 1-5) at the CVAO on sampling days of the case study (4/10/2017, 6/10/2017, 7/10/2017) and as an averaged EF$_{aer}$**

van Pinxteren et al. (2017) showed that the EF_{aer} of OC in the submicron marine ambient aerosols were between 10^3 up to 10^5. The averaged EF_{aer} of WSOC during our campaign in the submicron size range was between $2\cdot10^3$ and $1\cdot10^4$ and between $3\cdot10^2$ and $4\cdot10^2$ in the supermicron size range (Table S13) and in good agreement with van Pinxteren et al. (2017). Comparing the EF_{aer} of $\sum$FAA ($1\cdot10^1$-$6\cdot10^4$) with the EF_{aer} of WSOC ($1\cdot10^1$-$2\cdot10^4$) in the submicron size range, both EF_{aer} are in the same

5   order of magnitude and showed high enrichments compared to the SML. Furthermore, similar percentages of $\sum$FAA to DOC in SML (up to 7.6%) (section 3.1) and to WSOC on the submicron aerosol particles (up to 5.3%) (section 3.2) were observed. Previous studies showed that organic material ejected into the atmosphere during bubble bursting, resulting in sea spray aerosol particles containing similar organic material to that of the SML (Russell et al. (2010);Cunliffe et al. (2013) and references therein). Especially the film droplets have been reported to be enriched with OM and are suggested to transfer OM from the

10 SML to submicron aerosol particles (Wilson et al., 2015). The supermicron aerosol particles rather form from the larger jet droplets and therefore represent the ULW composition (Blanchard, 1975;Wilson et al., 2015). From the ambient measurements performed here, we cannot derive mechanistic transfer characterizations. However, the constant FAA enrichment in the SML together with the strong FAA enrichment in the submicron aerosol particles strongly suggest that film droplets form the submicron particles. However, Wang et al. (2017) showed that also jet drops (transferring OM from the ULW) have the

15 potential to contribute significantly to the formation of submicron sea spray aerosol particles therefore jet droplets can contribute to FAA formation as well.

3.4.5 High FAA concentrations in cloud water

The concentration of FAA in cloud water (Fig. 3, Table S11) were, although varying, always significant higher compared to

20 the aerosol particles (Table S8) with $\sum$FAA concentrations between 11.2 and 489.9 ng m^{-3}. The inorganic marine tracers in cloud water (Na$^+$: 5.7 µg m^{-3}, MSA: 25.1 ng m^{-3}, Table S11) were also present in higher concentrations compared to the aerosol particle samples at the CVAO (submicron: Na$^+$: 72.3 ng m^{-3}, MSA: 6.0 ng m^{-3}) and at the MV (submicron: Na$^+$: 17.0 ng m^{-3}, MSA: 1.8 ng m^{-3}, Table S10), indicating an enrichment in cloud water. This enrichment was even stronger visible when comparing $\sum$FAA in cloud water and in the SML resulting in an enrichment facotr of $\sum$FAA in cloud water (EF_{CW}, Eq. (2)),

25 with $EF_{CW(\sum FAA)} = 4\cdot10^3$. The reason for the high concentrations and enrichment of FAA in cloud water remains speculative to date and will be subject to further investigations. Contributions to FAA cloud water concentrations by non-marine sources can not be ruled out, however, the investigated period was rather of marine origin and dust concentrations were low. In addition, the majority of low-level clouds over the islands were locally formed (van Pinxteren et al., 2019a) and the presence of the marine tracers (sodium, MSA) suggest a strong link to oceanic sources. In situ-formation of FAA in cloud water, maybe due

30 to biogenic formation or enzymatic degradation of proteins, selective enrichment processes as well as pH dependent chemical reactions might be potential sources.

4   Conclusion

Concerted measurements i.e., simultaneous measurements of seawater, size-segregated aerosol particles and cloud water samples during the MarParCloud campaign at the CVAO and MV station allowed to investigate FAA on molecular level that are important contributors to marine OM. The similarities between the FAA composition in the seawater (SML) and on the submicron aerosol particle samples as described in section 3.4 indicated that a large contribution of FAA, especially of the hydrophilic amino acids in the submicron particles at the CVAO probably resulted from local sea spray. For the non-hydrophilic amino acids, additional sources, such as long-range transport and chemical transformation can be important and aromatic amino acids are either not transferred from the ocean into the atmosphere or react very fast. By distinguishing between the submicron and the supermicron aerosol particles, differences in the chemical composition of these aerosol size classes could be elaborated (section 3.2). FAA were present in the size range for aerosol particles connected to CCN activity and cloud water, and might be connected to CCN activity due to their hygroscopicity and soluble character, however this effect was not investigated here. Altogether, the here presented measurements suggest that several amino acids were transported from the ocean up to cloud level (Asp, Glu, Pro) where others might not be transferred or quickly degraded (Phe, Tyr) or produced (e.g. GABA from Glu). Some amino acids were present to a larger extent than others in the atmosphere compared to seawater, indication a selective transfer of the individual amino acids. To quantify the transfer of OM and FAA from the ocean into the aerosol particles, the EF_{aer} was calculated (section 3.4). The EF_{aer} of $\sum$FAA was found to be between $1\cdot10^1$-$2\cdot10^1$ (supermicron) and $2\cdot10^2$-$6\cdot10^4$ (submicron size range). The similar composition together with the significant enrichment of $\sum$FAA in SML and on submicron aerosol particles indicated that the transfer of FAA from the ocean into the atmosphere happens most likely via film droplet formation. Moreover, marine cloud water exhibited very high concentrations of FAA, enriched by a factor of $4\cdot10^3$ compared to the SML. These high concentrations can currently not be explained and possible sources such as biogenic formation or enzymatic degradation of proteins, selective enrichment processes or pH dependent chemical reactions are subject to future work. Altogether, the presence of high concentrations of FAA in general and of biologically produced FAA (Asp) in particular together with the presence of inorganic marine tracers showed the influence of oceanic sources on the local clouds. To the best of our knowledge, this study was the first to analyse FAA simultaneously in all marine compartments - seawater including the SML, size-segregated aerosol particles and cloud water – in such detail to obtain indications on their sources and interconnections.

Data availability. Data can be made available by the authors upon request.

Acknowledgements. This work was funded by Leibniz Association SAW in the project "Marine biological production, organic aerosol particles and marine clouds: a Process Chain (MarParCloud)" (SAW-2016-TROPOS-2) and within the Research and Innovation Staff Exchange EU project MARSU (69089). The authors also thank Susanne Fuchs, Anett Dietze, Sontje Krupka,

René Rabe and Anke Rödger for providing additional data and filter samples and all MarParCloud and MARSU project partners, especially Malena Manzi, for a good cooperation and support. Additional thanks to Khanneh Wadinga Fomba and his support in context of mineral dust and cloud water analytics, to Thomas Schaefer regarding the kinetic analysis and to Tobias Spranger concerning data visualization.

Author contributions. NT wrote the manuscript with contributions from MvP, HH and AE. NT and MvP performed as part of the MarParCloud campaign team the field sampling and NT the chemical measurements of amino acids. The chemical data evaluation was done by NT in consultation with HH and MvP and with the mentioned researcher in the acknowledgement. All authors discussed the results and further analysis after the campaign. All co-authors proofread and commented the manuscript.

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

References

15   Aluwihare, L. I., Repeta, D. J., Pantoja, S., and Johnson, C. G.: Two Chemically Distinct Pools of Organic Nitrogen Accumulate in the Ocean, Science, 308, 1007-1010, 10.1126/science.1108925, 2005.

Antia, N. J., Harrison, P., and Oliveira, L.: The Role of Dissolved Organic Nitrogen in Phytoplankton Nutrition, Cell Biology and Ecology, 30, 1-89, 10.2216/i0031-8884-30-1-1.1, 1991.

Barbaro, E., Zangrando, R., Moret, I., Barbante, C., Cescon, P., and Gambaro, A.: Free amino acids in atmospheric particulate matter of
20   Venice, Italy, Atmos. Environ., 45, 5050-5057, 10.1016/j.atmosenv.2011.01.068, 2011.

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

Bianco, A., Voyard, G., Deguillaume, L., Mailhot, G., and Brigante, M.: Improving the characterization of dissolved organic carbon in cloud
25   water: Amino acids and their impact on the oxidant capacity, Scientific Reports, 6, 7, 10.1038/srep37420, 2016.

Blanchard, D. C.: Bubble Scavenging and the Water-to-Air Transfer of Organic Material in the Sea, in: Applied Chemistry at Protein Interfaces, Advances in Chemistry, 145, American Chemical Society, 360-387, 1975.

Bradford, M. M.: Rapid and sensitive method for quantitation of microgram quantities of protein utilizing principle of protein-dye binding, Anal. Biochem., 72, 248-254, 10.1006/abio.1976.9999, 1976.

30   Bronk, D.: Dynamics of DON, in, 153-247, 2002.

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

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

40   Chan, M. N., Choi, M. Y., Ng, N. L., and Chan, C. K.: Hygroscopicity of Water-Soluble Organic Compounds in Atmospheric Aerosols: Amino Acids and Biomass Burning Derived Organic Species, Environ. Sci. Technol., 39, 1555-1562, 10.1021/es049584l, 2005.

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

Cunliffe, M. a. W., O.: Guide to best practices to study the ocean's surface. , Plymouth, UK, Marine Biological Association of the United Kingdom for SCOR, 118pp., 2014.

Dauwe, B., Middelburg, J. J., Herman, P. M. J., and Heip, C. H. R.: Linking diagenetic alteration of amino acids and bulk organic matter reactivity, Limnol. Oceanogr., 44, 1809-1814, doi:10.4319/lo.1999.44.7.1809, 1999.

Demoz, B. B., Collett, J. L., and Daube, B. C.: On the Caltech Active Strand Cloudwater Collectors, Atmos. Res., 41, 47-62, 10.1016/0169-8095(95)00044-5, 1996.

Dhakal, R., Bajpai, V. K., and Baek, K. H.: Production of GABA (gamma-aminobutyric acid) by microorganisms: a review, Braz. J. Microbiol., 43, 1230-1241, 2012.

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

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

Engel, A., Sperling, M., Sun, C., Grosse, J., and Friedrichs, G.: Organic Matter in the Surface Microlayer: Insights From a Wind Wave Channel Experiment, Frontiers in Marine Science, 5, 10.3389/fmars.2018.00182, 2018.

Feltracco, M., Barbaro, E., Kirchgeorg, T., Spolaor, A., Turetta, C., Zangrando, R., Barbante, C., and Gambaro, A.: Free and combined L- and D-amino acids in Arctic aerosol, Chemosphere, 220, 412-421, 10.1016/j.chemosphere.2018.12.147, 2019.

Fischer, M., Cox, J., Davis, D. J., Wagner, A., Taylor, R., Huerta, A. J., and Money, N. P.: New information on the mechanism of forcible ascospore discharge from Ascobolus immersus, Fungal Genetics and Biology, 41, 698-707, 10.1016/j.fgb.2004.03.005, 2004.

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

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

Fomba, K. W., van Pinxteren, D., Müller, K., Iinuma, Y., Lee, T., Collett Jr, J. L., and Herrmann, H.: Trace metal characterization of aerosol particles and cloud water during HCCT 2010, Atmos. Chem. Phys., 15, 8751-8765, 10.5194/acp-15-8751-2015, 2015.

Gantt, B., Meskhidze, N., Facchini, M. C., Rinaldi, M., Ceburnis, D., and O'Dowd, C. D.: Wind speed dependent size-resolved parameterization for the organic mass fraction of sea spray aerosol, Atmos. Chem. Phys., 11, 8777-8790, 10.5194/acp-11-8777-2011, 2011.

Gioda, A., Mayol-Bracero, O. L., Morales-García, F., Collett, J., Decesari, S., Emblico, L., Facchini, M. C., Morales-De Jesús, R. J., Mertes, S., Borrmann, S., Walter, S., and Schneider, J.: Chemical Composition of Cloud Water in the Puerto Rican Tropical Trade Wind Cumuli, Water, Air, and Soil Pollution, 200, 3-14, 10.1007/s11270-008-9888-4, 2009.

Gutiérrez-Castillo, M. E., Olivos-Ortiz, M., De Vizcaya-Ruiz, A., and Cebrián, M. E.: Chemical characterization of extractable water soluble matter associated with PM_{10} from Mexico City during 2000, Chemosphere, 61, 701-710, 10.1016/j.chemosphere.2005.03.063, 2005.

Hammer, K. D., and Kattner, G.: Dissolved free amino acids in the marine environment: a carbon to nitrogen ratio shift during diatom blooms, Mar. Ecol.-Prog. Ser., 31, 35-45, 1986.

Jiaxian, P., Shumin, Z., Kai, X., Junyang, Z., Chuanhe, Y., Senlin, L., Wei, Z., Yuzhen, F., Yuxiang, Y., Xinhui, B., Guohua, Z., and Qingyue, W.: Diversity of bacteria in cloud water collected at a National Atmospheric Monitoring Station in Southern China, Atmos. Res., 218, 176-182, 10.1016/j.atmosres.2018.12.004, 2019.

Kristensson, A., Rosenørn, T., and Bilde, M.: Cloud Droplet Activation of Amino Acid Aerosol Particles, The Journal of Physical Chemistry A, 114, 379-386, 10.1021/jp9055329, 2010.

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

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

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

5 Kyte, J., and Doolittle, R. F.: A simple method for displaying the hydropathic character of a protein, Journal of Molecular Biology, 157, 105-132, 10.1016/0022-2836(82)90515-0, 1982.

Lesworth, T., Baker, A. R., and Jickells, T.: Aerosol organic nitrogen over the remote Atlantic Ocean, Atmos. Environ., 44, 1887-1893, 10.1016/j.atmosenv.2010.02.021, 2010.

Letscher, R. T., Hansell, D. A., Carlson, C. A., Lumpkin, R., and Knapp, A. N.: Dissolved organic nitrogen in the global surface ocean:
10 Distribution and fate, Global Biogeochemical Cycles, 27, 141-153, doi:10.1029/2012GB004449, 2013.

M. Coggon, M., Sorooshian, A., Wang, Z., Metcalf, A., Frossard, A., Lin, J., Craven, J., Nenes, A., Jonsson, H., M. Russell, L., C. Flagan, R., and H. Seinfeld, J.: Ship impacts on the marine atmosphere: Insights into the contribution of shipping emissions to the properties of marine aerosol and clouds, 8439-8458 pp., 2012.

Mace, K. A., Duce, R. A., and Tindale, N. W.: Organic nitrogen in rain and aerosol at Cape Grim, Tasmania, Australia, Journal of
15 Geophysical Research: Atmospheres, 108, doi:10.1029/2002JD003051, 2003.

Mandalakis, M., Apostolaki, M., Tziaras, T., Polymenakou, P., and Stephanou, E. G.: Free and combined amino acids in marine background atmospheric aerosols over the Eastern Mediterranean, Atmos. Environ., 45, 1003-1009, 10.1016/j.atmosenv.2010.10.046, 2011.

Maria, S. F., Russell, L. M., Gilles, M. K., and Myneni, S. C. B.: Organic Aerosol Growth Mechanisms and Their Climate-Forcing Implications, Science, 306, 1921-1924, 10.1126/science.1103491, 2004.

20 Matos, J. T. V., Duarte, R., and Duarte, A. C.: Challenges in the identification and characterization of free amino acids and proteinaceous compounds in atmospheric aerosols: A critical review, Trac-Trends Anal. Chem., 75, 97-107, 10.1016/j.trac.2015.08.004, 2016.

Matsumoto, K., and Uematsu, M.: Free amino acids in marine aerosols over the western North Pacific Ocean, Atmos. Environ., 39, 2163-2170, 10.1016/j.atmosenv.2004.12.022, 2005.

McGregor, K. G., and Anastasio, C.: Chemistry of fog waters in California's Central Valley: 2. Photochemical transformations of amino
25 acids and alkyl amines, Atmos. Environ., 35, 1091-1104, 10.1016/S1352-2310(00)00282-X, 2001.

Milne, P. J., and Zika, R. G.: Amino acid nitrogen in atmospheric aerosols: Occurrence, sources and photochemical modification, J. Atmos. Chem., 16, 361-398, 10.1007/bf01032631, 1993.

Mueller, K., Lehmann, S., van Pinxteren, D., Gnauk, T., Niedermeier, N., Wiedensohler, A., and Herrmann, H.: Particle characterization at the Cape Verde atmospheric observatory during the 2007 RHaMBLe intensive, Atmos. Chem. Phys., 10, 2709-2721, 10.5194/acp-10-2709-
30 2010, 2010.

Pommié, C., Levadoux, S., Sabatier, R., Lefranc, G., and Lefranc, M.-P.: IMGT standardized criteria for statistical analysis of immunoglobulin V-REGION amino acid properties, Journal of Molecular Recognition, 17, 17-32, 10.1002/jmr.647, 2004.

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

35 2014.

Rastelli, E., Corinaldesi, C., Dell'Anno, A., Lo Martire, M., Greco, S., Cristina Facchini, M., Rinaldi, M., O'Dowd, C., Ceburnis, D., and Danovaro, R.: Transfer of labile organic matter and microbes from the ocean surface to the marine aerosol: an experimental approach, Scientific Reports, 7, 11475, 10.1038/s41598-017-10563-z, 2017.

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

Rinaldi, M., Fuzzi, S., Decesari, S., Marullo, S., Santoleri, R., Provenzale, A., von Hardenberg, J., Ceburnis, D., Vaishya, A., O'Dowd, C. D., and Facchini, M. C.: Is chlorophyll-a the best surrogate for organic matter enrichment in submicron primary marine aerosol?, Journal of Geophysical Research: Atmospheres, 118, 4964-4973, 10.1002/jgrd.50417, 2013.

Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K., and Bates, T. S.: Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting, Proc. Natl. Acad. Sci. U. S. A., 107, 6652-6657, 10.1073/pnas.0908905107, 2010.

Scalabrin, E., Zangrando, R., Barbaro, E., Kehrwald, N. M., Gabrieli, J., Barbante, C., and Gambaro, A.: Amino acids in Arctic aerosols, Atmos. Chem. Phys., 12, 10453-10463, 10.5194/acp-12-10453-2012, 2012.

5 Sorooshian, A., Padró, L. T., Nenes, A., Feingold, G., McComiskey, A., Hersey, S. P., Gates, H., Jonsson, H. H., Miller, S. D., Stephens, G. L., Flagan, R. C., and Seinfeld, J. H.: On the link between ocean biota emissions, aerosol, and maritime clouds: Airborne, ground, and satellite measurements off the coast of California, Global Biogeochemical Cycles, 23, 10.1029/2009gb003464, 2009.

Szyrmer, W., and Zawadzki, I.: Biogenic and anthropogenic sources of ice-forming nuclei: A review, Bull. Amer. Meteorol. Soc., 78, 209-228, 10.1175/1520-0477(1997)078<0209:baasoi>2.0.co;2, 1997.

10 van Pinxteren, M., Muller, C., Iinuma, Y., Stolle, C., and Herrmann, H.: Chemical Characterization of Dissolved Organic Compounds from Coastal Sea Surface Micro layers (Baltic Sea, Germany), Environ. Sci. Technol., 46, 10455-10462, 10.1021/es204492b, 2012.

van Pinxteren, M., Barthel, S., Fomba, K. W., Muller, K., von Tumpling, W., and Herrmann, H.: The influence of environmental drivers on the enrichment of organic carbon in the sea surface microlayer and in submicron aerosol particles - measurements from the Atlantic Ocean, Elementa-Sci. Anthrop., 5, 21, 10.1525/elementa.225, 2017.

15 van Pinxteren, M., Fomba, K. W., Triesch, N., Stolle, C., Wurl, O., Bahlmann, E., Gong, X., Voigtländer, J., Wex, H., Robinson, T. B., Barthel, S., Zeppenfeld, S., Hoffmann, E. H., Roveretto, M., Li, C., Grosselin, B., Daële, V., Senf, F., van Pinxteren, D., Manzi, M., Zabalegui, N., Frka, S., Gašparović, B., Pereira, R., Li, T., Wen, L., Li, J., Zhu, C., Chen, H., Chen, J., Fiedler, B., von Tümpling, W., Read, K. A., Punjabi, S., C. Lewis, A. C., Hopkins, J. R., Carpenter, L. J., Peeken, I., Rixen, T., Schulz-Bull, D., Monge, M. E., Mellouki, A., George, C., Stratmann, F., and Herrmann, H.: Marine organic matter in the remote environment of the Cape Verde Islands - An introduction 20 and overview to the MarParCloud campaign, Atmos. Chem. Phys. Discuss., 2019, 1-63, 10.5194/acp-2019-997, 2019a.

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

Wang, X., Deane, G. B., Moore, K. A., Ryder, O. S., Stokes, M. D., Beall, C. M., Collins, D. B., Santander, M. V., Burrows, S. M., Sultana, 25 C. M., and Prather, K. A.: The role of jet and film drops in controlling the mixing state of submicron sea spray aerosol particles, Proceedings of the National Academy of Sciences, 114, 6978-6983, 10.1073/pnas.1702420114, 2017.

Wedyan, M. A., and Preston, M. R.: The coupling of surface seawater organic nitrogen and the marine aerosol as inferred from enantiomer-specific amino acid analysis, Atmos. Environ., 42, 8698-8705, 10.1016/j.atmosenv.2008.04.038, 2008.

Wilson, T. W., Ladino, L. A., Alpert, P. A., Breckels, M. N., Brooks, I. M., Browse, J., Burrows, S. M., Carslaw, K. S., Huffman, J. A., 30 Judd, C., Kilthau, W. P., Mason, R. H., McFiggans, G., Miller, L. A., Najera, J. J., Polishchuk, E., Rae, S., Schiller, C. L., Si, M., Temprado, J. V., Whale, T. F., Wong, J. P. S., Wurl, O., Yakobi-Hancock, J. D., Abbatt, J. P. D., Aller, J. Y., Bertram, A. K., Knopf, D. A., and Murray, B. J.: A marine biogenic source of atmospheric ice-nucleating particles, Nature, 525, 234-+, 10.1038/nature14986, 2015.

Zhang, Q., and Anastasio, C.: Free and combined amino compounds in atmospheric fine particles (PM$_{2.5}$) and fog waters from Northern California, Atmos. Environ., 37, 2247-2258, 10.1016/s1352-2310(03)00127-4, 2003.

35