

The manuscript of Triesch et al. focuses on the measurements of free amino acids (FAA) in different marine compartments (underlayer water samples, sea surface microlayer, size segregated aerosol samples at different heights, cloud water) at the Cape Verde Atmospheric observatory (CVAO) and at the Mt. Verde during September/October 2017. Further, through the case study authors discuss the possible transfer of specific FAA from the ocean to the atmosphere up to the cloud level. This work for the first time aims to provide a detail chemical analyses of FAA, of both the sea surface layers as well as of atmospheric samples (size segregated aerosols and cloud water), thus representing a promising approach to contribute to the fundamental state-of-the-art knowledge on the linkage between the ocean and atmosphere. In addition, this work reports on unique marine and atmospheric organic matter data from remote tropical areas, being rare in comparison to continental/coastal ones. Thus, my opinion is that this manuscript presents valuable data sets and after some revision, it will be definitely worth to publish.

We thank the reviewer for the careful examination of the manuscript and the supporting information. In the following, please find a point-by-point response to the questions and concerns. All references to the manuscript (e.g. page and line numbers) listed in our replies refer to the clean version of the manuscript (without track changes).

### **Major comments**

**R#1-1)** The authors should comment and discuss that some specific FAA were not detected in particular compartments possibly due to their high LOQ (in particular matrices) and the fact that maybe not enough material was available for their analysis. This is particularly relevant for the selected hydrophilic FAA in comparison to other FAA groups and should be considered when discussing the selective transfer of FAA groups from the ocean to the atmosphere.

We agree with the reviewer's comment that a more detailed discussion of the LOQ of the individual analytes is needed and revised several parts of the manuscript accordingly.

In the SI (Table S1), we listed the LOQ of each FAA in the respective matrices (seawater, cloud water, aerosol particles). In the manuscript, we referred to these LOQs in a number of different places as described in the following:

In section “2.2.1 Seawater analyses” (page 6, line 20-23), we added: “The LOQs were mostly below 10 nmol L<sup>-1</sup>, however, GABA and Met exhibited LOQs with 24.2 nmol L<sup>-1</sup> and 16.8 nmol L<sup>-1</sup>, respectively (due to high blank values). A quantification of some FAAs in seawater, mainly in the ULW with its generally lower FAA concentrations compared to the SML, is therefore partly limited.”

In addition, we mentioned that “The limit of quantification (LOQ) of the individual FAAs in seawater samples is in good agreement with the FAA analysis in seawater samples (e.g. Kuznetsova et al. (2004)) and listed in Table S1” (page 6, line 19-20)

In section “2.2.2 Aerosol particle filter analyses” (page 7, line 6-8), we added: “Although a variance in LOQs between the individual FAAs is apparent, FAAs with relatively high LOQs (39.5 pg m<sup>-3</sup>) on aerosol particles such as Ala, GABA, Asp in submicron and supermicron aerosol particles could be quantified (as discussed in section 3.2 and 3.4).”

In section “2.2.3 Cloud water analyses” (page 7, line 31-33), we added “Since the LOQs of the FAAs in cloud water are below 0.3 ng m<sup>-3</sup> and often below 0.06 ng m<sup>-3</sup>, a limitation of the FAA composition in cloud water due to the LOQs is rather unlikely despite the variance of FAA concentrations (11.2-489.9 ng m<sup>-3</sup>) in cloud water (section 3.3).”

This possible restriction of the results by the LOQ was also discussed in the results and discussion section in the individual sections on seawater (section 3.1), aerosol particles (section 3.2), cloud water (section 3.3) and concerted measurements (section 3.4).

In section “3.1 Seawater samples” (page 10, line 1-3), we added “As discussed in section 2.2.1, GABA and Met have the highest LOQs of the analytical method used here, which may be one reason why these two analytes could not be quantified in the seawater samples (ULW and SML).” In section “3.4.1 Hydrophilic amino acids” (page 18, line 19/20), we added “Although some limitations of GABA quantification (Table S1) in seawater exist, a relatively major abundance of it in seawater would not be restricted due to the high FAA concentrations.”

In section “3.4.3 Aromatic amino acids” (page 21 ,line 1-3), we added “Assuming that Phe and Tyr were contributing to  $\sum$ FAA in a very small fraction as reported in Barbaro et al. (2011), their concentrations would be below the detection limit and could thus probably not be detected.”

**R#1-2)** The experiments have been done carefully and the quality of data is good. Authors comprehensively presented the experimental approach and obtained data within the manuscript. Important data are also shown within the SI material. However, some SI Tables are not easily comparable to each other. For example, in the present form Table S9 does not follow the Table S8 format. Comparing Tables S8 and S10, I am wondering why data for all size fractions are presented within Table S10 and only submicron and supermicron classification is done within the Table S8. I suggest to reorganize and to uniform SI Tables to follow the main text clearly and to enable the data comparison more easily.

We thank the reviewer for his positive judgement and his comment. We agree regarding the SI Tables. In order to simplify the comparability of the individual information in the SI, the SI tables (Table S2, S7, S8, S10 and S11) have been standardized in the distinction between submicron and supermicron aerosol particles. This provides a better overview of the measurement data and allow a clearer and easier to understand discussion.

**R#1-3)** Some sentences/paragraphs require major rephrasing. I found the reading of several statements rather unclear and I proposed some changes accordingly. However, my main concern lies in the sentence style used throughout the manuscript. I believe that the paper should be thoroughly edited.

Following this comment, the manuscript and supporting information has been carefully revised by a professional English-speaking person. The main focus was on the comprehensibility of the sentences/paragraphs. In this context, the specific and technical comments were also implemented.

**R#1-4)** Once introduced, abbreviations should be used further throughout the text.

We agree with the reviewer's comments regarding the abbreviations. Some of these are taken up again and explained in more detail in the following section "specific and technical comments" for abbreviations such as CVAO, MV and FAA. When revising the manuscript and the Supporting Information, care was taken to ensure that abbreviations (e.g. CVAO, MV, FAA) were used consistently after their introduction. A detailed overview can be found in the change tracking of both scripts attached.

## **Specific and technical comments**

### **R#1-5) Page 2**

L23 Skip ...also.; it is confusing considering the previous paragraph

Due to the revision of the introduction and also in line with the suggestions from reviewer 2, we concentrated on the FAA from the beginning and deleted general parts (as the one mentioned by the reviewer) from the manuscript.

**R#1-6) Page 3**

L7-9 please rewrite;...into consideration for the accurate prediction of marine organic matter transfer to the atmosphere (van Pinxteren et al., 2017).

As mentioned above, due to the revision of the introduction and also following the suggestions from reviewer 2, this part was deleted from the manuscript.

**R#1-7) Page 4**

L1-3 Repetition with the L27-34; I suggest to skip it or rewrite the overall paragraph to avoid repetition.

We agree with the reviewer's comment and have removed the detailed information on the sampling sites of the campaign in the introduction and concentrated on the different sampling approaches for seawater, aerosol particles and cloud water. The text now reads as follows in the Introduction (page 3, line 31 – page 4, line 5): "So, the aim of the present study is to investigate the occurrence of FAA in the marine environment regarding all important compartments; i.e. the ULW, the SML, the aerosol particles and finally cloud water in the remote tropical North Atlantic Ocean at the Cape Verde Atmospheric Observatory (CVAO). Their abundance, origin and possible transfer from the seawater as well as their transport within the atmosphere are studied in particular. Therefore, the FAA are measured on a molecular level and divided into hydrophilic (glutamic acid, aspartic, GABA), neutral (serine, glycine, threonine, proline, tyrosine) and hydrophobic compounds (alanine, valine, phenylalanine, isoleucine, leucine) according to their hydrophathy index. Especially the similarities and differences between the amino acid composition in submicron (0.05-1.2  $\mu\text{m}$ ) and supermicron (1.2-10  $\mu\text{m}$ ) aerosol particles are elucidated. Finally, the potential of individual FAA as proxies or tracers for specific sources of aerosol particles and cloud water in the tropical marine environment is outlined."

**R#1-8) L14-15 Unclear/confusing sentence, please rewrite**

We agree with the comments of the reviewer and have reworded the sentence and also added a figure of the sampling locations based on the comments of reviewer 2. It now reads (page 4, line 16-19): "During this campaign, concerted measurements were performed including the sampling of size-segregated aerosol particles at the CVAO and seawater sampling at the ocean site ( $\sim 16^{\circ}53'17''\text{N}$ ,  $\sim 24^{\circ}54'25''\text{E}$ ). The location was carefully chosen with minimal influence of the island and located in wind direction to the CVAO as shown in Fig. S1."

**R#1-9) L15 The abbreviations for the sampling sites (CVAO and MV stations) were introduced within the Introduction, thus please use it further throughout the text (e.g. .P4 L30, P5 L6, P12 L30...)**

We agree with the reviewer's comment and following the introduction we now use the abbreviations CVAO and MV.

**R#1-10) L19: I suggest avoiding abbreviations within the title (*Seawater sampling*). Types of samples could be specify within the following paragraph**

Following the advice of the reviewer, we have changed the title of section 2.1.1 to "Seawater sampling" (page 4, line 23). As noted by the reviewer, the two collected seawater sample types (SML and ULW) are described in more detail in this section.

**R#1-11) L20: Please correct ..were taken from a fishing boat...**

The sentence (page 4, line 24) was changed to “The seawater samples were taken from a fishing boat, starting from Bahia das Gatas, São Vicente.”

**R#1-12)** L22 and L23: Skip -pre-cleaned- as it is stated in L25-26 that all sampling material was pre -cleaned

Following this comment, we have omitted the additional description of the sample bottles by "pre-cleaned". The text is now written (page 4, line 25-28) as “The surface films adhered to the surface of the glass plate and were removed with Teflon wipers directly into a bottle. This glass plate approach is described in detail by Cunliffe (2014). The ULW was sampled in a depth of 1 m into a plastic bottle fitted on a telescopic rod. To avoid influences from the SML, the bottles were opened underwater at the intended sampling depth.”

## Page 5

**R#1-13)** L16 I suggest to use the FAA abbreviation throughout the text

As mentioned in comment R#1-4, we agree to the continuous use of the abbreviation “FAA” and have integrated it in the manuscript and in the Supporting Information.

**R#1-14)** L22 Add...include *determination of glycine* (Gly)...

Following the comment of the reviewer, we included “determination of”. It is now written (page 6, line 1-4) as “Besides, the FAA analysis includes the determination of 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  $\gamma$ -aminobutyric acid (GABA) (purity  $\geq$  99 %, Sigma-Aldrich, St. Louis, Missouri, USA).”

**R#1-15)** L34 Unclear sentence part (..in 0.1 min back to 5 % B and...); please rewrite

We agree with the comment of the reviewer and rewrote this sentence part (page 6, line 12-14). Now it reads: “The flow rate of the eluent was 0.3 mL min<sup>-1</sup> 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 from 100 % B to 5 % B and the 5 % B was then kept constant for 3.9 min.”

**R#1-16)** L34 Please correct: ...This *analytics OR analytical procedure* can be used...

The sentence was corrected to “This analytical procedure can be used for amines, too, as described in van Pinxteren et al. (2019).” (page 6, line 14/15)

## Page 6

**R#1-17)** L2-5 Unclear/confusing sentence, please rewrite

We agree with the comment of the reviewer and rewrote this sentence (page 6, line 15/16), which now reads: “Since no chiral column was used in the UHPLC separation, we cannot differentiate between L- and D- amino acids in our ambient samples.”

**R#1-18)** L6 Introduce the LOQ abbreviation here instead within L24

Following the comment, we introduced the LOQ abbreviation on page 6, line 19/20. It is now written as: “The limit of quantification (LOQ) of the individual FAAs in seawater samples is in good agreement with the FAA analysis in seawater samples (e.g. Kuznetsova et al. (2004)) and listed in Table S1.”

Moreover, we used only the LOQ abbreviation on page 7, line 4-6: “The LOQs of the individual FAAs in aerosol particle samples are listed in Table S1 and are in good agreement with the sensitivity of other analytical methods for FAAs in aerosol particles (e.g. Matsumoto and Uematsu (2005)).”

**R#1-19) L13** Please add the method used for the trace metal determination

The method for the trace metal determination was described in more detail on page 7, line 9-11: “The analysis of mineral dust tracers on nucleopore foils sampled with the Berner impactor was performed with the Total Reflection X-Ray Fluorescence S2 PICOFOX (Bruker AXS, Berlin, Germany) equipped with a Mo-X-ray source on polished quartz substrates as can be seen in Fomba et al. (2013).”

**R#1-20) L13** Remove a space before -total-

We agree with the comment of the reviewer and removed the space before -total-. On page 6, line 27-29 it is written now: “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.”

**R#1-21) L23** Rewrite to be clear that data obtained for the aerosol samples were blank corrected

Following the comment, we rewrote this sentence. Now it reads: All values presented here for aerosol particle samples are field blank corrected.” (page 7, line 4)

**R#1-22) Page 7**

Please explain the calculation of  $EF_{SML}$  based on LOQ/2 estimation (Figure 1) in the case of the missing ULW data within the 2.2.4 Section.

To better describe this procedure, we added in section “2.2.4 Enrichment factors” an explanation for the calculation of  $EF_{SML}$  based on LOQ/2 in the case of missing ULW data. Now it reads (page 8, line 11-14): “The FAA concentration in the ULW was assumed to be based on the concentration (LOQ/2) of individual amino acids for seawater samples from the same campaign day when individual FAA could be quantified in the SML samples, but not in the corresponding ULW ones due to FAA values below the LOQs (listed in Table S1). For the calculation of this estimated  $EF_{SML}$ , specially marked in the following, the concentration  $25.2 \text{ nmol L}^{-1}$  was used for  $c(analyte)_{ULW}$  in equation (1).”

**R#1-23) L28** I suggest to name the  $EF_{aer}$  as the -aerosol enrichment factor- instead of the -enrichment factor aerosol- (see accordingly the Fig 5 caption) 3

Following the comment of the reviewer we changed the name of  $EF_{aer}$  to aerosol enrichment factor throughout the manuscript.

**R#1-24) Page 8**

Authors should discuss if the observed variability of FFA concentrations in seawater samples (especially in the SML) was comparable to the variability of the overall DOC and/or TDN pools. It seems to me that high variability of DOC and/or TDN content actually caused the variability of their FAA constituents.

To put the FAA data in context with the DOC/TDN data, we included the DOC/TDN data in Figure 1 and we evaluated a possible connection between FAA variability in seawater (ULW and SML) and DOC and TDN variability in seawater (ULW and SML). However, no statistical relevant correlation/link between FAA and DOC or TDN in terms of variability was found. The study of the

correlation of variability (FAA and DOC/TDN) was included in the revised manuscript (page 10, line 12-14) as follows: “Nevertheless, the variance of the  $\sum$ FAA concentrations in the SML or ULW observed here could neither be explained by the variance of DOC or TDN values, nor by wind speed and chl-*a* concentrations (see Fig. 1, Table S2, S5), since no correlation between these parameters and the concentration or enrichment of FAA was found.”

**R#1-25)** In the context of further FAA transfer discussion, it would be useful to follow the FFA classification into hydrophilic, neutral and hydrophobic groups as done for the atmospheric samples.

We agree with the reviewer's comment and have extended the FAA's illustrations (Fig. 1, 2, 3, 4) and discussion in the different marine compartments not only to the individual amino acids but also to the amino acid groups.

In section “3.1 Seawater samples” (page 10, line 4-5) the text now reads: “Looking at the percentage composition within the ULW (10.1 % hydrophilic, 57.0 % neutral, 32.8 % hydrophobic) and the SML (10.6 % hydrophilic, 61.7 % neutral, 27.7 % hydrophobic), the values are similar to each other.”

In section “3.3 Cloud water samples” the sentence “In terms of the hydropathy classification, the first part of the campaign (27/09/2017-5/10/2017) was dominated by neutral FAAs, whereas a sudden increase of the hydrophilic FAAs was observed in its second part (06/10/2017-08/10/2017).” was added on page 16, line 18 – page 17, line 2.

## Page 9

**R#1-26)** L2 Add ...Mediterranean Sea of 0.07-0.60  $\mu\text{mol L}^{-1}$ ...

We agree with the reviewer's comment and added ‘of’. Now it reads (page 11, line 3-5): “Reinthaler et al. (2008) considered concentrations of dissolved FAA of 0.02-0.13  $\mu\text{mol L}^{-1}$  (ULW) and of 0.43-11.58  $\mu\text{mol L}^{-1}$  (SML) in the subtropical Atlantic Ocean as well as values of 0.07-0.60  $\mu\text{mol L}^{-1}$  (ULW) and of 0.77-3.76  $\mu\text{mol L}^{-1}$  (SML) in the western Mediterranean Sea.”

**R#1-27)** L4-6 Add .... in the SML or in the ULW *since* no correlation between...

The reviewer's comment was implemented in the new sentence. It now reads (page 10 line 12-14): “Nevertheless, the variance of the  $\sum$ FAA concentrations in the SML or ULW observed here could neither be explained by the variance of DOC or TDN values, nor by wind speed and chl-*a* concentrations (see Fig. 1, Table S2, S5), since no correlation between these parameters and the concentration or enrichment of FAA was found.”

**R#1-28)** L23-24 The sentence should be supplemented to indicate the particular oceanic regions with the comparable FFA levels as at the CVAO.

We agree with the comment and have specified the region of study accordingly.

In section “2.1 Study area” the following sentences (page 4, line 13-16) were inserted: “In accordance with the classification of Longhurst (2007), the ocean around the Cape Verde Islands belongs to the region “North Atlantic Tropical Gyral Province (NATR)”, which is described as the region with the lowest surface chlorophyll in the North Atlantic Ocean having a greater annual variability than seasonality.”

In section “3.1 seawater samples” the discussion (page 10, line 32- page 11, line 7) reads as follows: “Altogether, it can be concluded that there is some variability within the FAA concentration in the SML and in the ULW, with a clear trend of its strong enrichment in the SML. The fact that the FAA concentrations were in accordance with the ones measured at the same location in 11/2013 (0.64  $\mu\text{mol L}^{-1}$ , Table S4), supports the suggestion that the FAA concentrations reported here can be considered representative of the NATR region as part of the North Atlantic Ocean. These

concentrations are generally similar comparing them to FAA concentrations in other marine regions (Kuznetsova and Lee, 2002;Reinthal et al., 2008). Reinthal et al. (2008) considered concentrations of dissolved FAA of 0.02-0.13  $\mu\text{mol L}^{-1}$  (ULW) and of 0.43-11.58  $\mu\text{mol L}^{-1}$  (SML) in the subtropical Atlantic Ocean as well as values of 0.07-0.60  $\mu\text{mol L}^{-1}$  (ULW) and of 0.77-3.76  $\mu\text{mol L}^{-1}$  (SML) in the western Mediterranean Sea. Consequently, the FAA concentrations in the NATR region, with its very low surface chlorophyll and a greater annual variability than seasonality, are in the same order of magnitude compared to other marine regions (i.e. subtropical Atlantic and western Mediterranean Sea (Reinthal et al., 2008)).”

## Page 10

**R#1-29** L16 Add ...of dissolved FAA ( $PM_{10}$ ; sum of B1-5)...

This sentence was omitted in the revision of the manuscript. The FAA's concentration discussion is now more focused on the distinction between submicron and supermicron aerosol particles and reads as follows (page 12, line 3-7): “In the submicron aerosol particles, the concentration of  $\sum\text{FAA}$  was between 1.3  $\text{ng m}^{-3}$  (1/10/2017) and 6.3  $\text{ng m}^{-3}$  (7/10/2017). Whilst the concentration  $\sum\text{FAA}$  varied between 0.2  $\text{ng m}^{-3}$  (6/10/2017) and 1.4  $\text{ng m}^{-3}$  (22/09/2017) in the supermicron size range, the highest atmospheric concentrations of  $\sum\text{FAA}$  were found in the submicron aerosol particles (mean of 3.2  $\text{ng m}^{-3}$ ) compared to the supermicron ones (mean of 0.6  $\text{ng m}^{-3}$ ).”

**R#1-30** L17-21 Please indicate the PM size fraction citing the Matsumoto and Uematsu (2005) as well as Barbaro et al, 2015

Following the comment of the reviewer we defined the PM size fraction of both studies, Matsumoto and Uematsu (2005) and Barbaro et al, 2015, in more detail. Now it reads (page 12, line 23-28): “Matsumoto and Uematsu (2005) found averaged total concentrations of dissolved FAA with 4.5  $\text{ng m}^{-3}$  on aerosol particles (average of  $< 2.5 \mu\text{m}$  and  $> 2.5 \mu\text{m}$ ) in the western North Pacific Ocean. Moreover, Wedyan and Preston (2008) observed an average concentration of dissolved FAA of 2.5  $\text{ng m}^{-3}$  on total suspended particles (TSP) during a transect ship cruise in the Atlantic Ocean. For Antarctic aerosol particles, the observed mean total FAA concentration on size-segregated aerosol particle samples ( $< 0.49\text{-}10 \mu\text{m}$ ) at the Mario Zucchelli Station was 4.6  $\text{ng m}^{-3}$  (Barbaro et al., 2015).”

## Page 12

**R#1-31** Please explain why would the low percentage of hydrophobic FAA and higher percentages of hydrophilic FAA point to the local oceanic origin of FAA in aerosol size fractions. As marked previously, it would be useful to refer to the seawater FAA classification in this study.

This part was thoroughly revised.

In the Introduction (page 3, line 17-20), we stated “This divides them into hydrophilic, neutral and hydrophobic amino acids as discussed in Barbaro et al. (2015) for FAA in Antarctic aerosol particles. They also observed that hydrophilic FAA in the Antarctic were predominant in locally produced marine aerosol particles, while hydrophobic amino acids prevailed in aerosol particles collected at the continental station.”

We intensively discussed the single FAA contributing to the hydrophilic fraction and the text now reads (page 14, line 21-27): “Following this hydrophobicity classification, the submicron aerosol particles consisted on average of 5 % hydrophobic, 15 % hydrophilic and 80 % neutral amino acids, while the supermicron aerosol particles contained on average only 7 % hydrophobic and 93 % neutral amino acids (Table S7). During the campaign, an increase in the contribution of hydrophilic amino acids was observed with a maximum of 55 % on 7/10/2017. Barbaro et al. (2015) reported that hydrophilic components were predominant (60 %) in locally produced marine Antarctic aerosol particles, whereas hydrophobic compounds were rather dominate aerosol particles collected at the continental station (23 % and 27 %). According to the conclusions by Barbaro et al. (2015), the

relatively high content of hydrophilic FAA found here points at least at some influence of local oceanic sources.”

**R#1-32)** L31-32 Unnecessary sentence, repetition

Following the comment of the reviewer, we removed that sentence.

### Page 13

**R#1-33)** L6-10 The PM mass concentrations of size segregated samples at the MV were substantially lower than those obtain at the CVAO. Thus, it could be expected that the levels of Na and MSA constituents will be accordingly lower at MV in comparison to CVAO. For the sake of comparison of aerosol tracer levels at different stations, it is more reasonable to consider the contribution of Na and MSA to the PM mass (of corresponding size fraction) instead of comparing the concentration levels.

We strongly revised this part and following the suggestions of the reviewer, we included and discussed ratios of FAAs to other aerosol particle constituents (PM, Na<sup>+</sup>, MSA, WSOC) of the corresponding size fractions regarding CVAO and MV. The section (page 15, line 23-32) now reads: “The particles at the MV exhibited lower particle masses, as well as lower concentrations of the aerosol particle constituents. The decrease in concentrations of  $\Sigma$ FAA, PM, sodium, MSA and WSOC was reduced by a factor of three to four regarding the submicron aerosol particles. However, no uniform depletion ratio between their concentration at the CVAO and the MV was found for the supermicron aerosol particles (Table S11). While the PM of the supermicron particles was reduced by a factor of four at the MV (similar to the submicron aerosol particles), sodium and WSOC were depleted more strongly (factor of 11-12) compared to their respective concentrations at the CVAO. This suggests that the submicron particles were rather uniformly affected and depleted, likely by cloud processes, while the supermicron particles were influenced by clouds, and potentially other sources, in a non-uniform way. Nevertheless, the abundance of the marine tracers (sodium, MSA), together with the presence of FAA in the aerosol particles (which mainly had a similar composition compared to the oceanic and ground-based particulate FAA) indicated an oceanic contribution to the aerosol particles at cloud level.”

**R#1-34)** L24-27 Authors should comment on the fact that high LOQ of particular FAA could resulted in their variabilities or selective determination in cloud water samples.

We agree with this comment and have added on page 7, line 31-33 a statement to a possible limitation of the FAA composition in cloud water due to the LOQ.

It reads now: “Since the LOQs of the FAAs in cloud water are below 0.3 ng m<sup>-3</sup> and often below 0.06 ng m<sup>-3</sup>, a limitation of the FAA composition in cloud water due to the LOQs is rather unlikely despite the variance of FAA concentrations (11.2-489.9 ng m<sup>-3</sup>) in cloud water (section 3.3).”

**R#1-35)** L28-32 to P14 L4-8 This paragraph deals with the possible dominant origin of FAA in the cloud water collected at the MV as within the 3.4.5. Section. I suggest skipping this paragraph 4 and combining the cloud water source discussion within the 3.4.5 section to avoid the repetition.

We agree with the reviewer and included the entire cloud water discussion in section “3.3 Cloud water samples”. Section 3.4.5 has been deleted and section “3.4.4 Transfer of amino acids from the ocean into the atmosphere” now contains only some sentences on the enrichment factor in cloud water, which reads now (page 22, line 20-24): “Applying the concept of the enrichment factor to cloud water and calculating the EF<sub>CW</sub> (Eq. (2)), the EF<sub>CW( $\Sigma$ FAA)}</sub> = 4·10<sup>3</sup> (based on SML) and 1·10<sup>4</sup> (based on ULW) could be determined. As mentioned in section 3.3, several atmospheric processing (aging), oceanic transfer and biogenic-driven processes might contribute to this high enrichment



and need to be addressed in future studies. The high FAA concentrations and enrichments might have implications on OM processing through clouds and are worth further studying.”

**R#1-36)** L33-34 Please specify the study location of Gioda et al. (2009)

Following the comment of the reviewer we specified the study location of Gioda et al., (2009). Now the text reads (page 16, line 11-13): “The concentrations of cloud water sulfate (average:  $2.9 \mu\text{g m}^{-3}$ , Table S12) and sodium were higher than in cloud water samples, collected at East Peak in Puerto Rico, which can be seen in Gioda et al. (2009).”

### **Page 15**

**R#1-37)** The authors should comment and discuss that some specific FAA were not detected in particular compartments possibly due to their high LOQ (in all matrices) and/or the fact that not enough material was collected for their analysis. This is particularly relevant for selected hydrophilic FAA in comparison to other FAA classes/groups and should be considered when discussing the selective transfer of FAA groups from the ocean to the atmosphere.

We agree with the reviewer and carefully discussed LOQ restrictions in several parts of the manuscript as follows: In the experimental part section “2.2. Analyses” an estimation was given for which amino acids due to the LOQ a restriction of the sensitivity in the marine compartment would be possible and thus no quantitative statement on the analyte would be possible.

This possible restriction of the results by the LOQs was also discussed in the results and discussion section in the individual sections on seawater (section 3.1), aerosol particles (section 3.2), cloud water (section 3.3) and concerted measurements (section 3.4). The detailed response and citations from the manuscript can be found under comment R#1-1.

### **Page 17**

**R#1-38)** Although beyond the scope of this paper, I suggest discussing the potential connection of hydrophilic, hydrophobic and neutral FFA to CCN activity.

We included on page 2, line 27-30: “Due to their structure and hygroscopic properties, amino acids can act as both ice-forming particles (INP) (Wolber and Warren, 1989; Szyrmer and Zawadzki, 1997; Pandey et al., 2016; Kanji et al., 2017) as well as cloud condensation nuclei (CCN) (Kristensson et al., 2010) in the atmosphere when amino acids such as arginine and asparagine can exist as metastable droplets instead of solid particles at low relative humidity; this showed a laboratory study (Chan et al., 2005).”

However, we are not aware of a study that investigates amino acids within their hydrophilic, hydrophobic and neutral characteristics. As no CCN studies with regards to amino acids were performed here, we would like to not stress this topic too much in the manuscript.

### **Page 18**

**R#1-39)** L11-13 Please correct: For the calculated  $EF_{\text{aer}}$ , it should be noted that no further FAA formation or degradation pathways on the aerosol particles are considered, including biological or photochemical atmospheric reactions, *and* a possible transport from other than marine sources *is excluded*.

We agree with the reviewer's note and have incorporated his correction comments for page 21. In the course of re-structuring parts of the manuscript according to the suggestions of reviewer 2, this part was changed to: “A quantitative metric for comparing compounds in the ocean and in the atmosphere is the  $EF_{\text{aer}}$  (Eq. (2)). The concept is mainly applied to closed systems (e.g. Quinn et al. (2015), Rastelli et al. (2017)) because FAA formation or degradation pathways on the aerosol particles including biological or photochemical atmospheric reactions, and possible transport from other than marine sources are excluded in this parameter.” (page 21, line 9-12)

**R#1-40)** L14 remove -as-

In the course of re-structuring to address the comments of reviewer 2, this sentence was changed and reads now (page 21, line 13-15): “The averaged  $EF_{aer}$  of  $\Sigma$ FAA in the individual Berner stages of the case study at the CVAO based on SML and ULW concentrations are shown in Fig. 5.”

#### **Page 17**

**R#1-41)** L7-9 Please correct: Previous studies showed that organic material ejected into the atmosphere during bubble bursting, *results* in the formation of sea spray aerosol particles containing similar organic.....

We agree with the reviewer's comment and corrected the sentence on page 22, line 10-11. Now it reads: “Previous studies have shown that OM ejected into the atmosphere during bubble bursting, results in the formation of sea spray aerosol particles containing OM similar to SML (Russell et al. (2010);Cunliffe et al. (2013) and references therein).”

#### **Page 19**

**R#1-42)** L18 I suggest to change the title to -Origins of FFA in cloud water-, to be consistent with previous section

Taking into account the review comment R1#-35, the section 3.4.5 was removed.

#### **SI material**

**R#1-43)** Page 2, L17 ..and *is* discussed in more...

We agree with the reviewer's comment and corrected the sentence in the SI (page 3, line 5-6) to “It was generally low but increased during the campaign from  $0.1 \mu\text{g L}^{-1}$  to  $0.6 \mu\text{g L}^{-1}$  and is discussed in more detail by van Pinxteren et al., (2020).”

#### **Additional changes performed by the authors**

Due to the comments by reviewer 2 several parts of the manuscript were changed and adopted to the reviewer's suggestions. This affected the following parts:

- The introduction: here the focus was more clearly placed on the FAA
- Discussion about the amino acid groups (hydrophilic, neutral and hydrophobic) in all marine compartments (seawater, aerosol particles and cloud water)
- Discussion about the concerted measurements of FAA in marine compartments
- Discussion about the aerosol enrichment factor
- Discussion and conclusion in general: stronger focus on the novelty value of the main findings shown here in the context of previous studies

When discussing the mean lifetime  $\tau$  of individual amino acids (section 3.4 and Table S13), the unit of  $\tau$  was changed from days (d) to hours (h).

In addition, the acknowledgement was also revised to thank the people from the OSCM. The added sentence is now as follows: “We further acknowledge the professional support provided by the Ocean Science Centre Mindelo (OSCM) and the Instituto do Mar (IMar)” (page 24, line 3-4)  
The measured data were published on PANGAEA. The data availability statement was therefore updated and reads as follows: “Data availability. The data are available through the World Data Centre PANGAEA under the following link: <https://doi.pangaea.de/10.1594/PANGAEA.914220>.” (page 23, line 26/27)

The previous citation of van Pinxteren (submitted 2019) was updated to van Pinxteren et al. (2020) in the revised manuscript and supporting information.

## References

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., 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 and overview to the MarParCloud campaign, *Atmos. Chem. Phys.*, 20, 6921-6951, 10.5194/acp-20-6921-2020, 2020.

van Pinxteren, M. F., K. W.; Triesch, N.; Stolle, C.; Wurl, O.; Bahlmann E.; Gong, X.; Voigtländer J.; Wex, H.; Robinson, B.; Barthel, S.; Zeppenfeld, S.; Hoffmann, E. H.; Roveretto, M.; Li, C.; Grosselin, B.; Daele, V.; Senf, F.; van Pinxteren, D.; Manzi, M.; Zabalegui, N.; Frka, S.; Gašparović, B.; Pereira, R.; Li, T.; Xue, L.; Wen, L.; Wang, X.; Wang, W.; Li, J.; Chen, J.; Zhu, C.; Chen, H.; Chen, J.; Fiedler, B.; von Tümpling, W.; Read, K. A.; Punjabi, S.; 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.; Herrmann, H.: Marine organic matter in the remote environment of the Cape Verde Islands - An introduction and overview to the MarParCloud campaign, *Atmos. Chem. Phys.*, submitted 2019.

We thank the reviewer for the careful examination of the manuscript and the supporting information. In the following, please find a point-by-point response to the questions and concerns. All references to the manuscript (e.g. page and line numbers) listed in our replies refer to the clean version of the manuscript (without track changes).

### **General Comments**

R#2-1 a) This paper describes the measurement of free amino acids in seawater (microlayer and underlying water), aerosol, and cloud water at Cape Verde Island. The types and abundances of individual amino acids present in different sample types are compared. Enrichment factors are calculated for amino acid concentrations between the microlayer and underlying water, and between the water and aerosol. The contribution the amino acids make to the pools of organic carbon and total dissolved nitrogen in water and aerosol are presented. The work largely presents an inventory of amino acids for this location and the given sample types.

We have strongly revised the manuscript and added a lot of additional interpretation which represents clearly more than an inventory of amino acids and is explained in more detail in R#2-2 point 4. We agree that the implications were not well enough elaborated. From the revised results, we derived the atmospheric implication that simple parameters alone cannot describe the abundance and enrichment of FAA in the diverse marine environments. This work shows that, for a proper representation of FAA in oceanic/atmospheric models, their drivers need to be better understood and more studies are needed to unravel their complex composition.

R#2-1 b) The concerted measurement of amino acids in underlying seawater, microlayer, aerosol, and cloud water are novel. The authors also mention that these are the first reported free amino acids concentrations for marine clouds. Enrichment factors between seawater and aerosol are useful for comparison but I urge the authors to elaborate a little on the caveats of their use in an open system, namely that it is unlikely that a high fraction of the aerosol (and cloud droplets) measured came from the location of the measured seawater (and even less likely they emerged from those waters when the water was sampled). Concentrations in the atmosphere are also subject to ageing. This differs from other work on sea spray aerosol in closed systems where all particles are emitted from the contained source waters and minimal ageing occurs on the nascent particles (at least upon collection).

We thank the reviewer for his comments. We agree with the reviewer that the caveats of the concept of enrichment factor between seawater and aerosol were not treated well enough in the manuscript. It is true that the concept of the aerosol enrichment factor originally originates from controlled tank experiments and therefore does not take into account e.g. ageing processes or long-range transport processes of the aerosol particles, which does not completely correspond to the real conditions of field investigations. However, having pointed this out, we believe that the  $EF_{\text{aer}}$  is still a useful metric for comparison purposes. In recent studies, enrichment factors have been calculated from open systems and therefore provide a basis for comparative studies (e.g. Russell et al. (2010) or van Pinxteren et al. (2017)). In the revised version of our manuscript, we have underlined the uncertainties related to this concept and explained that the  $EF_{\text{aer}}$  might be useful for comparison purposes, but should be treated with caution.

The same applies to the enrichment factor between cloud water and seawater, which was calculated in the same way. Again, in the revised version, we point out that this is simplified approach, which only considers a possible transfer from the ocean to the aerosol particles and cloud water (neglecting

e.g. atmospheric processing). To illustrate the  $EF_{CW}$ , we included the values (with respect to the SML and the ULW, respectively) in Figure 5 in the revised version.

As a result, we have very carefully addressed these points in the following parts of the revised manuscript: In section 3.4.4 it is written now (page 21, line 9-13): “A quantitative metric for comparing compounds in the ocean and in the atmosphere is the  $EF_{aer}$  (Eq. (2)). The concept is mainly applied to closed systems (e.g. Quinn et al. (2015), Rastelli et al. (2017)) because FAA formation or degradation pathways on the aerosol particles including biological or photochemical atmospheric reactions, and possible transport from other than marine sources are excluded in this parameter. However, for comparison purposes, it might be useful to calculate the  $EF_{aer}$  also from open systems as done e.g. by Russell et al. (2010) or van Pinxteren et al. (2017).”

In addition, we have revised the abstract and the conclusion accordingly: The abstract (page 1, line 29-31) now reads: “Considering solely ocean-atmosphere transfer and neglecting atmospheric processing, high FAA enrichment factors were found in both aerosol particles in the submicron range ( $EF_{aer(\Sigma FAA)}: 2 \cdot 10^3 - 6 \cdot 10^3$ ) and medium enrichment factors in the supermicron range ( $EF_{aer(\Sigma FAA)}: 1 \cdot 10^1 - 3 \cdot 10^1$ ).”

The conclusion (page 23, line 10-14) is adopted as follows: “In a simplified approach, considering only a possible transfer from the ocean onto the aerosol particles and cloud water (neglecting e.g. atmospheric processing), the aerosol enrichment factor was calculated. A high FAA enrichment in the submicron aerosol particles of  $EF_{aer(\Sigma FAA)}: 2 \cdot 10^1 - 6 \cdot 10^3$  and a medium enrichment on supermicron aerosol particles  $EF_{aer(\Sigma FAA)}: 1 \cdot 10^1 - 3 \cdot 10^1$  were observed. Applying the same concept to cloud water, an enrichment of  $4 \cdot 10^3 - 1 \cdot 10^4$  was obtained.”

Besides the concept of the enrichment factor, the revised manuscript deals with possible atmospheric processes/ aging, which are discussed in sections 3.4.1, 3.4.2 and 3.4.3 when discussing the individual amino acids or amino acid classes.

To address the representativeness of the aerosol particle measurements, we added the information about the aerosol particle measurements at the CVAO on the 30 m tower, which represent the conditions in the open ocean (and not just the surf zone), as follows (page 4, line 33 – page 5, line 2): “Size-segregated aerosol particles were sampled using five stage Berner-type impactors (Hauke, Gmunden, Austria) at the top of a 30 m sampling tower at the CVAO since this location best represents the conditions above the ocean pursuant to previous studies. The internal boundary layer (IBL), which can form when air passes a surface with changing roughness (i.e. the transfer from open water to island) is mainly beneath 30 m (Niedermeier et al., 2014).”

R#2-2) This work could be strengthened by: 1. elaborating on the significance of amino acids in the ocean and atmosphere and how the scientific community benefits from their inventory. 2. investigating the drivers of their observations by further relationships amongst their datasets and incorporating other datasets, e.g. Did variations in measured aerosol volume drive variations in amino acid concentrations? Did primary productivity (via remotely sensed chlorophyll-a) influence FAA concentrations in water and air? 3. further exploration of commonalities among and differences between their amino acid data across different sample types. 4. what implications can be drawn from the analyses accomplished and those I suggest? Are there certain ratios of amino acids in seawater that hold constant in seawater samples but not in the aerosol and clouds? What could cause this? 5. better connecting to past work. How do the observations compare not just to the values reported in other work but to the conclusions drawn in other research? How do drivers of amino acid concentrations differ between the ocean and atmosphere? What are the surface activities of the amino acids and can they predict their transfer in sea spray aerosol?

We thank the reviewer for this comment and the suggestions to improve the manuscript. We have addressed the points raised by the reviewer as shown in the following:

1. elaborating on the significance of amino acids in the ocean and atmosphere and how the scientific community benefits from their inventory.

1) *Significance of amino acids*: Amino acids are important in the oceans and in the atmosphere for a number of reasons. Due to their chemical structure, amino acids contribute to both dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) and are therefore important biologically available sources of nitrogen and carbon. Especially in oligotrophic regions, such as the NATR region investigated here, the amino acids are an important source of nutrients for bacteria and other microorganisms. Besides the biogenic formation of amino acids in seawater and probably also on aerosol particles (e.g. GABA, see R#2-31), amino acids (as parts of proteins) also play an important role as ice-forming particles (INP) (Wolber and Warren, 1989; Szyrmer and Zawadzki, 1997; Pandey et al., 2016; Kanji et al., 2017) or cloud condensation nuclei (CCN) (Chan et al., 2005; Kristensson et al., 2010) in the marine environment. Besides abiotic and biotic conversion processes of amino acids, secondary organic aerosol particles (SOA) can be formed by the reaction of glyoxal with amino acids (Haan et al., 2009). These are important reasons why amino acids in the marine environment have been studied both in seawater and on the aerosol particles in different regions.

With our concerted FAA measurements in all marine compartments (seawater (ULW, SML), size-segregated aerosol particles and cloud water), it was possible not only to investigate the individual compartments (section 3.1, 3.2 and 3.3), but also to focus on the individual FAA and amino acid groups to identify similarities and differences. These are discussed in detail in the comments R#2-2 3), R#2-2 4), R#2-21, R#2-27. Furthermore, for the first time the FAA concentrations and compositions in cloud water were determined (section 3.3) and compared with the other two compartments (seawater and aerosol particles) in section 3.4.

In the revised version, we stronger elaborated the significance of the amino acids, as outlined in the Introduction: “Amino acids, either free (FAA) or in combined form (CAA), contribute to the global nitrogen and carbon cycle and to the atmosphere-biosphere nutrient cycle (Zhang and Anastasio, 2003; Wedyan and Preston, 2008). They are produced in the ocean and are reported to be 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 aerosol particles within the marine environment (Cunliffe et al., 2013; Engel et al., 2017; Wurl et al., 2017). Specific organic groups of compounds, including nitrogenous OM (Engel and Galgani, 2016) can be strongly enriched in the SML. From the ocean, amino acids as part of the class of proteinaceous compounds can be transferred into the atmosphere via bubble bursting (Kuznetsova et al., 2005; Rastelli et al., 2017). These proteinaceous compounds are often analyzed as sum parameter ‘proteins’ using an analytical staining method with Coomassie blue developed by Bradford (1976) and often applied in previous studies (Gutiérrez-Castillo et al., 2005; Mandalakis et al., 2011; Rastelli et al., 2017). Despite their attribution to proteins the FAAs are better utilizable forms of nitrogen instead of proteins for an aquatic organism such as phytoplankton and bacteria (Antia et al., 1991; McGregor and Anastasio, 2001).” (page 2, line 14-26)

Furthermore, we have added the following text in the introduction about the significance of amino acids in the atmosphere (page 2, lines 27-30): “Due to their structure and hygroscopic properties, amino acids can act as both ice-forming particles (INP) (Wolber and Warren, 1989; Szyrmer and Zawadzki, 1997; Pandey et al., 2016; Kanji et al., 2017) as well as cloud condensation nuclei (CCN) (Kristensson et al., 2010) in the atmosphere when amino acids such as arginine and asparagine can exist as metastable droplets instead of solid particles at low relative humidity; this showed a laboratory study (Chan et al., 2005).”

*Benefits:* Although FAA measurements in the marine atmosphere have been available so far, there is a lack of measurements considering both the abundance and molecular composition of amino acids simultaneously in the different marine compartments, especially in the tropical Atlantic Ocean. The measurements performed here, together with the interpretation of the data, will provide better insights into the FAA abundance, origins and possible transfer from the seawater and their transport within the atmosphere in the marine environment regarding all important compartments; i.e. the ULW, the SML, the aerosol particles and finally cloud water in the remote tropical North Atlantic Ocean.

We would like to mention that the concerted FAA measurements performed here have already been included in a discussion paper published at “Biogeoscience” as “Free AA concentrations ... recently quantified in cloud droplets ... on the Cape Verde islands” (Jaber et al., 2020).

2. investigating the drivers of their observations by further relationships amongst their datasets and incorporating other datasets, e.g. Did variations in measured aerosol volume drive variations in amino acid concentrations? Did primary productivity (via remotely sensed chlorophyll-a) influence FAA concentrations in water and air?

2) We agree that the incorporation of other data sets was partly missing in the manuscript. Consequently, we included additional available parameters with the aim to explain the variation of FAA concentrations.

For seawater, DOC and TDN measurements (in ULW and SML), chl-*a* concentrations (as an indicator for primary productivity) and wind speed were included to investigate the observed variance of FAA concentrations in seawater. However, no statistically significant correlations could be found (in more detail in R#2-5).

For the aerosol particles, wind speed, wind direction, the particulate mass (PM) of the aerosol particles and the chl-*a* concentrations in the seawater were considered to describe the variance of the atmospheric FAA concentrations. However, again no statistically relevant correlations could be found (detailed information in R#2-6).

The surface activity of the individual amino acids was also considered in the revised version. The octanol-water partition coefficient ( $K_{OW}$ ), the topological polar surface area (TPSA) and the density were included (Table S9). However, we found that these simple physico-chemical parameters could not explain the variance of the FAA by statistically relevant correlations. In addition to the parameters representing the surface activity, the mean lifetime  $\tau$  of the aerosol particles (Table S13) was also taken into account. However, no statistically relevant correlations were found here either. For a detailed answer to the investigations on surface activity and mean lifetime we would like to refer to the comment R#2-33.

3. further exploration of commonalities among and differences between their amino acid data across different sample types.

3) In the revised manuscript version, a clearer focus is put on the comparison of amino acid profiles (in terms of individual amino acids and amino acid groups) in the different marine compartments. After the introduction of the individual marine compartments, seawater (section 3.1), aerosol particles (section 3.2) and cloud water (section 3.3), the composition of the amino acid profiles was examined in more detail in section 3.4. A distinction was made between hydrophilic (section 3.4.1), neutral and hydrophobic (section 3.4.2) and aromatic amino acids (section 3.4.3).

The main results are summarized in the Conclusion (page 22, line 29-34): “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 certain FAA contribution, in particular the hydrophilic amino acids Asp and Glu in the submicron aerosol particles at the CVAO, was probably caused by sea spray and might be transferred up to cloud level. The neutral and hydrophobic amino acids were also present in all marine compartments, suggesting some interconnections. Stable amino acids like

Gly are often reported as long-range tracers, but their abundance in seawater and marine air masses prevailing during the sampling period suggest an (additional) oceanic source.”

For a detailed overview of the individual discussion of the amino acid profiles (in the individual compartments and the cross-compartment comparison in the marine environment), we would like to refer to the comments R#2-20, R#2-21, R#2-22, R#2-24 and R#2-27.

4. what implications can be drawn the analyses accomplished and those I suggest? Are there certain ratios of amino acids in seawater that hold constant in seawater samples but not in the aerosol and clouds? What could cause this?

The main points (summarized in the revised conclusion of the present study) are:

- A certain FAA contribution, particularly the hydrophilic amino acids Asp and Glu in the submicron aerosol particles at the CVAO, was probably caused by sea spray and might be transferred up to cloud level.
- Stable amino acids like Gly are often reported as long-range tracers, but their abundance in seawater and the marine air masses prevailing during the sampling period suggest an (additional) oceanic source.
- Indications for biological production of amino acids on the aerosol particles (GABA) were observed, supporting recent finding of a high active enzymatic activity on marine aerosol particles.
- The high FAA concentrations and enrichments in cloud water, which have been reported here for the first time. Their composition, together with the high concentrations of inorganic marine tracers (sodium, MSA), indicate at least to some extent to an oceanic transfer and biogenic formation that remains subject to future work.

From these findings, together with the now added additional interpretations to our data, we derived the atmospheric implications (see answer to R#2-1 a) and added the following in the Abstract and in the Conclusion: ”Finally, the varying composition of the FAA in the different matrices shows that their abundance and ocean-atmosphere transfer are influenced by additional biotic and abiotic formation and degradation processes. Simple physico-chemical parameters (e.g. surface activity) are not sufficient to describe the concentration and enrichments of the FAA in the marine environment. For a precise representation in organic matter (OM) transfer models, further studies are needed to unravel their drivers and understand their composition.” (page 2, line 3-8) and “Altogether, the varying composition of FAAs in the different matrices shows that their abundance and their enrichments in the SML and their atmospheric transfer are not determined by single environmental drivers (e.g. wind speed) and/or simple physico-chemical parameters (e.g. surface activity). The ocean-atmosphere transfer of FAAs is influenced by biotic and abiotic formation and degradation processes. Further studies are required to unravel their drivers and understand their complex composition that, finally, have to be considered in OM transfer models.” (page 23, line 17-23)

For more details, we would like to refer to our answer to the referee comment R#2-3.

These results and implications were derived from studying the ratios via the percentage composition of the FAA in the individual compartments together with other information (e.g. environmental parameters and physico-chemical properties). For a more detailed discussion of the amino acid ratios/ profiles, we would like to refer to our answers to the Review comments R#2-21 R#2-26 and R#2-27, R#2-31.

5. better connecting to past work. How do the observations compare not just to the values reported in other work but to the conclusions drawn in other research? How do drivers of amino acid concentrations differ between the ocean and atmosphere? What are the surface activities of the amino acids and can they predict their transfer in sea spray aerosol?



We agree that the connection of our work to previous studies was not strong enough. In the revised manuscript version, we have significantly extended the comparison of our observations to the conclusions drawn in earlier studies. We have also outlined the uncertainties of sources and drivers of amino acids in the marine environment and connected our findings to literature studies at several parts of the manuscript as follows:

In the Introduction, we have included the following (page 3, line 3-14): "Based on a cluster and factor analysis, Scalabrin et al. (2012) suggested two possible sources for the amino acids in the ultrafine Arctic aerosol particles. First, the authors mentioned the regional development (isoleucine, leucine, threonine) and long-range transport (glycine) of amino acids from marine areas; secondly, the influence of local sources such as of marine primary production (proline, valine, serine, tyrosine, glutamic acid). A different approach of Mashayekhy Rad et al. (2019) investigated the atmospheric proteinogenic aerosol particles in the Arctic and attributed them to different sources based among others on the reactivity of the distinct amino acids. The authors differentiated here between long-range transport (glycine), terrestrial and marine aerosol particles (proline, valine, serine, tyrosine) and coastal and marine phytoplankton and bacteria (isoleucine, leucine and threonine) as important sources for amino acids (Mashayekhy Rad et al., 2019). In fact, previous studies have assigned individual amino acids to specific marine biogenic sources and used them as biomarkers. Hammer and Kattner (1986) reported correlations between aspartic acid, diatoms and zooplankton in seawater. GABA ( $\gamma$ -aminobutyric acid) was referred to as an indicator for the microbiological decomposition of OM (Dauwe et al., 1999; Engel et al., 2018) and is probably used as a microbiological proxy in aerosol particles."

In section 3.1, we carefully revised the section on FAA enrichment in the SML and it reads now as follows (page 10, line 16-30): "The results of the individual FAA concentrations in seawater (ULW, SML) and their  $EF_{SML}$ , listed in Table S3, show clear differences between the individual amino acids and the amino acid classes. The most highly enriched amino acids in the SML are the neutral ones with values of up to 203 compared to the hydrophilic ( $EF_{SML}$ : 2-98) and hydrophobic ( $EF_{SML}$ : 1-96) amino acids. This may be related to the fact that Ser, Thr and Gly as part of the neutral amino acids, are main components of cell wall proteins (Hecky et al., 1973). The direct release of FAAs through cell lysis and the associated destruction of the cell wall can thus explain the increased enrichment of neutral amino acids in the SML. Our study confirmed that the SML is often non-uniformly enriched with FAAs as outlined from previous observations (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, the in-situ production by an extracellular hydrolysis of CAA or a direct release of FAA by cell lysis probably cause the observed enrichment of FAA in the SML. Kuznetsova and Lee (2002) showed that the rapid extracellular hydrolysis of CAA in the SML was not the cause of the non-uniformly enrichment in SML. Moreover, they suggested that the intracellular pools of organisms rich in DFAA and DCAA compared to seawater can be leached out by stressed microorganisms, resulting in the release of DFAA which in turn influences the pools of both DFAA and DCAA in seawater. Based on previous studies, the transportation and releasing mechanisms seem most likely to be the reasons for the observed enrichment of FAA."

And in section 3.2.1, we revised the discussion as follows (page 14, line 21-27): "Following this hydrophathy classification, the submicron aerosol particles consisted on average of 5 % hydrophobic, 15 % hydrophilic and 80 % neutral amino acids, while the supermicron aerosol particles contained on average only 7 % hydrophobic and 93 % neutral amino acids (Table S7). During the campaign, an increase in the contribution of hydrophilic amino acids was observed with a maximum of 55 % on 7/10/2017. Barbaro et al. (2015) reported that hydrophilic components were predominant (60 %) in locally produced marine Antarctic aerosol particles, whereas hydrophobic compounds were rather dominate aerosol particles collected at the continental station (23 % and 27 %). According to

the conclusions by Barbaro et al. (2015), the relatively high content of hydrophilic FAA found here points at least at some influence of local oceanic sources.”

As mentioned above (R#2-2, point 2), we included a variety of environmental factors and also considered substance-specific properties as well as the mean lifetime  $\tau$  to explain the amino acid concentrations in seawater or on the aerosol particles and to predict the transfer. However, no statistically relevant correlations could be found for all additionally investigated parameters. Therefore, the drivers of amino acid concentrations between ocean and atmosphere could not be distinguished.

R#2-3) Ultimately I would like the authors to demonstrate that they have done more than make some measurements and that we have gained new insight into the ocean-atmosphere system beyond an inventory of amino acids. The manuscript needs to set up what was done on top of our current understanding of sea spray aerosol formation and the transfer of different compounds/-classes into sea spray aerosol. By building on past research the present work is prepared to more clearly communicate its findings and to also contribute new knowledge to the field.

Based on the new measurement data obtained in our work, we have now added many more additional interpretations to our data. Our novel approach of the concerted measurements (ULW, SML, aerosol particles and cloud water) – which is clearly more than ‘some measurements - together with the analysis at molecular level provided a rich data set of the ambient amino acids. These measurements allowed to study similarities and differences of FAA in the various compartments and indicated that a certain FAA contribution, in particular the hydrophilic amino acids Asp and Glu in the submicron aerosol particles at the CVAO, was probably caused by sea spray and might be transferred up to cloud level. We showed that the neutral and hydrophobic amino acids were also present in all marine compartments, suggesting some interconnections. Stable amino acids like Gly are often reported as long-range tracers, but their abundance in seawater and the marine air masses prevailing during the sampling period suggest an (additional) oceanic source. The oceanic link is supported by a high atmospheric concentration of ocean-derived compounds (sodium, MSA), a high fractional residence time of the air masses above water and a low-to-medium impact of other non-marine sources (based e.g. on the mass concentration of trace metals). In addition, we could derive some indications for the biological production of amino acids on the aerosol particles (GABA), supporting the recent finding of a high active enzymatic activity on marine aerosol particles. We found that aromatic amino acids are either not transferred from the ocean into the atmosphere or react very quickly, in any case they are present in low concentrations close to the LOQ. By distinguishing between submicron and supermicron aerosol particles, differences in the chemical composition of these aerosol particle size classes could be identified, which show a much higher complexity of the FAA composition in the submicron aerosol particles. FAA were present in the size range for aerosol particles associated with CCN activity and cloud water, and might be connected to CCN activity due to their hygroscopicity and soluble character, but this effect was not investigated here.

Regarding the enrichment factor (see our answer to the comment R#2-1 b).

These aspects are summarized in the conclusions of the revised version: “In a simplified approach, considering only a possible transfer from the ocean onto the aerosol particles and cloud water (neglecting e.g. atmospheric processing), the aerosol enrichment factor was calculated. A high FAA enrichment in the submicron aerosol particles of  $EF_{\text{aer}(\Sigma\text{FAA})}: 2 \cdot 10^1 - 6 \cdot 10^3$  and a medium enrichment on supermicron aerosol particles  $EF_{\text{aer}(\Sigma\text{FAA})}: 1 \cdot 10^1 - 3 \cdot 10^1$  were observed. Applying the same concept to cloud water, an enrichment of  $4 \cdot 10^3 - 1 \cdot 10^4$  was obtained. The high FAA concentrations ( $11.2 - 489.9 \text{ ng m}^{-3}$ ) and enrichments in cloud water were reported here for the first time. Their composition, together with the high concentrations of inorganic marine tracers (sodium, MSA),

indicate at least to some extent an oceanic transfer and biogenic formation that remains subject to future work. Altogether, the varying composition of FAAs in the different matrices shows that their abundance and their enrichments in the SML and their atmospheric transfer are not determined by single environmental drivers (e.g. wind speed) and/or simple physico-chemical parameters (e.g. surface activity). The ocean-atmosphere transfer of FAAs is influenced by biotic and abiotic formation and degradation processes. Further studies are required to unravel their drivers and understand their complex composition that, finally, have to be considered in OM transfer models. To the best of our knowledge, this study was the first that simultaneously analyzed the FAA in all marine compartments - seawater including the ULW and the SML, size-segregated aerosol particles and cloud water – in such detail to obtain indications on their sources and interconnections.” (page 23, line 10-24).

Altogether, we believe that the results mentioned above provide new insight into the ocean-atmosphere system beyond an inventory of amino acids.

R#2-4) Introduction. page 3. line 22. 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 line 24. Although there are several studies in different marine regions, there is a lack of ambient measurements of FAA simultaneously in seawater and in size-segregated aerosol particles in the tropical Atlantic Ocean It would strengthen the justification for the work if it was stated why we must know this information specifically for the Atlantic Ocean and atmosphere.

As stated correctly by the reviewer, there are several studies of amino acids in marine samples. However, source attributions of amino acids are still not clear and might vary between different marine locations. In addition, there is mostly a lack of measurements that regard the abundance and molecular composition of amino acids simultaneously in marine compartments - in seawater and in the atmosphere – especially in the tropical Atlantic Ocean. Such studies are, however, crucial to learn more about sources and fate of the amino acids in the ambient marine environment. Besides, cloud water studies of amino acids are lacking. However, such studies are needed to investigate if these important compounds (see answer to the comment R#2-2) are transferred or maybe produced in marine clouds.

We referred to these points more clearly in the introduction and reads as follows (page 3, line 22-30): “Despite several studies of FAAs also conducted in the marine environment, there is still a huge uncertainty to the question whether FAAs are of marine origin or not. Matsumoto and Uematsu (2005) showed that the long-range transport of land-derived sources largely contributes to the amino acid concentration in the North Pacific. On the other hand, based on a positive correlation between amino acids in seawater and the atmosphere, Wedyan and Preston (2008) pointed out the particulate amino acids in the Southern Ocean to be of marine origin. These findings are likely due to regional varying source strengths, given different meteorological and biological conditions, which require further measurements in distinct marine regions necessary. Unfortunately, measurements are lacking that regard the abundance and molecular composition of amino acids in both seawater and size-segregated aerosol particles, especially in the tropical Atlantic Ocean.”

The region investigated here, the NATR region around the Cape Verde Islands (see R#2-5), is an interesting but rarely studied oligotrophic region. The region of study is of huge interest as it is home to a remote marine time-series observatory with low anthropogenic influences where particles during the campaign were predominantly of marine origin. Therefore, our studies provide a better understanding of the FAA in such a region on a molecular level, in order to be able to describe their sources and fate in the marine environment more precisely.

The main statements of this study concerning amino acids in the atmosphere in this marine region in view of the present state of knowledge and the new main findings of this study are summarized in more detail in answer R#2-8. For the general importance of the amino acids, please see our answer to the referee comment R#2-2.

R#2-5) There is little effort made to investigate the drivers of amino acids data for the ULW and SML. The data are not plotted against other measurements. We are merely offered (page 9, line 19): "On the basis of previous studies, the transportation and the releasing mechanisms seems to be most likely for the observed enrichment of FAA." At this point, we were not given a strong motivation for the measurements and we haven't learned anything from them. Then it is explained that the data are in agreement with other datasets and then this one dataset is extrapolated to the entire North Atlantic Ocean. I wouldn't extrapolate data from one location to the entire North Atlantic Ocean.

We agree that not sufficient effort was made to investigate the drivers of amino acids data for the ULW and SML and have consequently included correlations to environmental parameters in the revised version. However, correlations of the FAA data with either wind speed, chl-*a*, DOC or TDN could not explain the variance in FAA concentrations or enrichments. That was, however, in agreement to results of previous studies.

The transportation and releasing mechanisms is discussed in section 3.1. We found high enrichments of FAA in the SML that we considered interesting. The environmental parameters could not explain the observed FAA enrichment in the SML of neither the individual nor the amino acid groups. However, we could observe that the neutral amino acids in particular are more abundant than the hydrophilic or hydrophobic ones. This may be related to the fact that neutral amino acids are the main components of cell wall proteins and are directly released by cell lysis, as we concluded by comparing our findings to results from the literature.

The motivation for the measurements are summarized in the revised introduction, please see our answer to the referee comments R#2-2 and R#2-8.

Several changes according to these aspects were done in the revised manuscript. For a better visualization, we have included the temporal variation of the respective additional parameters (wind speed, chl-*a*, DOC and TDN) in Figure 1. The discussion of the correlations to environmental parameters was added and reads (page 10, line 12-14): "Nevertheless, the variance of the  $\sum$ FAA concentrations in the SML or ULW observed here could neither be explained by the variance of DOC or TDN values, nor by wind speed and chl-*a* concentrations (see Fig. 1, Table S2, S5), since no correlation between these parameters and the concentration or enrichment of FAA was found." For explanations of the observed enrichment of the FAA in the SML we want to refer to the referee comment R#2-2 point 5).

R#2-5\_1) Then it is explained that the data are in agreement with other datasets and then this one dataset is extrapolated to the entire North Atlantic Ocean. I wouldn't extrapolate data from one location to the entire North Atlantic Ocean.

We agree that we might not extrapolate the local data to the entire North Atlantic Ocean, as it appeared in the first version of the manuscript. In the revised version we have subdivided the marine regions in more detail according to Longhurst (2007). Thus, in the revised manuscript version we refer to the "North Atlantic Tropical Gyral Province (NATR)" region (introduced by Longhurst (2007)). This region is defined as follows in the manuscript (page 4, line 13-16): "In accordance with the classification of Longhurst (2007), the ocean around the Cape Verde Islands belongs to the region "North Atlantic Tropical Gyral Province (NATR)", which is described as the region with the lowest surface chlorophyll in the North Atlantic Ocean having a greater annual variability than seasonality."

We compared our measurements with previous own FAA measurements at the same location (data from 2013, shown here for the first time in Table S4) and the good agreement allowed us to conclude that FAA concentrations shown in this study can be considered as representative for the NATR region surrounding the Cape Verde Islands.

Moreover, we compared the FAA concentrations obtained here to published FAA data from the subtropical Atlantic Ocean the western Mediterranean Sea and concluded that "the FAA concentrations in the NATR region, with its very low surface chlorophyll and a greater annual

variability than seasonality, are in the same order of magnitude compared to other marine regions (i.e. subtropical Atlantic and western Mediterranean Sea (Reinthal et al., 2008)).” (page 11, line 5-7).

R#2-6) Similar to the seawater measurements, the atmospheric research would be stronger if it explored the drivers of the amino acid data. Particularly lacking from the aerosol work are aerosol sizing measurements. In their absence, we do not know if the variability in amino acid concentrations in the air are driven by changes in particle concentrations. Similarly, amino acid concentrations in the air could be related to wind direction.

Following the comment of the reviewer, and similar to the seawater results, we have tested to correlate the particulate FAA concentrations with wind speed, wind direction, chl-*a* data in seawater as well as the particulate mass concentrations of the aerosol particle samples to explain the variance of amino acid concentrations in the aerosol particle samples. However, statistically relevant correlations could not be found. In the manuscript the text now reads (page 12, line 10-12): “Correlations between the  $\Sigma$ FAA concentrations of the size-segregated aerosol particles (considered as submicron, supermicron and PM<sub>10</sub>) and the wind speed were not observed for here reported data (Fig. 2, Table S2).”

and on page 12, line 18/19: “No significant correlation could be observed between the  $\Sigma$ FAA concentration of size-segregated aerosol particle samples (submicron, supermicron and PM<sub>10</sub>) and the chl-*a* concentration in seawater.”

and on page 14, line 13-15: “However, the reasons for the high concentration of hydrophilic FAAs within these respective sampling days remain unclear, since no change in the environmental parameters determined (e.g. wind speed, wind direction, chl-*a* concentration, Fig. 2a) was observed.”

For a better visualization, we have included the temporal variation of the respective additional parameters (wind speed, wind direction and chl-*a*) in Figure 2.

Other:

R#2-7) Did particle type vary across the different aerosol sampling periods?

We have included the discussion of several meteorological parameters and back trajectories as well as particulate mass concentrations and included the new small chapter “*First indications of aerosol particle origin*”. From these discussed measurements we could not observe changes in the type of particles across the different aerosol sampling periods. In the revised manuscript it reads now as follows: “To obtain a first indication of the particle origin, that might help to explain the differences in the particle composition concerning amino acids, the particles were associated with the origin of the air masses and with marine and dust tracers. Overall, the CVAO station experienced north-easterly trade winds during this campaign, which are typical for this season within this region (Fomba et al., 2014; van Pinxteren et al., 2020). According to physical and chemical specifications such as the air mass origins, particulate MSA concentrations and MSA/sulfate ratios as well as particulate mass concentrations of dust tracers, aerosol particles predominantly of marine origin with low to medium dust influences were observed. It has to be noted that dust generally influences the supermicron particles to a larger extent than the submicron particles (Fomba et al., 2013). Further information on the classification of the air masses are given in the overview paper of this campaign (van Pinxteren et al., 2020).” (page 11, line 25-33)

R#2-8) If amino acids have already been measured in remote marine air/aerosol, how does the present manuscript advance our knowledge?

Although some studies on amino acids in marine aerosol particles have been published so far, the source of the amino acid as well as their transfer and fate is still not clear. Especially with regard to the connection between ocean and atmosphere, the gap in the simultaneous investigation of both marine compartments is problematic with regard to FAA. We have briefly summarized the current

state of knowledge on this subject in the revised introduction. This now reads as follows (page 3, line 21-30): “Although the study and characterization of amino acids are of paramount importance for atmospheric scientists, the true role and the fate of amino acids in the atmosphere are still poorly understood (Matos et al., 2016). Despite several studies of FAAs also conducted in the marine environment, there is still a huge uncertainty to the question whether FAAs are of marine origin or not. Matsumoto and Uematsu (2005) showed that the long-range transport of land-derived sources largely contributes to the amino acid concentration in the North Pacific. On the other hand, based on a positive correlation between amino acids in seawater and the atmosphere, Wedyan and Preston (2008) pointed out the particulate amino acids in the Southern Ocean to be of marine origin. These findings are likely due to regional varying source strengths, given different meteorological and biological conditions, which require further measurements in distinct marine regions necessary. Unfortunately, measurements are lacking that regard the abundance and molecular composition of amino acids in both seawater and size-segregated aerosol particles, especially in the tropical Atlantic Ocean.”

We wanted to investigate the already mentioned knowledge gap about the ocean-atmosphere relationship more closely through our methodological approach and the associated FAA analysis, and to introduce new aspects or support previous assumptions of other studies in this marine region as well. To this end, we have summarized the main objectives of our work in the revised introduction as follows (page 3, line 31 – page 4, line 5): “So, the aim of the present study is to investigate the occurrence of FAA in the marine environment regarding all important compartments; i.e. the ULW, the SML, the aerosol particles and finally cloud water in the remote tropical North Atlantic Ocean at the Cape Verde Atmospheric Observatory (CVAO). Their abundance, origin and possible transfer from the seawater as well as their transport within the atmosphere are studied in particular. Therefore, the FAA are measured on a molecular level and divided into hydrophilic (glutamic acid, aspartic, GABA), neutral (serine, glycine, threonine, proline, tyrosine) and hydrophobic compounds (alanine, valine, phenylalanine, isoleucine, leucine) according to their hydropathy index. Especially the similarities and differences between the amino acid composition in submicron (0.05-1.2  $\mu\text{m}$ ) and supermicron (1.2-10  $\mu\text{m}$ ) aerosol particles are elucidated. Finally, the potential of individual FAA as proxies or tracers for specific sources of aerosol particles and cloud water in the tropical marine environment is outlined.”

The main findings that are beyond the state of knowledge are summarized in the conclusion and have been outlined in our answer to the referee comment R#2-3.

### **Specific Comments**

R#2-9) Abstract. page 1. line 20. “The total concentration (PM10) was between 1.8–6.8  $\mu\text{g m}^{-3}$  and tended to increase during the campaign.” Perhaps instead of “during the campaign”, give the time period or relate to a potential/suspected driver of the observation.

Following the comment of the reviewer the added the time period of the campaign in the Abstract and it reads now (page 1, line 12-14): “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 were performed at the MarParCloud campaign at the Cape Verde islands in autumn 2017.”

### **Introduction.**

page 2.

R#2-10) lines 8-12. The marine nitrogen cycle is alluded to but vaguely. "(T)he bulk DON pool CAN BECOME bioavailable" or "IS bioavailable"? What is remineralized nitrogen? Perhaps get straight to proteniaceous compounds and amino acids as being large members of the DON pool.

Due to the revision of the introduction and also following the suggestions from the reviewer's, we focused on the FAA right from the beginning and therefore general parts (as the one mentioned by the reviewer) were deleted from the manuscript.

R#2-11)line 21. much more work has been done on amino acids as ice nucleating entities (and as antifreeze entities) than just Szyrmer and Zawadzki, 1997 and should be acknowledged because it gives importance to this work.

We agree with the comment of the reviewer. We have added more references in the reference to the INP ability of amino acids. It reads now (page2, line 27-30): "Due to their structure and hygroscopic properties, amino acids can act as both ice-forming particles (INP) (Wolber and Warren, 1989;Szyrmer and Zawadzki, 1997;Pandey et al., 2016;Kanji et al., 2017) as well as cloud condensation nuclei (CCN) (Kristensson et al., 2010) in the atmosphere when amino acids such as arginine and asparagine can exist as metastable droplets instead of solid particles at low relative humidity; this showed a laboratory study (Chan et al., 2005)."

R#2-12)line 23. "Amino acids are also present and have been described in the marine environment." This has already been established. The first 3 sentences of this paragraph feel like we are going backwards. In the previous paragraph we went from the ocean to the atmosphere and now we are back to describing amino acids in the ocean.

We agree with the comment of the reviewer and have removed the noted sentences in the course of restructuring the introduction. With the revised introduction, the focus should now be more clearly on amino acids and the structure of the introduction should also be more coherent with the revision (as outlined in the answer to the referee comment R#2-2).

R#2-13)line 28. (Engel et al., 2017) lacking other citations for the microlayer's importance in the ocean and sea spray aerosol.

Following the comment of the reviewer, we added other citations in this sentence. Now it reads (page 2, line 17-19): "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 aerosol particles within the marine environment (Cunliffe et al., 2013;Engel et al., 2017;Wurl et al., 2017)."

page 3.

R#2-14) line 7. "However, chl-a concentration solely does not adequately describe the complete spectrum of biological activity (Quinn et al., 2014)" should reference a paper on marine microbiology, like Azam and Malfatti. 2007. Microbial Structuring of Marine Ecosystems. DOI: 10.1038/nrmicro1747

We agree with the comment of the reviewer and have removed the noted sentences in the course of restructuring the introduction. With the revised introduction, the focus should now be more clearly on amino acids and the structure of the introduction should also be more coherent with the revision (as stated in the answer to the referee comment R#2-2).

page 4.

R#2-15) line 13. "During this campaign, concerted measurements were performed including sampling of sizesegregated aerosol particles at the CVAO and seawater sampling at the ocean site (16.53°N, 24.54°W). The location was carefully chosen with minimal influence of the island and located in wind direction to the CVAO" This second sentence is crucial to the rationale of the study and should be demonstrated. I'm surprised to not see a figure referenced here.

We agree with the comment of the reviewer and added a Figure S1 in the SI. Figure S1 shows an overview of the sampling locations MV, CVAO and seawater sampling site now and additionally the prevailing wind direction was added. In the manuscript, now it reads (page 4, line 13-19): “In accordance with the classification of Longhurst (2007), the ocean around the Cape Verde Islands belongs to the region “North Atlantic Tropical Gyral Province (NATR)”, which is described as the region with the lowest surface chlorophyll in the North Atlantic Ocean having a greater annual variability than seasonality. During this campaign, concerted measurements were performed including the sampling of size-segregated aerosol particles at the CVAO and seawater sampling at the ocean site (~16°53'17'N, ~24°54'25'E). The location was carefully chosen with minimal influence of the island and located in wind direction to the CVAO as shown in Fig. S1.”

In addition, we would like to point out that a general introduction to the campaign and the setting is given by the (now published) article by van Pinxteren et al., 2020 that we refereed to (for example: “van Pinxteren et al. (2020) provide further details on the MarParCloud campaign.”, page 4, line 20/21).

R#2-16) line 20. "The seawater samples were taken with a fishing boat, starting from Bahia das Gatas, São Vicente." A study site map with water and aerosol locations and winds during sampling periods would be good to "connect the dots". Figure S1 does not do this.

We agree with this comment and the previous comment (R#2-15) of the reviewer and added Fig. S1 as an overview of the sampling locations MV, CVAO and seawater sampling site in the SI.

page 6.

R#2-17) line 2. "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." So why not simply report them as L- and D-amino acids instead of reporting them as L-amino acids but acknowledging that is not accurate?

We thank the reviewer for this comment and have changed the sentence so that it now reads as follows: “Since no chiral column was used in the UHPLC separation, we cannot differentiate between L- and D- amino acids in our ambient samples” (page 6, line 15/16).

Furthermore, the following manuscript does not differentiate between D- and L-amino acids.

R#2-18) 2.2.4 Enrichment Factors

For calculating enrichment factors (EFs) between aerosol and the SML, I wonder if it would be more appropriate to first calculate the aerosol-ULW EF using equation 2 and then apply the SML-ULW EF (EF\_SML) from equation 1 for that analyte. So there would be EFs for aerosol relative to the underlying water and relative to the SML and they would differ by the EF\_SML (Eq.1). Ideally this would resolve the current inconsistency in invoking the Na<sup>+</sup> concentration of the SML when comparing to aerosol to SML (Eq. 2) but not when comparing SML to ULW. The way it stands now, if you calculate aerosol EFs relative to the ULW and the SML they won't differ by the EF\_SML and instead will differ by an EF\_SML calculated using equation 2.

As mentioned above (answer to the reviewer comment R#2-1b), we strongly revised the here applied concept of the calculation of the EF<sub>aer</sub> and pointed out the relating caveats. We used the EF<sub>aer</sub> for comparison purposes and in this regard, we included the EF<sub>aer</sub> based on ULW (besides the EF<sub>aer</sub> based on SML). The Na<sup>+</sup> concentration in the ULW and SML was very similar (12.45 g L<sup>-1</sup> in the ULW and 12.53 g L<sup>-1</sup> in the SML), therefore differences in the EF<sub>aer</sub> (related to the SML and to the ULW, respectively) are mainly due to the different concentrations, i.e. the high SML enrichments of the FAAs.



To calculate the  $EF_{\text{aer}}$  (Equation 2), we followed previous studies. In these studies, the enrichment of a substance was calculated by using on the aerosol particles the concentration of the substance in relation to the sodium concentration in relation to the substance concentration and sodium concentrations present in seawater. This was done, for example, under controlled conditions as described in Rastelli et al. (2017), but also in ambient studies such as Russell et al. (2010) and van Pinxteren et al. (2017).

page 10.

R#2-19) line 1. This sentence is confusing: "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." Is it DFAA in seawater accounting for ~12% of DOC (in seawater), and DFAA in SML accounting for ~30% of DON in the SML?

We agree with the reviewer and have reworded the sentence (page 11, line 17-19) as follows: "In the SML of the Atlantic Ocean and the western Mediterranean Sea, the DFAA contributed with ~12 % of the DOC and ~30 % of the dissolved organic nitrogen (DON) (Reinthaler et al., 2008)."

R#2-20) line 28. The characterization of FAA into the hydrophilic, hydrophobic, and neutral classes is nice. What might be the drivers and implications?

The FAA's division into hydrophilic, hydrophobic and neutral amino acid classes was used to ensure better comparability with previous studies. Often different analytical methods are used to study the FAA in different marine compartments, mostly seawater or aerosol particles, and often different individual FAA standards are used. In order to be able to make statements about the FAA with similar physico-chemical properties, the classification of the amino acids is based on the 'hydropathy index'. This classification was used, for example, in previous studies to classify the FAA results in the aerosol particles at the CVAO. This can be read as follows in the revised manuscript (page 14, line 21-27): "Following this hydropathy classification, the submicron aerosol particles consisted on average of 5 % hydrophobic, 15 % hydrophilic and 80 % neutral amino acids, while the supermicron aerosol particles contained on average only 7 % hydrophobic and 93 % neutral amino acids (Table S7). During the campaign, an increase in the contribution of hydrophilic amino acids was observed with a maximum of 55 % on 7/10/2017. Barbaro et al. (2015) reported that hydrophilic components were predominant (60 %) in locally produced marine Antarctic aerosol particles, whereas hydrophobic compounds were rather dominant in aerosol particles collected at the continental station (23 % and 27 %). According to the conclusions by Barbaro et al. (2015), the relatively high content of hydrophilic FAA found here points at least at some influence of local oceanic sources."

Moreover, the classification within this study was used to investigate the FAA composition in the different marine compartments (section 3.1, 3.2 and 3.3) and also to compare the compartments with each other. This is done after subdividing the amino acid classes in sections "3.4.1 Hydrophilic amino acids" and "3.4.2 Neutral and hydrophobic amino acids".

page 11

R#2-21) line 11. "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." If amino acids can indicate aerosol type or source, this should be central to this work, explained in the introduction, and examined for each sample. Also, how did the amino acid profiles of the different sample types (and individual samples) compare? Were the same relative abundances consistent across the ULW, SML, and different aerosol size classes? Are all the amino acids measured commonly found in the ocean and are they exclusive to the ocean?

There is still a high uncertainty about source attributions of FAA in the marine atmosphere. In the revised manuscript, we addressed this issue in several parts in the revised manuscript as outlined in the following. In the introduction we listed the results concerning the attribution of FAAs to distinct sources from other studies (detailed changes are shown in our response to comment R#2-8) and concluded: “Despite several studies of FAAs also conducted in the marine environment, there is still a huge uncertainty to the question whether FAAs are of marine origin or not. Matsumoto and Uematsu (2005) showed that the long-range transport of land-derived sources largely contributes to the amino acid concentration in the North Pacific. On the other hand, based on a positive correlation between amino acids in seawater and the atmosphere, Wedyan and Preston (2008) pointed out the particulate amino acids in the Southern Ocean to be of marine origin. These findings are likely due to regional varying source strengths, given different meteorological and biological conditions, which require further measurements in distinct marine regions necessary. Unfortunately, measurements are lacking that regard the abundance and molecular composition of amino acids in both seawater and size-segregated aerosol particles, especially in the tropical Atlantic Ocean.” (page 3, line 22-30)

In our work we performed a proper comparison of the FAA in the different matrices and concluded: “The high complexity of FAA observed in seawater was also found in the aerosol particles as well as in cloud water, and generally shows a high similarity between FAA in the different compartments. All marine compartments contained Gly, Ser, Glu and Ala as dominant species, i.e. representatives of the hydrophilic, neutral and hydrophobic groups. However, the percentage contribution of the individual FAAs to the  $\sum$ FAA varies within the different compartments.” (page 18, line 3-7)

The individual FAA are discussed in section 3.4.1, 3.4.2 and 3.4.3.

Important findings from our work show:

“Consequently, the usage of the major FAAs as chemical biomarkers seems to be restricted to some extent due to their lack of source-specificity” (page 14, line 9/10)

Still, we could conclude from our investigations that “...a certain FAA contribution, in particular the hydrophilic amino acids Asp and Glu in the submicron aerosol particles at the CVAO, was probably caused by sea spray and might be transferred up to cloud level. The neutral and hydrophobic amino acids were also present in all marine compartments, suggesting some interconnections. Stable amino acids like Gly are often reported as long-range tracers, but their abundance in seawater and marine air masses prevailing during the sampling period suggest an (additional) oceanic source.” (page 22, line 30-34)

This is in agreement with results from Barbaro et al. (2015). “Barbaro et al. (2015) reported that hydrophilic components were predominant (60 %) in locally produced marine Antarctic aerosol particles, whereas hydrophobic compounds were rather dominant aerosol particles collected at the continental station (23 % and 27 %). According to the conclusions by Barbaro et al. (2015), the relatively high content of hydrophilic FAA found here points at least at some influence of local oceanic sources.” (page 14, line 24-27)

Furthermore, we found “In addition, some indications for the biological production of amino acids on the aerosol particles (GABA) were observed, supporting the recent finding of a high active enzymatic activity on marine aerosol particles. Aromatic amino acids are either not transferred from the ocean into the atmosphere or react very quickly; in any case, they are present only in small concentrations close to the LOQ.” (page 23, line 3-6)

We think that the results summarized here, together with the reported high FAA concentrations in cloud water (see Comment R#2-27), are new and interesting and help to gain better insights into sources and transfer of FAA to the marine environment.

page 12

R#2-22) line 2. "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." Similar to previous comment. The different amino acid characterizations: hydrophathy index of Kyte & Doolittle 1982; Pommie et al. 2004; and Barbaro et al. 2005 should be explained early on and would add value to the present work.

Following the reviewers' suggestion, we have described the concept of the hydrophathy index already in the introduction. It reads now (page 3, line 14-18): "Grouping amino acids as regards their physico-chemical properties ('hydrophathy' index (Kyte and Doolittle, 1982)) allows different studies to better compare them what Pommie et al. (2004) suggested pursuant to the partition coefficient between water and ethanol. This divides them into hydrophilic, neutral and hydrophobic amino acids as discussed in Barbaro et al. (2015) for FAA in Antarctic aerosol particles."

And on page 3, line 34 – page 4, line 2: "Therefore, the FAA are measured on a molecular level and divided into hydrophilic (glutamic acid, aspartic, GABA), neutral (serine, glycine, threonine, proline, tyrosine) and hydrophobic compounds (alanine, valine, phenylalanine, isoleucine, leucine) according to their hydrophathy index."

Furthermore, this classification of amino acids, introduced in the introduction, is taken up in the discussions of the individual marine compartments (section 3.1, 3.2 and 3.3) and in the comparison of the marine compartments with regard to the FAA classifications (section 3.4.1, 3.4.2, 3.4.3).

R#2-23) line 5. "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)." It would be nice to lay this out because we make it this far into the manuscript wondering about the presence of aerosols from land in these samples. I would characterize the air masses early on. Do the back trajectories differ for the samples collected at 2 different elevations? And which back trajectories were used? Hysplit or Flexpart? Is this mentioned in the Experimental section?

We thank the Reviewer for his comments regarding the missing discussion of the aerosol particle origins and the air mass characterization in the manuscript.

Information about the calculation of the backward trajectories and the validity of those for both sampling stations (CVAO and MV) was added in the experimental part, section 2.2.2 (page 7, line 12-17) and it reads now: "Back trajectory analyses provided information regarding the origins of air masses. Seven-day back trajectories were calculated on an hourly basis within the sampling intervals, using the NOAA HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, <http://www.arl.noaa.gov/ready/hysplit4.html>, 26.11.16) in the ensemble mode at an arrival height of 500 m ± 200 m (van Pinxteren et al., 2010); van Pinxteren et al. (2020) provide more details. The calculated backward trajectories are representative for both aerosol particle sampling stations (CVAO and MV)."

Moreover, a short characterization of the air masses was added at the beginning of section 3.2.1, which reads now (page 11, line 24-33):

*"First indications of aerosol particle origin*

To obtain a first indication of the particle origin, that might help to explain the differences in the particle composition concerning amino acids, the particles were associated with the origin of the air masses and with marine and dust tracers. Overall, the CVAO station experienced north-easterly trade winds during this campaign, which are typical for this season within this region (Fomba et al., 2014; van Pinxteren et al., 2020). According to physical and chemical specifications such as the air mass origins, particulate MSA concentrations and MSA/sulfate ratios as well as particulate mass concentrations of dust tracers, aerosol particles predominantly of marine origin with low to medium dust influences were observed. It has to be noted that dust generally influences the supermicron particles to a larger extent than the submicron particles (Fomba et al., 2013). Further information on the classification of the air masses are given in the overview paper of this campaign (van Pinxteren et al., 2020)."

R#2-24) line 7. "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." Yes, that is good, and I would encourage the authors to leverage this resolution in their data. See previous comments regarding the comparison of amino acid "profiles" for different sample types and what do the presence of each amino acid tell us.

We thank the reviewer for this comment.

In the revised manuscript version, a clearer focus has been placed on the comparison of amino acid profiles (in terms of individual amino acids and amino acid groups). Above all, this comparison is made between the individual marine compartments in section 3.4.1, 3.4.2 and 3.4.3. After introduction of the individual compartments and their FAA specifications in the individual section 3.1 (seawater), 3.2 (aerosol particles) and 3.3 (cloud water). For detailed answers to the amino acid profiles, please refer to the comments R#2-2, R#2-20, R#2-21, R#2-22 and R#2-27.

R#2-25) line 10. "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." Please simplify this sentence.

During the revision of the manuscript, this reference to section 3.4 was removed.

R#2-26 )3.2.2 Size-segregated aerosol particles at the mountain station (MV) This section reports particulate matter (PM) masses for both the MV and CVAO stations. The Experimental section only reports particle volume measured for cloud water sampling at Mount Verde, and not at CVAO, with liquid water content (LWC) somehow derived. I am in favor of reporting what is measured directly. Here, is particle mass derived from the particle volume measurements or from the mass of filter samples (at CVAO) and cloud water (at MV) recovered? I assume there was a particle volume monitor at both CVAO and MV. I encourage plotting all particle volume data against other particle measurements like FAA. Does FAA abundance track particle volume?

We thank the reviewer for this comment. The measurement technique of the PM was added in the section 2.2.2 and it reads now (page 7, line 11-12): "The particulate mass (PM) of the aerosol particle samples was determined by weighing the filter before and after sampling (van Pinxteren et al., 2015)."

We have explicitly outlined all parameters that were measured in the aerosol particles at both, the CVAO and the MV (e.g. PM, WSOC, Na<sup>+</sup> and MSA) in the Table S11 in the SI and referred to this Table in the manuscript.

We also refer to the online particle size distributions (PSND), which were also taken at both sampling stations (CVAO and MV) during the campaign. In the revised manuscript it reads as follows (page 15, line 16-19): "Additional online measurements of particle size number distributions (PSND) at the CVAO and the MV, described in Gong et al. (2020) were in good agreement with one another during cloud-free times. This indicated that, for cloud-free conditions, the aerosol particles measured at ground level represented the aerosol particles at cloud level, i.e. the aerosol particles within the marine boundary layer were well mixed."

Moreover, in the manuscript, in section 3.2.2 we compared the chemical composition of the aerosol particles at the CVAO and at the MV. It reads now (page 15, line 23-32): "The particles at the MV exhibited lower particle masses, as well as lower concentrations of the aerosol particle constituents. The decrease in concentrations of  $\sum$ FAA, PM, sodium, MSA and WSOC was reduced by a factor of three to four regarding the submicron aerosol particles. However, no uniform depletion ratio between their concentration at the CVAO and the MV was found for the supermicron aerosol particles (Table S11). While the PM of the supermicron particles was reduced by a factor of four at the MV (similar to the submicron aerosol particles), sodium and WSOC were depleted more strongly (factor of 11-12) compared to their respective concentrations at the CVAO. This suggests

that the submicron particles were rather uniformly affected and depleted, likely by cloud processes, while the supermicron particles were influenced by clouds, and potentially other sources, in a non-uniform way. Nevertheless, the abundance of the marine tracers (sodium, MSA), together with the presence of FAA in the aerosol particles (which mainly had a similar composition compared to the oceanic and ground-based particulate FAA) indicated an oceanic contribution to the aerosol particles at cloud level.”

page 13

R#2-27) line 24. "In cloud water samples with  $\Sigma$ FAA  $<65 \text{ ng m}^{-3}$ , usually Gly was dominant followed by Ser. Cloud water samples with  $\Sigma$ FAA  $>290 \text{ ng m}^{-3}$  showed a higher complexity in the FAA composition, especially towards the end of the campaign, including the appearance of Asp." Did the relative abundances of the FAA vary, indicating different FAA profiles, or were they similar, indicating a consistent FAA profile? What was the profile of hydrophobic, hydrophilic, and neutral amino acids and how did that compare to the aerosol samples?

We thank the reviewer for this comment. Not only the FAA concentrations in cloud water varied during the campaign, but also the composition of these. Samples with a total FAA concentration of  $<65 \text{ ng m}^{-3}$  showed a low variance in composition, because Gly was dominant, followed by Ser. A higher complexity of the FAA composition could be found at FAA concentrations in cloud water with  $>290 \text{ ng m}^{-3}$ . Besides Gly and Ser, Ala and Asp played an important role and Thr, Leu and Ile also contributed to the FAA complexity. Thus, it is not possible to speak about a uniform FAA profile over the whole campaign, but a certain variance was observed.

Looking at the amino acid classes in the cloud water, it can be seen that the neutral FAA were dominant in the first part of the campaign (27/09/2017-05/10/2017) and towards the end of the campaign (06/10/2017-08/10/2017) the proportion of hydrophilic amino acids increased significantly. Similar to the observations in the submicron aerosol particles at CVAO. However, here above all GABA was higher concentrated FAA in submicron aerosol particles at the CVAO. But GABA, for example, was not detected in cloud water.

A detailed comparison of the individual amino acids/amino acid classes in the individual compartments, also with regard to aerosol particles and cloud water, can be found in sections 3.4.1, 3.4.2 and 3.4.3.

In order to clarify and discuss the composition of the individual amino acids and amino acid groups in the cloud water sample, Figure 3 was extended and the hydrophilic, neutral and hydrophobic amino acid groups were clearly pointed out. The variability of FAA composition in cloud water of the individual amino acids and amino acid classes were addressed as follows in the revised manuscript (page 16, line 16 – page 17, line 4): “In cloud water samples with  $\Sigma$ FAA  $<65 \text{ ng m}^{-3}$ , Gly was usually dominant, followed by Ser. However, cloud water samples with  $\Sigma$ FAA  $>290 \text{ ng m}^{-3}$  showed a higher complexity in FAA composition, including the concentrations of Asp and Ala. Other abundant FAA were Thr, Leu and Ile. In terms of the hydrophobicity classification, the first part of the campaign (27/09/2017-5/10/2017) was dominated by neutral FAAs, whereas a sudden increase of the hydrophilic FAAs was observed in its second part (06/10/2017-08/10/2017). Comparative studies on the FAA composition of cloud water in the marine environment are lacking, but especially in the second part of the campaign, it pointed to a local marine (biogenic) influence.”

R#2-28) Were the sodium, sulfate, and MSA measurements made on cloud water also made on the aerosol samples? Other than FAA (in section 3.4) which other data are common to the two sample types - aerosol and cloud water - that would allow us to compare them?

Sodium, sulfate and MSA measurements were made for both, cloud water and aerosol particle samples. The results of the measurements of inorganic ions in cloud water are listed in Table S12 and are discussed in sections 3.3 and 3.4. For aerosol particles at the CVAO, the results of inorganic ion measurements are listed in Table S8 and are discussed in section 3.2. For the comparison

between the aerosols of both stations (CVAO and MV) regarding inorganic ions and PM, the results are listed in Table S11 and are also discussed in section 3.2.

In the manuscript we addressed this topic in section 3.3. It reads now (page 16, line 9-13): “The inorganic marine tracers in cloud water ( $\text{Na}^+$ :  $5.7 \mu\text{g m}^{-3}$ , MSA:  $25.1 \text{ ng m}^{-3}$ , Table S12) were also present in higher concentrations compared to the aerosol particle samples at the CVAO (submicron:  $\text{Na}^+$ :  $72.3 \text{ ng m}^{-3}$ , MSA:  $6.0 \text{ ng m}^{-3}$ ) and the MV (submicron:  $\text{Na}^+$ :  $17.0 \text{ ng m}^{-3}$ , MSA:  $1.8 \text{ ng m}^{-3}$ , Table S11). The concentrations of cloud water sulfate (average:  $2.9 \mu\text{g m}^{-3}$ , Table S12) and sodium were higher than in cloud water samples, collected at East Peak in Puerto Rico, which can be seen in Gioda et al. (2009).”

and on page 17, line 9-12: “The presence of the marine tracers (sodium, MSA) in cloud water supports a coupling to oceanic sources. In addition, the majority of low-level clouds were formed over the ocean and ocean-derived components are expected to have some influence on cloud formation (van Pinxteren et al., 2020). Nevertheless, contributions from the desert and other non-marine sources cannot be excluded.”

And on page 2, line 2-3: “The abundance of inorganic marine tracers (sodium, methane-sulfonic acid) in cloud water suggests an influence of oceanic sources on marine clouds.”

R#2-29) page 15

line 10. "the reactivity/ mean life time \_ of the amino acids" Please explain.

A definition of the mean life time was added in the manuscript. Now it reads: “The mean life time  $\tau$  of the individual amino acids depends on the pH-dependent rate constant  $k$  and the OH radical concentration of the different atmospheric scenarios (SI, Eq. (3)).” (page 18, line 11-13)

Additionally in the SI (page 17) the equation for the calculation as well as a short discussion about the mean lifetime was added.

R#2-30) line 22. "The mean lifetime \_ of Glu (remote aerosol case: 0.02 d" Thats 29 minutes.

Is that considered long?

Comparing the mean lifetime  $\tau$  of the individual amino acids in the remote aerosol case (valid for conditions at the CVAO) listed in Table S13, it can be shown that amino acids with a mean lifetime  $\tau$  of 1.20 h (Ala) and 0.48 h (Gly, Glu) have a comparatively longest lifetime  $\tau$ . Whereas some amino acids have a much shorter mean lifetime with e.g. 0.007 h (Tyr) or 0.014 h (Phe). The estimation method for the mean lifetime is discussed in detail in the SI on page 17. Thus, it can be concluded that when comparing FAA under remote aerosol conditions, FAA with e.g. a mean lifetime of 0.48 h have a longer mean lifetime than most other FAA.

We have integrated the discussion of mean lifetime  $\tau$  into the discussion about Gly ( $\tau$ : 0.48 h), because Gly is often used as a long-range tracer with comparatively high stability (within the FAA). This can be read as follows in the revised manuscript (page 20, line 10-16): “Compared to other amino acids, Gly and Ser have a very low atmospheric reactivity (McGregor and Anastasio, 2001) and therefore a higher mean lifetime  $\tau$  (Gly: 0.48 h, Ser: 0.24 h; remote aerosol case, Table S13). Due to its atmospheric stability, Gly is proposed as an indicator for long-range transport (Barbaro et al. (2015) and references therein) and has a very low atmospheric reactivity (McGregor and Anastasio, 2001). However, our results clearly show that Gly and Ser are also present in seawater to a high extend, likely resulting from the siliceous exoskeleton of diatom cell walls (e.g. Hecky et al. (1973)). Hence, besides long-range transport, a transfer from the ocean via bubble bursting might be an additional likely source of the stable, long-lived FAA in the atmosphere.”

R#2-31) line 30. "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." Until the authors demonstrate that GABA cannot exist outside of a (marine) microorganism, this statement is unfounded. The opposite is a safe assumption: that any compound produced by marine microorganisms will also be found in the seawater, either by active release by the living microorganism

or via release of the dead microorganism (residence times will vary).

We have carefully revised the discussion on hydrophilic FAA, including GABA. Our interpretation approach is based on previous studies regarding GABA in the marine environment (Dauwe et al., 1999; Engel et al., 2018) as already introduced in the Introduction (page 3, line 13/14). They reported GABA as an indicator for microbiological OM degradation and GABA can therefore be considered as a microbiological proxy in aerosol particles in the marine environment. Thereby GABA can be actively released by microorganisms on the aerosol particles or passively, e.g. by the death of the microorganisms. Based on these previous studies, the finding that the air masses were mainly marine (indicating non-marine sources of minor importance) and the high GABA concentrations on the submicron aerosol particles at CVAO, we have addressed the discussion in the revised manuscript as follows (page 18, line 17-33): “A conspicuous finding is the high concentration of GABA, which is present exclusively in the submicron aerosol particles (B1 and B2: 0.05-0.42  $\mu\text{m}$ ) at the CVAO. Despite the relatively high LOQ of GABA in seawater (Table S1), a major abundance of GABA in seawater would be detectable. GABA is a metabolic product of the decarboxylation of Glu, which has been detected in all marine compartments. Furthermore, it can be produced by microorganisms (Dhakal et al., 2012) and is considered as an indicator for the microbiological decomposition of OM (Dauwe et al., 1999; Engel et al., 2018). The abundance of GABA on the submicron aerosol particles suggests that (marine) microorganisms were present on the aerosol particles and likely produced GABA via microbiological decarboxylation of Glu. Microbial processes on marine particles have recently been reported by Malfatti et al. (2019). The authors observed a diverse array of microbial enzymes transferred from the ocean into the atmosphere with an even higher activity on the particles compared to seawater. On this basis, they hypothesized that active enzymes can dynamically influence the composition of marine aerosol particles after ejecting from the ocean. The high GABA concentrations on the aerosol particles reported here are well in line with this hypothesis. Interestingly, GABA was not detected in cloud water samples, although bacteria were found during the campaign in cloud water (van Pinxteren et al., 2020) whose presence has been reported in the literature (Jardine, 2009; Vaitilingom et al., 2013; Jiaxian et al., 2019). It remains speculative whether GABA was degraded in cloud water despite its rather long lifetime (remote cloud case: 28.8 h, Table S13) or whether it was not produced by the bacteria in cloud water.”

R#2-32) page 17

line 2. "the presence of bacteria in cloud waters has been reported in the literature (Jiixian et al., 2019)." Microorganisms have been documented in the air since at least Darwin's HMS Beagle voyages so a few more citations here would be appropriate. A few of note:

Jardine, B. Between the Beagle and the barnacle: Darwin's microscopy, 1837-1854. *Stud. Hist. Philos. Sci. Part A* 40, 382–395 (2009).

Salisbury, J. H. On the Cause of Intermittent and Remittent Fevers. *Am. J. Med. Sci.* 51–75 (1866).

M. Vaitilingom et al., Potential impact of microbial activity on the oxidant capacity and organic carbon budget in clouds. *Proceedings of the National Academy of Sciences of the United States of America.* 110, 559–564 (2013).

Following the comment of the reviewer we included more citations regarding bacteria in cloud water as recommended. Now it reads (page 18, line 29-31): “Interestingly, GABA was not detected in cloud water samples, although bacteria were found during the campaign in cloud water (van Pinxteren et al., 2020) whose presence has been reported in the literature (Jardine, 2009; Vaitilingom et al., 2013; Jiixian et al., 2019).”

R#2-33) 3.4.2 Neutral and hydrophobic amino acids How do the surface activities vary across the different amino acids? Does abundance in aerosol correlate to surface activity? Or a combination of surface activity and reactivity/lifetime?

We thank the reviewer for his comment. To consider the surface activity of each individual amino acid, the  $K_{ow}$ , the TPSA and the density as listed in Table S9 were considered. These parameters were used to study the variation of the atmospheric FAA concentration on the aerosol particles. However, these simple physico-chemical parameters could not explain this variance by statistically relevant correlations.

In addition to the surface activity parameters, the mean lifetime  $\tau$  of the aerosol particles (Table S13) was also considered, as proposed, to study the variance of the FAA concentrations on the aerosol particles. However, no statistically relevant correlations were found here either. But for example, Gly, with a long mean lifetime  $\tau$ , occurs dominantly on the aerosol particles. Aromatic amino acids with a shorter mean lifetime  $\tau$ , were not found on the aerosol particles.

Therefore, neither the surface activity parameters nor the mean lifetime  $\tau$  of the individual amino acids are suitable to explain the variance of FAA concentrations on the aerosol particles in the marine region investigated here by statistically relevant correlations.

These points were addressed as follows in the revised manuscript (page 14, line 15-18): "In addition, we considered further FAA physico-chemical parameters such as the octanol-water partition coefficient ( $K_{ow}$ ), the topological polar surface area (TPSA), which describes the surface activity, and the density (Table S9) to describe the concentration changes. However, no statistically relevant correlations between the FAA concentration or composition and physico-chemical parameters were found here either."

page 18.

R#2-34) line 13. "a possible transport from other than marine sources is included in this parameter." The language is (not on purpose) vague and should clearly state that the waters measured and used for the enrichment factors have not been demonstrated to be the source of the aerosols measured.

As mentioned above (response to comment R#2-1b) we have carefully revised the discussion of the  $EF_{aer}$ , showed the uncertainties related to calculating the  $EF_{aer}$  in an open system.

R#2-35) line 16. "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."

Although not written altogether clearly, this statement seems to state that compound classes nor compounds have been resolved from ambient aerosol. This is false as there is a number of studies that have accomplished this. See:

Molecular diversity of sea spray aerosol particles: Impact of ocean biology on particle composition and hygroscopicity RE Cochran, O Laskina, JV Trueblood, AD Estillore, HS Morris, ... Chem 2 (5), 655-667

Quinn, P. K., Collins, D. B., Grassian, V. H., Prather, K. A., & Bates, T. S. (2015). Chemistry and Related Properties of Freshly Emitted Sea Spray Aerosol. Chemical Reviews. American Chemical Society. <https://doi.org/10.1021/cr500713g>

As part of the restructuring of the discussion part related to the  $EF_{aer}$  (review comment R#2-1b), section 3.4.4, this sentence was removed from the manuscript

R#2-36) Figure 5. Please include in the figure the size range for each Berner stage.

Following the comment of the reviewer we included in Figure 5 the size range of each Berner stage. Figure 5 can be found on page 21.

R#2-37) page 19.

line 7. "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)." This - the basics of sea spray aerosol formation - need to be brought up later and the investigation of hydrophilic/-phobic amino acids in different particle types needs to be established in this context.

We thank the reviewer for his comment. The current state of knowledge on primary marine aerosol formation by the bubble bursting process (incl. jet and film droplets) was briefly summarized in section 3.4.4, since this section deals with a possible transfer of FAA from the ocean into the atmosphere.

It should be noted that our ambient investigations cannot provide detailed mechanistic investigations of the bubble transfer. For this purpose, tank experiments under controlled conditions are necessary (that are currently performed in our group).

However, due to the FAA composition in the SML and on the submicron aerosol particles and the similar percentage contribution of FAA to DOC and WSOC in these two compartments, we suggested that film droplets contributed to the transfer of FAA.

The summary of the state of knowledge on primary marine aerosol formation via bubble bursting and the proposed interpretation of our observation is now included on page 22, line 10-19, and reads as follows in the revised manuscript: "Previous studies have shown that OM ejected into the atmosphere during bubble bursting, results in the formation of sea spray aerosol particles containing OM similar to SML (Russell et al. (2010); Cunliffe et al. (2013) and references therein). Especially the film droplets have been reported to be enriched in OM and are suggested to transfer OM from the SML onto submicron aerosol particles (Wilson et al., 2015). The supermicron aerosol particles tend to form from the larger jet droplets and thus represent the ULW composition (Blanchard, 1975; Wilson et al., 2015). We cannot derive mechanistic transfer characterizations from the ambient measurements performed here. Nevertheless, 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 jet drops (which transfer OM from the ULW) also have the potential to contribute significantly to the formation of submicron sea spray aerosol particles, so, jet droplets can also contribute to FAA formation."

R#2-38) line 29. "In situ-formation of FAA in cloud water, maybe due to biogenic formation or enzymatic degradation of proteins, selective enrichment processes as well as pH dependent chemical reactions might be potential sources." site Malfatti, F., Lee, C., Tinta, T., Pendergraft, M. A., Celussi, M., Zhou, Y., : : : Prather, K. A. (2019). Detection of Active Microbial Enzymes in Nascent Sea Spray Aerosol: Implications for Atmospheric Chemistry and Climate. *Environmental Science and Technology Letters*, 6(3), 171–177. <https://doi.org/10.1021/acs.estlett.8b00699>

We thank the reviewer for pointing out this interesting paper. In fact, the results, suggesting microbial activity on aerosol particles, shown by the transfer of enzymes, fits well with the observations made here and might explain the abundance of GABA on the aerosol particles. Please also note our reply to R#2-31.

We included this reference in the revised manuscript in the following context:

"The abundance of GABA on the submicron aerosol particles suggests that (marine) microorganisms were present on the aerosol particles and likely produced GABA via microbiological decarboxylation of Glu. Microbial processes on marine particles have recently been reported by Malfatti et al. (2019)." (page 18, line 23-25)

and "Altogether, the in-situ formation of FAA in cloud water by chemical processes in the cloud or by atmospheric biogenic formation or enzymatic degradation of proteins, as proposed by Malfatti et al. (2019), as well as by selective enrichment processes and pH dependent chemical reactions might be potential sources." (page 17, line 14-17)

## Technical Corrections

Introduction.

R#2-39) page 2. line 8. "surface global ocean" to "global surface ocean" line 16. "utilizable sources of nitrogen" to "utilizable FORMS of nitrogen"

Due to the revision of the Introduction and also following the suggestions from reviewer 2, we focused stronger on the FAA from the beginning and therefore general parts (as the one mentioned by the reviewer) were deleted from the manuscript.

On page 2, line 24-26 the suggested correction was implemented. Now it reads: "Despite their attribution to proteins the FAAs are better utilizable forms of nitrogen instead of proteins for an aquatic organism such as phytoplankton and bacteria (Antia et al., 1991;McGregor and Anastasio, 2001)."

R#2-40) page 3. line 31. "underline seawater" to "underlying seawater"

Following the commentary of reviewer 1 (R#1-4), we have used the abbreviations in the manuscript continuously after the introduction: This sentence (page 3, line 31-32) reads now: "So, the aim of the present study is to investigate the occurrence of FAA in the marine environment regarding all important compartments; i.e. the ULW, the SML, the aerosol particles and finally cloud water in the remote tropical North Atlantic Ocean at the Cape Verde Atmospheric Observatory (CVAO)."

R#2-41) page 4. line 4. "as proxies or tracer" to "as proxies or tracerS"

Following the comment of the reviewer we changed the sentence on page 4, line 4/5. And it reads now: "Finally, the potential of individual FAA as proxies or tracers for specific sources of aerosol particles and cloud water in the tropical marine environment is outlined."

R#2-42) In the Experimental section perhaps change "analytics" to "analyses"

We agree with the comment of the reviewer and changed in the experimental section "analytics" to analyses, e.g. page 5, line 25/26: "2.2 Analyses" and "2.2.1 Seawater analyses"; page 6, line 25 "2.2.2 Aerosol particle filter analyses" and page 7, line 19: "2.2.3 Cloud water analyses".

R#2-43) 2.2.1 Seawater sample analytics Was the standard addition method applied to samples to assess for recovery efficiency of the entire process?

The standard addition method was also used to evaluate the recovery efficiency in the development of desalination methods and analytical measurement methods. The recovery efficiency stated here is based on the fact that a defined concentration of amino acids was added to a seawater sample prepared from milli-Q water using sea salt standard (Sigma-Aldrich, Germany) and this sample was treated using the same procedure as the real seawater samples. The FAA concentration in the seawater sample was then determined after sample preparation. To consider the recovery efficiency, the percentage of the measured concentrations to the added FAA concentration was calculated. The recovery rate thus determined is consistent with tests using standard addition methods and proved to be less complex and more practical.

R#2-44) page 6. line 23. "All here presented values" to "All values presented here" line 29.

Following the comment of the reviewer we changed the sentence on page 7, line 4 to "All values presented here for aerosol particle samples are field blank corrected."

R#2-45) "The cloud water samples were operated the same as seawater samples". change "operated" to "handled" or "processed".

We agree with the reviewer's comment and changed the sentence on page 7, line 20/21 to “The cloud water samples were processed the same as seawater samples for the analysis of DOC/TDN and inorganic ions (section 2.2.1).”

R#2-46) line 31. "syringe filters filters" to "syringe filters" or "syringe tip filters"

We agree with the reviewer's comment and changed the sentence to “After the filtration with 0.2  $\mu\text{m}$  syringe filters (Acrodisc-GHP; 25 mm, Pall Corporation, New York, USA), an aliquot of the prepared cloud water was derivatized based on the AccQ-Tag™ precolumn derivatization method (Waters, Eschborn, Germany).” (page 7, line 22-24)

R#2-47) page 10. line 12. Remove "It is obvious that" as it is confusing language.

Following the comment of the reviewer we removed “it is obvious that”. Now it reads (page 12, line 4-7): “Whilst the concentration  $\Sigma\text{FAA}$  varied between 0.2  $\text{ng m}^{-3}$  (6/10/2017) and 1.4  $\text{ng m}^{-3}$  (22/09/2017) in the supermicron size range, the highest atmospheric concentrations of  $\Sigma\text{FAA}$  were found in the submicron aerosol particles (mean of 3.2  $\text{ng m}^{-3}$ ) compared to the supermicron ones (mean of 0.6  $\text{ng m}^{-3}$ ).”

R#2-48) line 14-15.

Reword. Use "neither" instead of "both".

Following the comment of the reviewer we changed “both” to “neither”. Now it reads (page 12, line 33/34): “ $\Sigma\text{FAA}$  included all investigated amino acids (listed in 2.2.1) except for Met and Gln, analytes which were neither detected in the size-segregated aerosol particle samples.”

R#2-49) page 12 line 32. "aerosol particles" is redundant. aerosols are particles. say just "aerosol" or "particle", here and elsewhere.

Since the term "aerosol" refers to the entirety of a gas with the particles suspended in it, we would prefer to use the term "aerosol particles" in the manuscript and in the SI. The term “aerosol particle” is also common in other publications, for example (Cochran et al., 2017; Forestieri et al., 2016; Frossard et al., 2019; Koulouri et al., 2008).

R#2-50) page 17. line 7. "Neutral amino acids" to "acids"

We changed the typo. Now it reads (page 20, line 8/9): “Neutral amino acids were generally the amino acid group with the highest concentration in all investigated marine compartments, accounting for more than 50% of the FAA total (Fig. 4a-d).”

R#2-51) line 10. "A further explanation approach" remove "approach"

Following the comment of the reviewer we restructured the sentence. Now it reads (page 20, line 15/16): “Hence, besides long-range transport, a transfer from the ocean via bubble bursting might be an additional likely source of the stable, long-lived FAA in the atmosphere.”

### **Additional changes performed by the authors**

When discussing the mean lifetime  $\tau$  of individual amino acids (section 3.4 and Table S13), the unit of  $\tau$  was changed from days (d) to hours (h).

The acknowledgement was also revised to thank the people from the OSCM. The added sentence is now as follows: “We further acknowledge the professional support provided by the Ocean Science Centre Mindelo (OSCM) and the Instituto do Mar (IMar)” (page 23, line 25-26)

The measured data were published on PANGAEA. The data availability statement was therefore updated and reads as follows: “Data availability. The data are available through the World Data Centre PANGAEA under the following link: <https://doi.pangaea.de/10.1594/PANGAEA.914220>.” (page 23, line 14/15)

The previous citation of van Pinxteren (submitted 2019) was updated to van Pinxteren et al. (2020) in the revised manuscript and supporting information.

## References

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.

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.

Cochran, R. E., Laskina, O., Trueblood, J. V., Estillore, A. D., Morris, H. S., Jayarathne, T., Sultana, C. M., Lee, C., Lin, P., Laskin, J., Laskin, A., Dowling, J. A., Qin, Z., Cappa, C. D., Bertram, T. H., Tivanski, A. V., Stone, E. A., Prather, K. A., and Grassian, V. H.: Molecular Diversity of Sea Spray Aerosol Particles: Impact of Ocean Biology on Particle Composition and Hygroscopicity, *Chem*, 2, 655-667, <https://doi.org/10.1016/j.chempr.2017.03.007>, 2017.

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.

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.

Forestieri, S. D., Cornwell, G. C., Helgestad, T. M., Moore, K. A., Lee, C., Novak, G. A., Sultana, C. M., Wang, X., Bertram, T. H., Prather, K. A., and Cappa, C. D.: Linking variations in sea spray aerosol particle hygroscopicity to composition during two microcosm experiments, *Atmos. Chem. Phys.*, 16, 9003-9018, 10.5194/acp-16-9003-2016, 2016.

Frossard, A. A., Gérard, V., Duplessis, P., Kinsey, J. D., Lu, X., Zhu, Y., Bisgrove, J., Maben, J. R., Long, M. S., Chang, R. Y. W., Beaupré, S. R., Kieber, D. J., Keene, W. C., Nozière, B., and Cohen, R. C.: Properties of Seawater Surfactants Associated with Primary Marine Aerosol Particles Produced by Bursting Bubbles at a Model Air–Sea Interface, *Environ. Sci. Technol.*, 53, 9407-9417, 10.1021/acs.est.9b02637, 2019.

Haan, D. O. D., Corrigan, A. L., Smith, K. W., Stroik, D. R., Turley, J. J., Lee, F. E., Tolbert, M. A., Jimenez, J. L., Cordova, K. E., and Ferrell, G. R.: Secondary Organic Aerosol-Forming Reactions of Glyoxal with Amino Acids, *Environ. Sci. Technol.*, 43, 2818-2824, 10.1021/es803534f, 2009.

Jaber, S., Joly, M., Brissy, M., Lereboure, M., Khaled, A., Ervens, B., and Delort, A. M.: Biotic and abiotic transformation of amino acids in cloud water: Experimental studies and atmospheric implications, *Biogeosciences Discuss.*, 2020, 1-27, 10.5194/bg-2020-250, 2020.

Kanji, Z. A., Ladino, L. A., Wex, H., Boose, Y., Burkert-Kohn, M., Cziczo, D. J., and Krämer, M.: Overview of Ice Nucleating Particles, *Meteorological Monographs*, 58, 1.1-1.33, 10.1175/amsmonographs-d-16-0006.1, 2017.

Koulouri, E., Saarikoski, S., Theodosi, C., Markaki, Z., Gerasopoulos, E., Kouvarakis, G., Mäkelä, T., Hillamo, R., and Mihalopoulos, N.: Chemical composition and sources of fine and coarse aerosol particles in the Eastern Mediterranean, *Atmos. Environ.*, 42, 6542-6550, <https://doi.org/10.1016/j.atmosenv.2008.04.010>, 2008.

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.

Longhurst, A. R.: Chapter 9 - THE ATLANTIC OCEAN, in: *Ecological Geography of the Sea (Second Edition)*, edited by: Longhurst, A. R., Academic Press, Burlington, 131-273, 2007.

Pandey, R., Usui, K., Livingstone, R. A., Fischer, S. A., Pfaendtner, J., Backus, E. H. G., Nagata, Y., Fröhlich-Nowoisky, J., Schmäser, L., Mauri, S., Scheel, J. F., Knopf, D. A., Pöschl, U., Bonn, M., and Weidner, T.: Ice-nucleating bacteria control the order and dynamics of interfacial water, *Science Advances*, 2, e1501630, 10.1126/sciadv.1501630, 2016.

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.

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.

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.

van Pinxteren, M., Barthel, S., Fomba, K. W., Müller, K., von Tümpling, 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.

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., 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 and overview to the MarParCloud campaign, *Atmos. Chem. Phys.*, 20, 6921-6951, 10.5194/acp-20-6921-2020, 2020.

van Pinxteren, M. F., K. W.; Triesch, N.; Stolle, C.; Wurl, O.; Bahlmann E.; Gong, X.; Voigtländer J.; Wex, H.; Robinson, B.; Barthel, S.; Zeppenfeld, S.; Hoffmann, E. H.; Roveretto, M.; Li, C.; Grosselin, B.; Daele, V.; Senf, F.; van Pinxteren, D.; Manzi, M.; Zabalegui, N.; Frka, S.; Gašparović, B.; Pereira, R.; Li, T.; Xue, L.; Wen, L.; Wang, X.; Wang, W.; Li, J.; Chen, J.; Zhu, C.; Chen, H.; Chen, J.; Fiedler, B.; von Tümpling, W.; Read, K. A.; Punjabi, S.; 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.; Herrmann, H.: Marine organic matter in the remote environment of the Cape Verde Islands - An introduction and overview to the MarParCloud campaign, *Atmos. Chem. Phys.*, submitted 2019.

Wolber, P., and Warren, G.: Bacterial-ice-nucleation proteins, *Trends in Biochemical Sciences*, 14, 179-182, 10.1016/0968-0004(89)90270-3, 1989.

# 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<sup>1</sup>, Manuela van Pinxteren<sup>1</sup>, Anja Engel<sup>2</sup> and Hartmut Herrmann<sup>1</sup>

<sup>1</sup>Leibniz-Institute for Tropospheric Research (TROPOS), Atmospheric Chemistry Department (ACD), Leipzig 04318, Germany

<sup>2</sup>GEOMAR Helmholtz Centre for Ocean Research, Kiel 24105, Germany

10 Correspondence to: Hartmut Herrmann ([herrmann@tropos.de](mailto:herrmann@tropos.de))

## Abstract.

~~This study presents measurements~~ 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. ~~were performed at the MarParCloud campaign at the Cape Verde islands in autumn 2017. According to physical and chemical specifications such as the behaviour of air masses, particulate MSA concentrations and MSA/sulfate ratios as well as particulate mass concentrations of dust tracers, aerosol particles predominantly of marine origin with low to medium dust influences were observed.~~ FAA were investigated in ~~different compartments: they were examined in two types of seawater (underlying water (ULW)) and in the sea surface microlayer (SML))~~ as well as in ambient marine size-segregated aerosol particle samples at two heights (ground based at the Cape Verde Atmospheric Observatory (CVAO) and at 744 m height at the Mt. Verde, ~~744 m height~~) and in cloud water using concerted measurements. The  $\Sigma$ FAA concentration in the SML varied between 0.13-3.64  $\mu\text{mol L}^{-1}$ , ~~in the ULW whereas it was~~ between 0.01-1.10  $\mu\text{mol L}^{-1}$  ~~and in the ULW; also,~~ a strong enrichment of  $\Sigma$ FAA ~~in the SML~~ ( $EF_{\text{SML}}$ : 1.1-298.4, average of 57.2) was ~~observed found in the SML~~. In the submicron (0.05-1.2  $\mu\text{m}$ ) aerosol particles at the CVAO, the composition of ~~FAA~~ FAAs was more complex and higher atmospheric ~~eonecentration~~ concentrations of  $\Sigma$ FAA (up to 6.3  $\text{ng m}^{-3}$ ) compared to the supermicron (1.2-10  $\mu\text{m}$ ) aerosol particles (maxima of 0.5  $\text{ng m}^{-3}$ ) were observed. The total  $\Sigma$ FAA concentration ( $\text{PM}_{10}$ ) was between 1.8-6.8  $\text{ng m}^{-3}$  and tended to increase during the campaign. Averaged  $\Sigma$ FAA concentrations on the aerosol particles at the Mt. Verde were lower (submicron: 1.5  $\text{ng m}^{-3}$ , supermicron: 1.2  $\text{ng m}^{-3}$ ) compared to the CVAO. A similar percentage contribution of  $\Sigma$ 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 aerosol particles ( $EF_{\text{aer}(\Sigma\text{FAA})}$ :  $4 \cdot 10^3$ - $3 \cdot 10^4$ ,  $EF_{\text{aer}(\text{WSOC})}$ :  $2 \cdot 10^3$ - $1 \cdot 10^4$ ), possibly resulting from film droplet formation. The enrichment in supermicron aerosol particles was several orders of magnitude lower compared to submicron size range with  $EF_{\text{aer}(\Sigma\text{FAA})}$ :  $1 \cdot 10^3$ - $2 \cdot 10^3$ ,  $EF_{\text{aer}(\text{WSOC})}$ :  $3 \cdot 10^2$ - $4 \cdot 10^2$ . A case study showed that several amino acids were transported from the ocean up to cloud level (e.g. aspartic acid, glutamic acid, proline)~~

Formatted: English (United Kingdom)

Formatted: English (United Kingdom)

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  $\Sigma$ FAA during the campaign (11.2-489.9 ng m<sup>-3</sup>). FAA in cloud water samples showed a strong enrichment by a factor of  $4 \cdot 10^3$  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. Considering solely ocean-atmosphere transfer and neglecting atmospheric processing, high FAA enrichment factors were found in both aerosol particles in the submicron range ( $EF_{aer(\Sigma FAA)}: 2 \cdot 10^3$ - $6 \cdot 10^3$ ) and medium enrichment factors in the supermicron range ( $EF_{aer(\Sigma FAA)}: 1 \cdot 10^1$ - $3 \cdot 10^1$ ). In addition, indications for a biogenic FAA formation were observed, that might be related to recently reported high biological enzymatic activity on aerosol particles. One striking finding was furthermore the high and varying FAA cloud water concentration (11.2-489.9 ng m<sup>-3</sup>) as well as enrichments ( $EF_{CW}: 4 \cdot 10^3$  and  $1 \cdot 10^4$  compared to the SML and ULW, respectively), which were reported here for the first time. The abundance of inorganic marine tracers (sodium, methane-sulfonic acid) in cloud water suggests an influence of oceanic sources on marine clouds. Finally, the varying composition of the FAA in the different matrices shows that their abundance and ocean-atmosphere transfer are influenced by additional biotic and abiotic formation and degradation processes. Simple physico-chemical parameters (e.g. surface activity) are not sufficient to describe the concentration and enrichments of the FAA in the marine environment. For a precise representation in organic matter (OM) transfer models, further studies are needed to unravel their drivers and understand their composition.

## Keywords

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 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 amino acids, either free (FAA) or in combined form (CAA), contribute to the global nitrogen and carbon cycle and to the atmosphere-biosphere nutrient cycle (Zhang and Anastasio, 2003; Wedyan and Preston, 2008). They are produced in the ocean and are reported to be ~~sum parameter 'proteins'~~ using an analytical staining method with Coomassie blue developed by Bradford (1976) and often applied in previous studies

~~(Gutiérrez-Castillo 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, 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). 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 aerosol particles within the marine environment (Cunliffe et al., 2013; Engel et al., 2017; Wurl et al., 2017). Specific organic groups of compounds, including nitrogenous OM (Engel and Galgani, 2016) can be strongly enriched in the SML. From the ocean, amino acids as part of the class of proteinaceous compounds can be transferred into the atmosphere via bubble bursting (Kuznetsova et al., 2005; Rastelli et al., 2017). These proteinaceous compounds are often analyzed as sum parameter 'proteins' using an analytical staining method with Coomassie blue developed by Bradford (1976) and often applied in previous studies (Gutiérrez-Castillo et al., 2005; Mandalakis et al., 2011; Rastelli et al., 2017). Despite their attribution to proteins the FAAs are better utilizable forms of nitrogen instead of proteins for an aquatic organism such as phytoplankton and bacteria (Antia et al., 1991; McGregor and Anastasio, 2001), compounds from the SML. It was shown that especially FAA exhibit a high enrichment in the SML ( $EF_{SML}$ ), e.g. in the subtropical Atlantic ( $EF_{SML(FAA)}: 7.6-229.4$ , average of  $59.3 \pm 68.8$ ) and in the western Mediterranean Sea ( $EF_{SML(FAA)}: 6.2-26.1$ , average of  $16.5 \pm 9.1$ ) (Reinthaler et al., 2008). Moreover, correlations between individual amino acids and (micro)biological lifeforms in the marine environment were observed. Due to their structure and hygroscopic properties, amino acids can act as both ice-forming particles (INP) (Wolber and Warren, 1989; Szyrmer and Zawadzki, 1997; Pandey et al., 2016; Kanji et al., 2017) as well as cloud condensation nuclei (CCN) (Kristensson et al., 2010) in the atmosphere when amino acids such as arginine and asparagine can exist as metastable droplets instead of solid particles at low relative humidity; this showed a laboratory study (Chan et al., 2005). In general, previous studies have shown that amino acids in aerosol particles can have both natural and anthropogenic sources. Having being detected in volcanic emissions (Scalabrin et al., 2012) and during biomass burning events (Chan et al., 2005; Feltracco et al., 2019), amino acids can be produced by plants, pollens, fungi, bacterial spores and algae (Milne and Zika, 1993; Zhang and Anastasio, 2003; Matos et al., 2016). Nevertheless, they are useful indicators for aerosol particle age and origin (Barbaro et al., 2011; Matsumoto and Uematsu, 2005; Scalabrin et al., 2012). Based on a cluster and factor analysis, Scalabrin et al. (2012)~~



suggested two possible sources for the amino acids in the ultrafine Arctic aerosol particles. First, the authors mentioned the regional development (isoleucine, leucine, threonine) and long-range transport (glycine) of amino acids from marine areas; secondly, the influence of local sources such as of marine primary production (proline, valine, serine, tyrosine, glutamic acid). A different approach of Mashayekhy Rad et al. (2019) investigated the atmospheric proteinogenic aerosol particles in the Arctic and attributed them to different sources based among others on the reactivity of the distinct amino acids. The authors differentiated here between long-range transport (glycine), terrestrial and marine aerosol particles (proline, valine, serine, tyrosine) and coastal and marine phytoplankton and bacteria (isoleucine, leucine and threonine) as important sources for amino acids (Mashayekhy Rad et al., 2019). In fact, previous studies have assigned individual amino acids to specific marine biogenic sources and used them as biomarkers. Hammer and Kattner (1986) reported correlations between aspartic acid and diatoms and zooplankton in seawater. GABA ( $\gamma$ -aminobutyric acid) is was referred to as an indicator for the microbiological decomposition of organic matter OM (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 and is probably used as a microbiological proxy in aerosol particles. Grouping amino acids as regards their physico-chemical properties ('hydropathy' index (Kyte and Doolittle, 1982)) allows different studies to better compare them what Pommié et al. (2004) suggested pursuant to the partition coefficient between water and ethanol. This divides them into hydrophilic, neutral and hydrophobic amino acids as discussed in Barbaro et al. (2015) for FAA in Antarctic aerosol particles. They also observed that hydrophilic FAA in the Antarctic were predominant in locally produced marine aerosol particles, while hydrophobic amino acids prevailed in aerosol particles collected at the continental station, via bubble bursting (Kuznetsova et al., 2005; Rastelli et al., 2017). 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. Although the study and characterization of amino acids are of paramount importance for atmospheric scientists, the true role and the fate of amino acids in the atmosphere are still poorly understood (Gantt Matos et al., 2011; Rinaldi et al., 2013, 2016). 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. Despite several studies of FAAs also conducted in the marine environment, there is still a huge uncertainty to the question whether FAAs are of marine origin or not. Matsumoto and Uematsu (2005) showed that the long-range transport of land-derived sources largely contributes to the amino acid concentration in the North Pacific. On the other hand, based on a positive correlation between amino acids in seawater and the atmosphere, (van Pinxteren et al., 2017) Wedyan and Preston (2008). Moreover, pointed out the particulate amino acids in the Southern Ocean to be of marine origin. These findings are likely due to regional varying source strengths, given different groups of OM, such as lipids, carbohydrates meteorological 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

Formatted: English (United States)

Formatted: Font color: Red, English (United States)

characteristics and the surface adsorption behaviour. To apply and biological conditions, which require further develop such parameterizations, distinct measurements of these organic compound groups, such as amino acids in different oceanic in distinct marine regions are urgently needed.

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 necessary. Unfortunately, measurements are lacking that regard the abundance and molecular composition of amino acids simultaneously in marine compartments—in the both 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 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 ( $>1 \mu\text{m}$ ) and fine mode aerosol ( $<1 \mu\text{m}$ ), 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 lack of ambient measurements of FAA simultaneously in seawater and in size-segregated aerosol particles in, especially in the tropical Atlantic Ocean.

The aim of the present study is to investigate the occurrence of FAA in the marine environment regarding all important compartments; i.e. the ULW, the SML, the aerosol particles and finally cloud water 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 as well as their transport within the atmosphere is investigated and studied in particular. Therefore, the FAA are measured on a molecular level and divided into hydrophilic (glutamic acid, aspartic, GABA), neutral (serine, glycine, threonine, proline, tyrosine) and hydrophobic compounds (alanine, valine, phenylalanine, isoleucine, leucine) according to their hydropathy index. Especially the similarities and differences between the amino acid composition in the submicron (0.05-1.2  $\mu\text{m}$ ) and the supermicron (1.2-10  $\mu\text{m}$ ) 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 tracers for specific sources of aerosol particles and cloud water shall be elucidated in the tropical marine environment is outlined.

## 2. Experimental

### 2.1 Study area

Formatted: English (United Kingdom)

Formatted: English (United Kingdom)

~~In~~Within 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 was performed at the Cape Verde Atmospheric Observatory (CVAO) from 13 September to 13 October 2017 ~~was performed. The CVAO, a. This~~ remote marine station, is located ~~at~~on the northeast coast of the island of São Vicente island, directly at the ocean (16°51'49"N 51' 49" N, 24°52'02"W) and is described ~~more detailed in~~52'02'E) which ~~Fomba et al. (2014); Carpenter et al. (2010). During this campaign, concerted measurements were performed including and Fomba et al. (2014) described in more detail. In accordance with the classification of Longhurst (2007), the ocean around the Cape Verde Islands belongs to the region "North Atlantic Tropical Gyral Province (NATR)", which is described as the region with the lowest surface chlorophyll in the North Atlantic Ocean having a greater annual variability than seasonality. During this campaign, concerted measurements were performed including the~~ sampling of size-segregated aerosol particles at the CVAO and seawater sampling at the ocean site (~16°53'30"N 53' 17" N, ~24°54'00"W 54' 25' E). The location was carefully chosen with minimal influence of the island and located in wind direction to the CVAO. ~~Additionally as shown in Fig. S1. Here,~~ aerosol particle sampler and cloud water sampler were installed at the mountain station on the top of the mountain Mt. 'Monte Verde' (MV). Further, 16°52' 11" N, 24°56'02' W. ~~van Pinxteren et al. (2020) provide 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~~from a fishing boat, starting from Bahia das Gatas, São Vicente. A glass plate with a sampling area of 2000 cm<sup>2</sup> was vertically immersed into the seawater and then slowly drawn upwards to sampletake the SML. The surface films adhered to the surface of the glass plate and were removed with Teflon wipers directly ~~in~~into 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 the seawater sampling were pre-cleaned usingwith a 10 % HCl solution and high purity water.

### 2.1.2 Aerosol particles sampling

~~The sampling of the size~~Size-segregated aerosol partiele samples ~~was performed~~particles were sampled using five stage Berner-type impactors (Hauke, Gmunden, Austria) at the top of a 30 m sampling tower at the CVAO ~~and~~since this location best represents the conditions above the ocean pursuant to previous studies. The internal boundary layer (IBL), which can form when air passes a surface with changing roughness (i.e. the transfer from open water to island) is mainly beneath 30 m (Niedermeier et al., 2014). Moreover, aerosol particles were sampled on the top of the mountain "Monte Verde" Mt. MV (744 m a.s.l.) using five stage Berner-type impactors (Hauke, Gmunden, Austria). To avoid the condensation of atmospheric water on the aerosol particle sampling substrate, a conditioning unit consisting of a 3 m long tube was installed between the impactor

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: English (United States)

inlet and the sampling unit. By heating the sampled air, the high relative humidity of the ambient air before collecting the aerosol particles was reduced to 75-80%. The temperature difference between the ambient air at the impactor inlet and the sampled air after the conditioning unit was below 9 K (van Pinxteren et al., 2020). The Berner impactors were operated with a flow rate of 75 L min<sup>-1</sup> for 24 h and pre-baked aluminium foils (350°C for two hours) were used ~~for~~as 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~~When it comes to the segregated aerosol particle samples, our study, the size segregated aerosol particle samples were distinguished in the differentiates between the ones of submicron size range (B1, B2, B3), the ones of supermicron size range (B4, B5) and ~~in~~as well as the ones of PM<sub>10</sub> (B1-5) aerosol particle samples. After the sampling, the aluminium foils were stored in aluminium boxes and stored at -20 °C until the time of analysis. It needs to be pointed out that the Berner impactors ran continuously, thus the impactor on the MV sampled aerosol particles also during cloud events. However, due to the pre-conditioning unit, the cloud droplets were efficiently removed before the aerosol particles were collected on the aluminium foils.▲

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: Not Bold, English (United Kingdom)

Formatted: Normal

### 2.1.3 Cloud water sampling

ForAt the sampling of cloud waterMV station, 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) to sample cloud water. During a 'cloud event' the bottles were changed every 2-3 h, whereas on the other days the sampling time was e.g. overnight (every 12 h). For each sampling, the used Teflon rods were pre-cleaned usingwith a 10 % HCl solution followed by high purity water. The liquid water content (LWC) of the cloud werewas measured continuously by a particle volume monitor (PVM-100, Gerber Scientific, USA). TheFinally, the collected cloud water was sampled in pre-cleaned plastic bottles and stored at -20 °C until the time of analysis.

## 2.2 Analyties

### 2.2 Analyses

#### 2.2.1 Seawater samples analytiesanalyses

For the DOC/TDN content and the analysis of inorganic ions, the seawater samples were first filtered first (0.45 µm syringe filter) and then quantified usingwith a TOC-VCPH analyser (Shimadzu, Japan) or an ion chromatography (ICS3000, Dionex, Sunnyvale, CA, USA) as described in van Pinxteren et al. (2017). For amino acid analysis,As the seawater samples need to must first undergo a desalination step first. To achieve thisfor the FAA analysis, 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 the 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 enabled the filtering of the enriched samples; then, a derivatization was performed usingwith the AccQ-Tag™ precolumn derivatization method

(Waters, Eschborn, Germany). ~~The amino acid~~ Besides, the FAA analysis includes the determination of 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  $\gamma$ -aminobutyric acid (GABA) (purity  $\geq$  99 %, Sigma-Aldrich, St. Louis, Missouri, USA). ~~The analytical measurements of the derivatized FAA were performed with ultra-~~ An ultra-high performance liquid chromatography with electrospray ionization and Orbitrap mass spectrometry (UHPLC/ESI-~~Orbitrap-MS~~) Orbitrap-MS) performed the analytical measurements of the derivatized FAAs. 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) therefore. The samples were subsequently separated using through an ACQUITY UPLC® HSS T3 column (Waters, Eschborn, Germany) with the dimensions 1.8  $\mu$ m, 2.1 x 100 mm at a constant temperature of 30 °C and a detection in positive mode. The eluent composition was consisted of (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<sup>-1</sup> 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 from 100 % B to 5 % B and held the 5 % B was then kept constant for 3.9 min. This analytical procedure can be used for amines, too, as described in van Pinxteren et al. (2019b). ~~The amino acid~~ van Pinxteren et al. (2019). The FAA 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. we cannot differentiate between L- and D- amino acids in our ambient samples.~~ 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~~ They consist of high purity water, which was filled in pre-cleaned plastic bottles and handled the same as the seawater samples. ~~The limit of quantification (LOQ) of the individual FAAFAAs in seawater samples is in good agreement with the FAA analysis in seawater samples (e.g. Kuznetsova et al. (2004)) and is listed in Table S1.) and listed in Table S1. The LOQs were mostly below 10 nmol L<sup>-1</sup>, however, GABA and Met exhibited LOQs with 24.2 nmol L<sup>-1</sup> and 16.8 nmol L<sup>-1</sup>, respectively (due to high blank values). A quantification of some FAAs in seawater, mainly in the ULW with its generally lower FAA concentrations compared to the SML, is therefore partly limited.~~

### 2.2.2 Aerosol particle filter ~~analyties~~ analyses

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 first filtered using with a 0.45  $\mu$ m 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  $\mu$ L) were filtered (0.45  $\mu$ m syringe filter) and investigated using ion chromatography (ICS3000, Dionex,

Formatted: Font: Times New Roman

Formatted: English (United States)

Formatted: English (United Kingdom)

Sunnyvale, CA, USA) as ~~described~~ outlined in Mueller et al. (2010). The aliquot (1.5 mL) of the aqueous particle extracts for FAA analysis was reduced to several  $\mu\text{L}$  using with a vacuum concentrator at  $T=30\text{ }^{\circ}\text{C}$  (miVac sample Duo, GeneVac Ltd., Ipswich, United Kingdom) and derivatized and analysed as well as analyzed using the UHPLC/ESI-~~Orbitrap~~ Orbitrap-MS method as ~~described~~ explained in section 2.2.1 for seawater samples. Amino acid FAA concentrations were calculated via external calibration, ~~measured~~; each sample was measured 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 values presented values here for aerosol particle samples are field blank corrected. The limit of quantification (LOQ) LOQs of the individual FAA FAAs in aerosol particle samples is are listed in Table S1 and is are in good agreement with the sensitivity of other analytical methods for FAA FAAs in aerosol particles (e.g. Matsumoto and Uematsu (2005)). ~~The analysis of mineral dust tracers of~~ Although a variance in LOQs between the individual Berner stages was performed FAAs is apparent. FAAs with relatively high LOQs ( $39.5\text{ pg m}^{-3}$ ) on aerosol particles such as described in Fomba et al. (2013); Ala, GABA, Asp in submicron and supermicron aerosol particles could be quantified (as discussed in section 3.2 and 3.4).

The analysis of mineral dust tracers on nucleopore foils sampled with the Berner impactor was performed with the Total Reflection X-Ray Fluorescence S2 PICOFOX (Bruker AXS, Berlin, Germany) equipped with a Mo-X-ray source on polished quartz substrates as can be seen in Fomba et al. (2013). The particulate mass (PM) of the aerosol particle samples was determined by weighing the filter before and after sampling (van Pinxteren et al., 2015). Back trajectory analyses provided information regarding the origins of air masses. Seven-day back trajectories were calculated on an hourly basis within the sampling intervals, using the NOAA HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, <http://www.arl.noaa.gov/ready/hysplit4.html>, 26.11.16) in the ensemble mode at an arrival height of  $500\text{ m} \pm 200\text{ m}$  (van Pinxteren et al., 2010); van Pinxteren et al. (2020) provide more details. The calculated backward trajectories are representative for both aerosol particle sampling stations (CVAO and MV).

### 2.2.3 Cloud water ~~samples~~ analytical analyses

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

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

were generated by rinsing the pre-cleaned Teflon rods with high purity water after its installation in the cloud water sampler. ~~The~~ Then, the blank samples were handled the same as the field cloud water samples including the derivatization and analytical separation as described in section 2.2.1. ~~The LOQ~~ Overall, the LOQs of the individual ~~FAA~~FAAs in cloud water samples ~~is~~are in good agreement with the reported sensitivity of the FAA analysis in cloud water (Bianco et al., 2016) and listed in Table S1. Since the LOQs of the FAAs in cloud water are below 0.3 ng m<sup>-3</sup> and often below 0.06 ng m<sup>-3</sup>, a limitation of the FAA composition in cloud water due to the LOQs is rather unlikely despite the variance of FAA concentrations (1.2-489.9 ng m<sup>-3</sup>) in cloud water (section 3.3). To calculate the atmospheric concentration of FAA in cloud water, the measured ~~concentration~~ concentrations were multiplied with the measured liquid water content (LWC) of the clouds as ~~described in Fomba et al. (2015)~~. Fomba et al. (2015) applied beforehand.

#### 2.2.4 Enrichment factors

The enrichment factor in the SML (EF<sub>SML</sub>) 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):

$$EF_{SML} = \frac{c(\text{analyte})_{SML}}{c(\text{analyte})_{ULW}} \quad (1)$$

Accordingly, both an enrichment in the SML ~~is indicated by~~with EF<sub>SML</sub> > 1, and a depletion in the SML with EF<sub>SML</sub> < 1, are indicated.

The FAA concentration in the ULW was assumed to be based on the concentration (LOQ/2) of individual amino acids for seawater samples from the same campaign day when individual FAA could be quantified in the SML samples, but not in the corresponding ULW ones due to FAA values below the LOQs (listed in Table S1). For the calculation of this estimated EF<sub>SML</sub>, specially marked in the following, the concentration 25.2 nmol L<sup>-1</sup> was used for c(analyte)<sub>ULW</sub> in equation (1).

To calculate the enrichment factor of the individual analytes in different matrices (M), the concentration of the analyte in matrix 1 (M<sub>1</sub>) ~~related~~relative to the sodium (Na<sup>+</sup>) concentration in M<sub>1</sub> was divided by the analyte concentration in matrix 2 (M<sub>2</sub>) ~~relation~~relative to the Na<sup>+</sup> concentration in M<sub>2</sub> using equation (2):

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

Therefore, it was possible to calculate the ~~The aerosol~~ enrichment factor in aerosol particles (EF<sub>acc</sub>) with the concentration of the analyte and Na<sup>+</sup> were calculated in each of the five Berner stages of the Berner impactor (B<sub>x</sub> with x = 1–5) as M<sub>1</sub> and of using the respective analyte and Na<sup>+</sup> concentration in relation to the SML or the ULW as M<sub>2</sub>. For this purpose, the aerosol particle concentrations, typically sampled ~~at in~~ in a 24-hour interval, were combined with SML/ULW concentrations, which

5 ~~have had~~ been collected during the aerosol particle 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/ULW. The calculation of the ~~enrichment factor aerosol~~  $EF_{\text{aer}}$  was limited to the availability of data in both matrices – size-segregated aerosol particles and SML/ULW samples. The  $EF_{\text{aer}}$  could only be calculated if both the analyte concentration ~~of the analyte as well as and~~ the sodium concentration could be quantified in the size-segregated aerosol particles and ~~in~~ the corresponding SML/ULW samples ~~could be quantified~~. To calculate the enrichment factor in cloud water ( $EF_{\text{CW}}$ ), the concentration of the analyte and of  $\text{Na}^+$  ~~of~~ in the cloud water were considered as  $M_1$  and those of the SML or the ULW as  $M_2$  ~~were considered~~. The determination of ~~the~~  $EF_{\text{aer}}$  was possible for  $n=3$  samples ~~and both on the determination basis of SML and ULW. The  $EF_{\text{CW}}$  was possible~~ could only be determined for  $n=1$  ~~and will be discussed sample though basing on the SML and ULW measurements. Section 3.4 discusses both the  $EF_{\text{aer}}$  and the  $EF_{\text{CW}}$  in more detail in section 3.4.~~

Formatted: Subscript

### 3. Results and Discussion

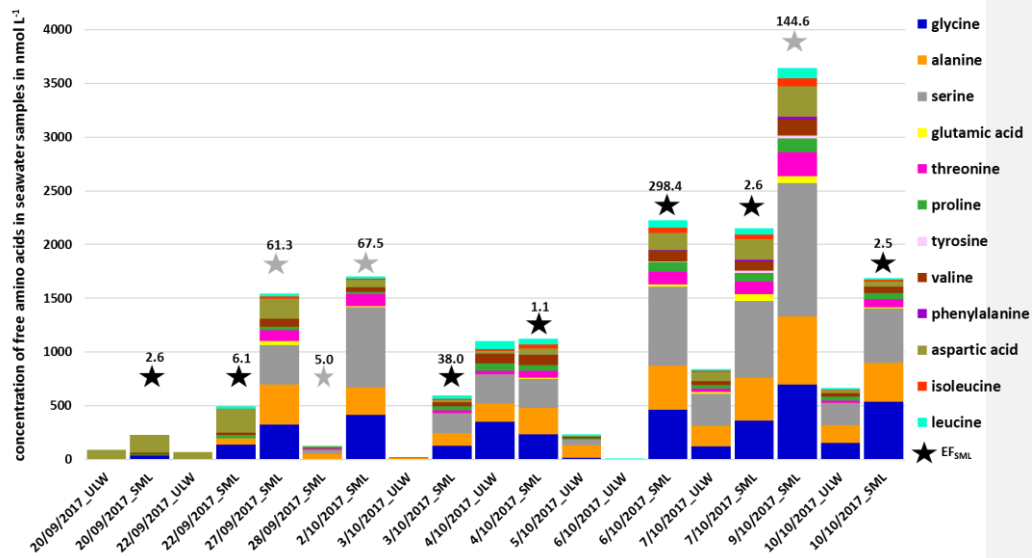
#### 3.1 Seawater samples

##### *Free amino acids in seawater samples*

15 FAA were measured in the seawater as a source region of FAA on primary marine aerosol particles. ~~In~~ Fig. 4, 1b shows the measured  $\Sigma$ FAA concentration in the SML and the ULW samples together with their enrichment factor  $EF_{\text{SML}}$  (Eq. 4) ~~are shown~~.

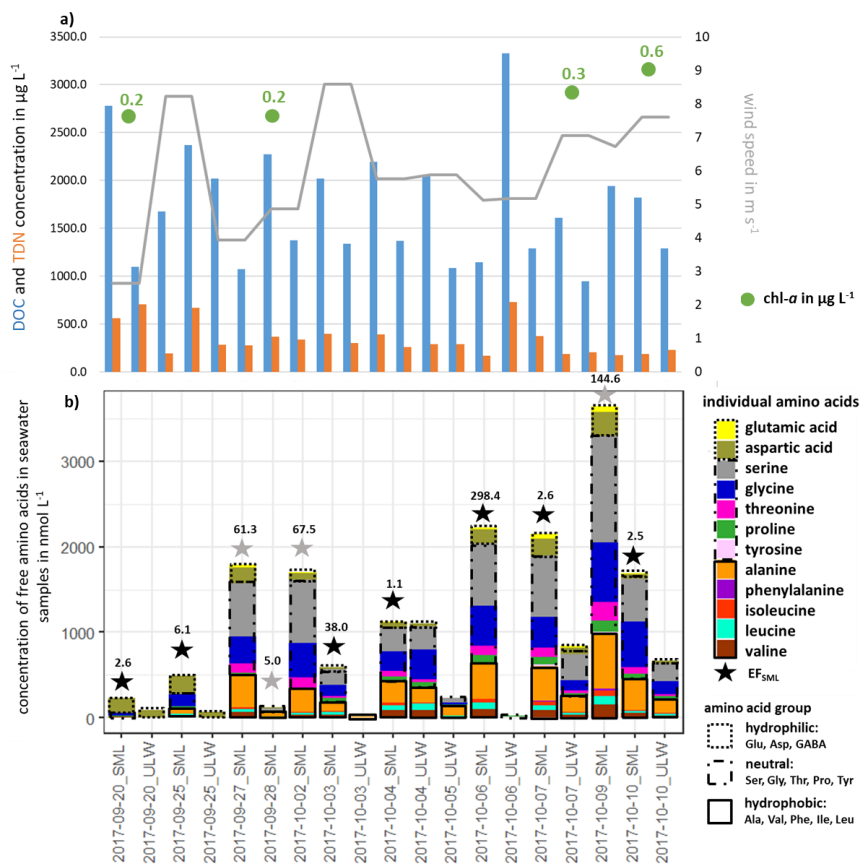
Formatted: English (United States)





1)

Formatted: English (United States)



**Figure 1: Individual a) DOC, TDN and chl- $\alpha$  concentration in seawater and windspeed and b) individual FAA concentration in the seawater samples (ULW, SML) in  $\text{nmol L}^{-1}$ , and the enrichment factor  $\text{EF}_{\text{SML}}$  of  $\Sigma\text{FAA}$ ;  $\text{EF}_{\text{SML}}$  based on measurements (black stars),  $\text{EF}_{\text{SML}}$  based on LOQ/2 estimation (grey stars)**

5  $\Sigma\text{FAA}$  included all investigated amino acids (listed in 2.2.1) with the exception of methionine, glutamine except for Met, Gln and GABA. These As discussed in section 2.2.1, GABA and Met have the highest LOQs of the analytical method used here, which may be one reason why these two analytes were could not detected or quantified, in the seawater samples (ULW and SML). The

Formatted: Font: +Body (Times New Roman)

Formatted: Font: Times New Roman

Formatted: Font: Times New Roman

Formatted: Font: Times New Roman

Looking at the percentage composition within the ULW (10.1 % hydrophilic, 57.0 % neutral, 32.8 % hydrophobic) and the SML (10.6 % hydrophilic, 61.7 % neutral, 27.7 % hydrophobic), the values are similar to each other. However, the concentration of  $\Sigma$ FAA varied between 0.01-1.10  $\mu\text{mol L}^{-1}$  in the ULW and between 0.13-3.64  $\mu\text{mol L}^{-1}$  in the SML. Interestingly, in the second half of the campaign, the  $\Sigma$ FAA concentration was higher than in the first part. A general strong variability of  $\Sigma$ FAA concentration, especially in the SML, were reported in previous studies 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  $\mu\text{mol L}^{-1}$  (ULW) and 0.43-11.58  $\mu\text{mol L}^{-1}$  (SML) and in the western Mediterranean Sea 0.07-0.60  $\mu\text{mol L}^{-1}$  (ULW) and 0.77-3.76  $\mu\text{mol L}^{-1}$  (SML). have already reported a general strong variability of  $\Sigma$ FAA concentration, especially in the 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, but without clear diel variations in their concentrations. The wind speed (Table S2) could not explain. Nevertheless, the variability of the  $\Sigma$ FAA concentrations in the SML or in the ULW and observed here could neither be explained by the variance of DOC or TDN values, nor by wind speed and chl-*a* concentrations (see Fig. 1, Table S2, S5), since no correlation between wind speed these parameters and the concentration or enrichment of FAA was observed. This is consistent with other publications, which observed that the 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 concentrations in seawater (ULW, SML) and their  $EF_{\text{SML}}$ , listed in Table S3, show clear differences between the individual amino acids: Ser was and the highest concentrated amino acid classes. The most highly enriched amino acids in the SML and clearly lower concentrated in the ULW, resulting in are the neutral ones with values of up to 203 compared to the highest value and variance of hydrophilic ( $EF_{\text{SML}}$ : 2-98) and hydrophobic ( $EF_{\text{SML}}$ : 1-1515.6) of the observed individual FAA. However, other 96 amino acids as e.g. Tyr showed smaller  $EF_{\text{SML}}$  (2.1-18.7) caused by significantly smaller concentration in ULW and. This may be related to the fact that Ser, Thr and Gly as part of the neutral amino acids, are main components of cell wall proteins (Hecky et al., 1973). The direct release of FAAs through cell lysis and the associated destruction of the cell wall can thus explain the increased enrichment of neutral amino acids in the SML samples (Table S3). Our study confirmed previous observations that the SML is often non-uniformly enriched with FAAs as outlined from previous observations (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, and the in-situ production via an extracellular hydrolysis of CAA or a direct release of FAA by cell lysis can probably 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 the cause of the non-uniformly enrichment in SML. Moreover, Kuznetsova and Lee (2002) they suggested that the intracellular pools of organisms, which are rich in DFAA and DCAA compared to seawater, can be leached out by stressed microorganisms, resulting in the release of DFAA and DCAA with an effect on which in turn influences the pools of both DFAA and DCAA pools in seawater. On the basis of Based on previous studies, the transportation and the releasing mechanisms seems to be most likely to be the reasons for the

Formatted: Font: Not Bold

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;Reinthal et al., 2008) and for~~ the here investigated region (Table S4). It can be concluded that the here observed FAA concentrations are representative for the tropical North Atlantic Ocean.

~~Altogether, it can be concluded that there is some variability within the FAA concentration in the SML and in the ULW, with a clear trend of its strong enrichment in the SML. The fact that the FAA concentrations were in accordance with the ones measured at the same location in 11/2013 (0.64  $\mu\text{mol L}^{-1}$ , Table S4), supports the suggestion that the FAA concentrations reported here can be considered representative of the NATR region as part of the North Atlantic Ocean. These concentrations are generally similar comparing them to FAA concentrations in other marine regions (Kuznetsova and Lee, 2002;Reinthal et al., 2008). Reinthal et al. (2008) considered concentrations of dissolved FAA of 0.02-0.13  $\mu\text{mol L}^{-1}$  (ULW) and of 0.43-11.58  $\mu\text{mol L}^{-1}$  (SML) in the subtropical Atlantic Ocean as well as values of 0.07-0.60  $\mu\text{mol L}^{-1}$  (ULW) and of 0.77-3.76  $\mu\text{mol L}^{-1}$  (SML) in the western Mediterranean Sea. Consequently, the FAA concentrations in the NATR region, with its very low surface chlorophyll and a greater annual variability than seasonality, are in the same order of magnitude compared to other marine regions (i.e. subtropical Atlantic and western Mediterranean Sea (Reinthal et al., 2008)).~~

#### *Contribution of FAA to DOC and TDN content in seawater*

~~The~~ DOC and TDN concentrations and their enrichment in the SML ( $EF_{\text{SML}}$ ) are listed in Table S5. The contribution of  $\Sigma\text{FAA}$  to DOC or ~~to~~ TDN in the seawater ~~washed been~~ calculated (~~considering taking into account~~ the carbon and nitrogen content of the amino acids, Table S6) and ~~are~~ also listed in Table S5. The carbon content of  $\Sigma\text{FAA}$  contributed to ~~the~~ DOC ~~with values~~ between 0.1-7.6 % in the seawater samples ~~with and~~ a median of 2.4 % (n=17), ~~differentiated in SML with differing between~~ 2.8 % (n=11) ~~and in in the SML and 1.8 % (n=6) in the~~ ULW samples ~~with 1.8 % (n=6). Considering. Looking~~ at the nitrogen content ~~offrom~~  $\Sigma\text{FAA}$  to TDN in the seawater samples, 0.1-42.4 % of ~~the~~ TDN consisted of  $\Sigma\text{FAA}$  with a median of 8.3 % (n=18). In the SML,  $\Sigma\text{FAA}$  contributed on average with 11.9 % (n=11) ~~and whereas they contributed~~ in the ULW with 3.2 % (n=7) to TDN. The observed daily variations ~~of within~~ the contribution of  $\Sigma\text{FAA}$  to DOC/TDN, result from ~~the~~ daily variations of ~~the~~  $\Sigma\text{FAA}$  concentration ~~of~~  $\Sigma\text{FAA}$  in seawater (Fig. 1) and of DOC/TDN (Table S5). In the ~~study of Reinthal et al. (2008) SML of the Atlantic Ocean and the western Mediterranean Sea, the~~  $\Sigma\text{FAA}$  contributed with ~~~12% to % of the~~ DOC and ~~with ~30% to % of the~~ dissolved organic nitrogen (DON) ~~in the SML of the Atlantic ocean and the western Mediterranean Sea. The (Reinthal et al., 2008). Our results concerning regarding the~~ contribution to DOC were ~~in of~~ the same order of magnitude, but slightly lower ~~compared to than those of~~ Reinthal et al. (2008).

### 3.2 Size-segregated aerosol particles

#### 3.2.1 Size-segregated aerosol particles at the CVAO

Formatted: English (United Kingdom)

Formatted: Font: Not Italic, No underline

Formatted: Font: Not Bold

### First indications of aerosol particle origin

To obtain a first indication of the particle origin, that might help to explain the differences in the particle composition concerning amino acids, the particles were associated with the origin of the air masses and with marine and dust tracers.

Overall, the CVAO station experienced north-easterly trade winds during this campaign, which are typical for this season

5 within this region (Fomba et al., 2014;van Pinxteren et al., 2020). According to physical and chemical specifications such as the air mass origins, particulate MSA concentrations and MSA/sulfate ratios as well as particulate mass concentrations of dust tracers, aerosol particles predominantly of marine origin with low to medium dust influences were observed. It has to be noted that dust generally influences the supermicron particles to a larger extent than the submicron particles (Fomba et al., 2013). Further information on the classification of the air masses are given in the overview paper of this campaign (van Pinxteren et  
10 al., 2020).

### Free amino acids in size-segregated aerosol particles-: Concentrations

The lower panel of Fig. 2b shows the atmospheric concentration of  $\Sigma$ FAA in each Berner stage at the CVAO is shown in Fig. 2 lower whereas the upper panel and represents the concentration in the submicron (B1-3), the supermicron (B4-5) and

15 PM<sub>10</sub> (B1-5) PM aerosol particle size range in the upper panel. In the submicron aerosol particles, the concentration of  $\Sigma$ FAA was between 1.3 ng m<sup>-3</sup> (1/10/2017) and 6.3 ng m<sup>-3</sup> (7/10/2017). In the supermicron size range, whilst the concentration of  $\Sigma$ FAA varied between 0.2 ng m<sup>-3</sup> (6/10/2017) and 1.4 ng m<sup>-3</sup> (22/09/2017). It is obvious that in the supermicron size range, the highest atmospheric concentrations of  $\Sigma$ FAA were found in the submicron aerosol particles (mean of 3.2 ng m<sup>-3</sup>) compared to the supermicron aerosol particles (mean of 0.6 ng m<sup>-3</sup>).  $\Sigma$ FAA included all Daily variations of the  $\Sigma$ FAA content on  
20 the investigated amino acids (listed in 2.2.1) with the exception of methionine and glutamine, both analytes were not detected in the size-segregated aerosol particle samples.

The were observed total atmospheric concentration of dissolved FAA (sum of B1-5) was between 1.76-6.82 ng m<sup>-3</sup> (averaged 3.82 ng m<sup>-3</sup>) and in good agreement with previous: the  $\Sigma$ FAA tended to increase slightly along the campaign. OM

25 parameterization studies focussing on marine aerosols in remote areas, showed that wind speed and chl-*a* concentrations were most important parameters for the regulation of the OM production in sea spray aerosol particles Matsumoto and Uematsu (2005)(Gantt et al., 2011;Rinaldi et al., 2013;van Pinxteren et al., 2017) reported averaged total concentrations of dissolved FAA with 4.5 ng m<sup>-3</sup> in the western North Pacific Ocean. Correlations between the  $\Sigma$ FAA concentrations of the size-

segregated aerosol particles (considered as submicron, supermicron and PM<sub>10</sub>) and the wind speed were not observed for here reported data (Fig. 2, Table S2). However, the available wind speed and wind direction data represented an average value of

30 24 hours. Therefore, shortly pronounced changes in the wind speed that might have affected the amino acids transfer would not have been visible in the averaged wind speed value. The major source of bubbles are whitecaps or breaking waves, that occur when the wind speed exceeds 3-4 m s<sup>-1</sup> (Blanchard, 1975), which was continuously reported during the campaign. Hence, the high wind speeds together with the constantly observed breaking waves indicated that the wind intensity in this region might be consistently sufficient to transfer the amino acids from the ocean into the atmosphere. No significant correlation

could be observed between the  $\Sigma$ FAA concentration of size-segregated aerosol particle samples (submicron, supermicron and  $PM_{10}$ ) and the chl-*a* concentration in seawater. Nevertheless, the increasing chl-*a* concentration along the campaign (Fig. 2, Table S2) could be a reason for the slight increase in the concentrations of  $\Sigma$ FAA in seawater and on submicron aerosol particles, indicating a possible connection between ocean and atmosphere, e.g. the transfer of amino acids from the ocean into the atmosphere.

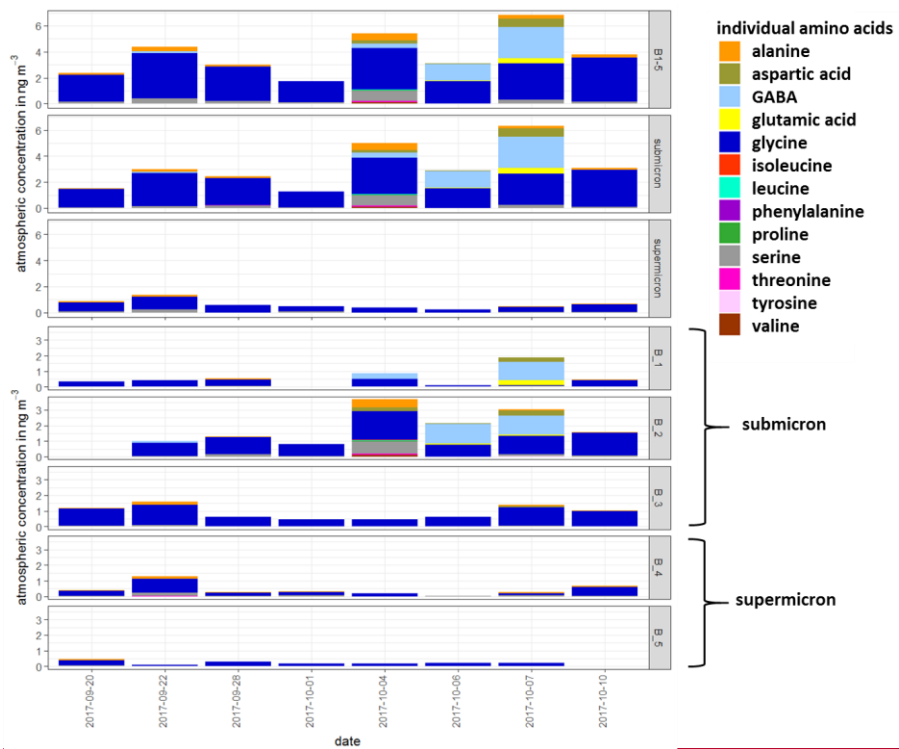
Overall, the concentrations reported here agree well with other FAA studies on marine aerosol particles. Matsumoto and Uematsu (2005) found averaged total concentrations of dissolved FAA with  $4.5 \text{ ng m}^{-3}$  on aerosol particles (average of  $< 2.5 \mu\text{m}$  and  $> 2.5 \mu\text{m}$ ) in the western North Pacific Ocean. Moreover, Wedyan and Preston (2008) observed during a transect ship cruise in the Atlantic Ocean a mean average concentration of dissolved FAA of  $2.5 \text{ ng m}^{-3}$  on total suspended particles (TSP). In) during a transect ship cruise in the Atlantic Ocean. For Antarctic aerosol particles, the observed mean FAA-total FAA concentration on size-segregated aerosol particle samples ( $< 0.49\text{-}10 \mu\text{m}$ ) at the Mario Zucchelli Station was  $4.6 \text{ ng m}^{-3}$  (Barbaro et al., 2015). Hence, regarding the sum of FAA, a striking similarity was found between FAA concentrations in different parts of the ocean that probably underlay different influences (e.g. pristine region in the Southern Ocean, continental-influenced aerosol particles in the North Pacific Ocean).

Especially

*Free amino acids in size-segregated aerosol particles: Composition*

$\Sigma$ FAA included all investigated amino acids (listed in 2.2.1) except for Met and Gln, analytes which were neither detected in the size-segregated aerosol particle samples. The most abundant FAA was Gly, which was consistently found in submicron and supermicron aerosol particles, followed by Ala and Ser. However, towards the end of the campaign (4/10/2017-7/10/2017), a high contribution of the hydrophilic FAAs GABA and Asp were detected (Fig. 2 shown in the 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  $3 \text{ ng m}^{-3}$ ) occur. Lower concentration of amino acids generally contained mainly Gly and in smaller concentrations Ala and Ser. However, on 10/10/2017, the  $\Sigma$ FAA concentration was high ( $3.8 \text{ ng m}^{-3}$ ) 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. of Fig. 2b), which caused the slight increase of the total FAA concentration.

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) 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 Pommić 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.



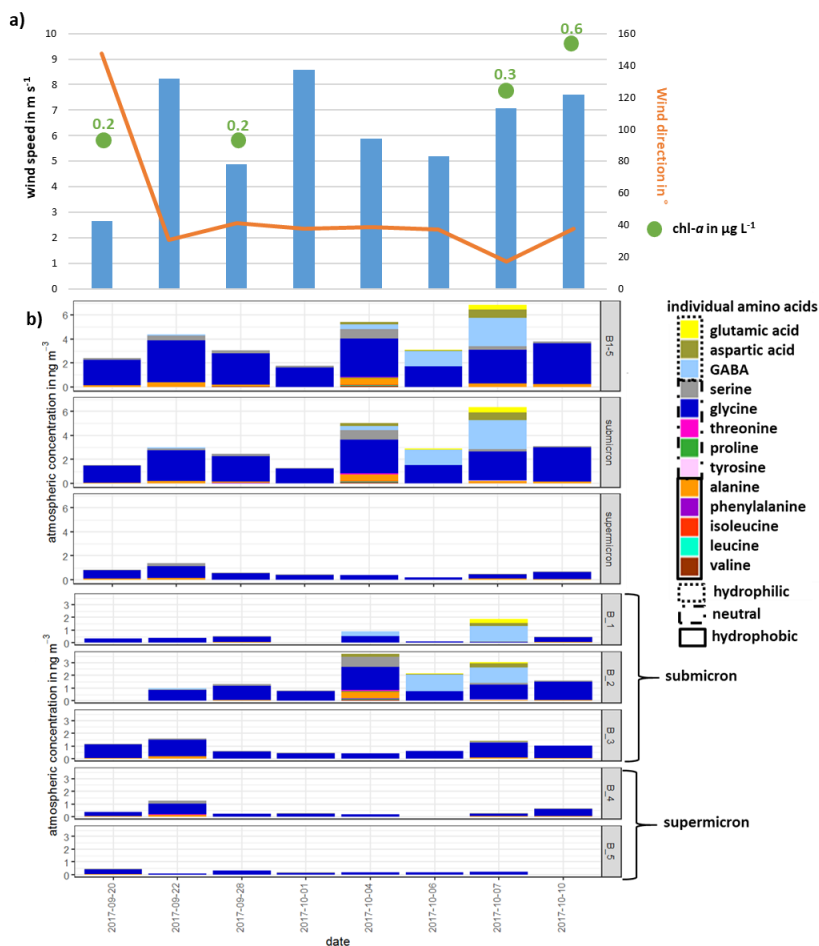


Figure 2: **Atmospheric** overview of wind speed and wind direction at the CVAO and the chl-a concentration in seawater; **b) atmospheric** concentration of individual amino acids contributing to the  $\Sigma$ FAA in different aerosol particle size classes: the sum of all Berner stages (B1 - 5), in the submicron (B1-3) and the supermicron (B4-5) size range (upper panel); and 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 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~~ was able to quantify the individual molecular FAA species. ~~With Such differentiation would not be possible 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 high abundance of Gly in the aerosol particles is in good agreement with the Gly occurrence in other marine studies. Gly seems to be the dominant FAA, independent of whether the particles were sampled in the Arctic (Scalabrin et al., 2012), Antarctic (Barbaro et al., 2015) or in the North Pacific (Matsumoto and Uematsu, 2005) and whether they are attributed to a local marine source (Wedyan and Preston, 2008; Barbaro et al., 2015) or are rather continental or long-range influenced (Matsumoto and Uematsu, 2005). Other abundant FAAs reported at the different locations are arginine (not analyzed here), Ser and Ala: the latter ones are also dominant FAAs found in the here reported study. Consequently, the usage of the major FAAs as chemical biomarkers seems to be restricted to some extent due to their lack of source-specificity. The high abundance of GABA found in the second half of the campaign has neither been partly regarded (i.e. included as a standard compound) in some marine studies, nor yet been reported in ambient marine aerosol particles, but seems to be special for this location. However, the reasons for the high concentration of hydrophilic FAAs within these respective sampling days remain unclear, since no change in the environmental parameters determined (e.g. wind speed, wind direction, chl-*a* concentration, Fig. 2a) was observed. In addition, we considered further FAA physico-chemical parameters such as the octanol-water partition coefficient ( $K_{ow}$ ), the topological polar surface area (TPSA), which describes the surface activity, and the density (Table S9) to describe the concentration changes. However, no statistically relevant correlations between the FAA concentration or 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 and physico-chemical parameters were found here either. Our observations could not clarify possible additional (i.e. non-marine) sources leading to the higher concentrations and

Formatted: Font: Not Bold, English (United States)

Formatted: English (United States)

~~complexity in the FAA composition with the seawater. The dynamics behind the varying FAA concentration and composition with at this location seem to be discussed more detailed complex.~~

~~Following this hydropathy classification, the submicron aerosol particles consisted on average of 5 % hydrophobic, 15 % hydrophilic and 80 % neutral amino acids, while the supermicron aerosol particles contained on average only 7 % hydrophobic and 93 % neutral amino acids (Table S7). During the campaign, an increase in section 3.4 the contribution of hydrophilic amino acids was observed with a maximum of 55 % on 7/10/2017. Barbaro et al. (2015) reported that hydrophilic components were predominant (60 %) in locally produced marine Antarctic aerosol particles, whereas hydrophobic compounds were rather dominate aerosol particles collected at the continental station (23 % and 27 %). According to the conclusions by Barbaro et al. (2015), the relatively high content of hydrophilic FAA found here points at least at some influence of local oceanic sources.~~

#### Contribution of FAA to WSOC and WSON

In consideration of the carbon or nitrogen content of the amino acids (Table S6), the contribution of  $\Sigma$ FAA to WSOC and water-soluble organic nitrogen (WSON) in the size-segregated aerosol particles was calculated (Table ~~S9S10~~). In the submicron size range,  $\Sigma$ FAA contributed up to 5.3 % (average 1.1 %) to WSOC, ~~whereas  $\Sigma$ FAA while~~ in the supermicron range,  $\Sigma$ FAA only contributed only up to 0.04 % to WSOC. ~~Considering the Looking at  $\Sigma$ FAA's~~ total contribution of  $\Sigma$ FAA to WSOC (PM<sub>10</sub>), 0.7 % of WSOC ~~exist~~ consists of  $\Sigma$ FAA, which ~~was~~ is in good agreement with the value of the study of by Mandalakis et al. (2011). Considering the nitrogen content of the amino acids,  $\Sigma$ 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 of 0.05 % in the supermicron size range. The observed daily variations of the contribution of  $\Sigma$ FAA to WSOC/WSON, ~~resulted were derived~~ from the daily ~~variation~~ variations of the atmospheric concentration of  $\Sigma$ FAA (Fig. 2) and of WSOC/ WSON (Table ~~S9S10~~). In summary,  $\Sigma$ FAA contributed up to 5.3 % to WSOC ~~or up and~~ to 1.8 % to WSON ~~on when it comes to~~ the submicron aerosol particles (7/10/2017) and up ~~until to~~ 0.15 % to WSOC ~~or up until and to~~ 0.1 % to WSON ~~on for~~ the supermicron aerosol particles. These percentages were in the same order of magnitude as ~~off for~~ other organic compound groups, e.g. amines. ~~van Pinxteren et al. (2019b) showed that amines contributed on average with van Pinxteren et al. (2019) showed that amines contributed on average~~ 5 % to the submicron WSOC content on marine aerosol particles. Especially, the percentage of  $\Sigma$ 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)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  $\Sigma$ FAA concentration of 1.5 ng m<sup>-3</sup> (0.8-1.9 ng m<sup>-3</sup>), similar to the  $\Sigma$ FAA concentration in the supermicron aerosol particles (1.2 ng m<sup>-3</sup>; 0.2-2.9 ng m<sup>-3</sup>). The averaged PM for the~~

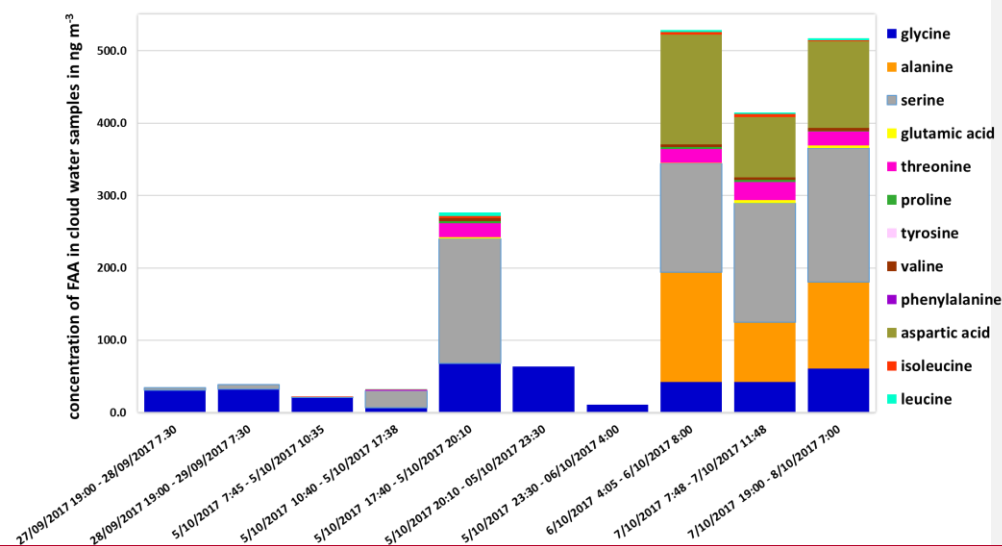
Formatted: Font: Times New Roman, 10 pt, English (United Kingdom), Highlight

submicron ( $2517 \text{ ng m}^{-3}$ ) and the supermicron ( $13669 \text{ ng m}^{-3}$ ) aerosol samples at the CVAO were 3–4 times higher compared to the MV (submicron:  $735 \text{ ng m}^{-3}$ , supermicron:  $3668 \text{ ng m}^{-3}$ ). Moreover, the averaged WSOC content on the submicron aerosol particles ( $2.6 \text{ ng m}^{-3}$ ) was similar to the supermicron aerosol particles ( $5.9 \text{ ng m}^{-3}$ ) at the MV station and considerably smaller as at the CVAO (submicron:  $22.1 \text{ ng m}^{-3}$ , supermicron:  $50.6 \text{ ng m}^{-3}$ ).  $\Sigma$ 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  $\text{Na}^+$  and MSA concentration were compared with the corresponding data at the CVAO. With concentration of  $\text{Na}^+$  (averaged  $17.0 \text{ ng m}^{-3}$ ) and of MSA ( $0.04\text{--}4.2 \text{ ng m}^{-3}$ ) in the submicron aerosol particles and in the supermicron aerosol particles (averaged  $\text{Na}^+$ :  $111.3 \text{ ng m}^{-3}$ , MSA:  $1.1\text{--}3.7 \text{ ng m}^{-3}$ ), the MV aerosol particle samples were lower concentrated in marine inorganic tracers as the corresponding CVAO samples (Table S10). The lower concentrations of marine compounds (e.g. MSA,  $\text{Na}^+$ ) 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.

### 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  $\Sigma$ FAA in cloud water had a strong variation during the investigated campaign days ( $11.2\text{--}489.9 \text{ ng m}^{-3}$ ) as shown in Fig. 3. Our observed carbon concentration of FAA in cloud water at the MV station showed a higher variance ( $17\text{--}757 \mu\text{g C L}^{-1}$ ) 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  $211 \pm 19 \mu\text{g C L}^{-1}$ . 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  $\Sigma$ FAA  $< 65 \text{ ng m}^{-3}$ , usually Gly was dominant followed by Ser. Cloud water samples with  $\Sigma$ FAA  $> 290 \text{ ng m}^{-3}$  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  $5.0 \mu\text{g m}^{-3}$  ( $1.6\text{--}7.2 \mu\text{g m}^{-3}$ ), of sulfate  $2.9 \mu\text{g m}^{-3}$  ( $1.8\text{--}3.6 \mu\text{g m}^{-3}$ ) and of MSA  $26.1 \text{ ng m}^{-3}$  ( $11.0\text{--}39.0 \text{ ng m}^{-3}$ ) 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).



From the MV samples, FAAs and additional parameters such as PM, WSOC, sodium and MSA were investigated. The results are listed in Table S11. The submicron aerosol particles at the MV had an averaged  $\Sigma$ FAA concentration of  $1.5 \text{ ng m}^{-3}$  ( $0.8\text{--}1.9 \text{ ng m}^{-3}$ ) and were about three times lower compared to the  $\Sigma$ FAA concentration at the CVAO. The  $\Sigma$ FAA concentration in the supermicron aerosol particles at the MV ( $1.2 \text{ ng m}^{-3}$ ;  $0.2\text{--}2.9 \text{ ng m}^{-3}$ ) was similar to the respective concentrations at the CVAO. Additional online measurements of particle size number distributions (PSND) at the CVAO and the MV, described in Gong et al. (2020) were in good agreement with one another during cloud-free times. This indicated that, for cloud-free conditions, the aerosol particles measured at ground level represented the aerosol particles at cloud level, i.e. the aerosol particles within the marine boundary layer were well mixed. However, as described above, the Berner measurements were (continuously) taken during cloud-free as well as during cloud times. The concentration and composition of the aerosol particles can therefore be affected by the clouds that formed and disappeared consistently during the sampling period of the aerosol particles at the Mt. Monte Verde (for further details on the frequency of the cloud events see Gong et al. (2020) and van Pinxteren et al. (2020)). The particles at the MV exhibited lower particle masses, as well as lower concentrations of the aerosol particle constituents. The decrease in concentrations of  $\Sigma$ FAA, PM, sodium, MSA and WSOC was reduced by a factor of three to four regarding the submicron aerosol particles. However, no uniform depletion ratio between their concentration at the CVAO and the MV was found for the supermicron aerosol particles (Table S11). While the PM of the supermicron particles was reduced by a factor of four at the MV (similar to the submicron aerosol particles), sodium and WSOC were depleted more strongly (factor of 11-12) compared to their respective concentrations at the CVAO. This suggests that the submicron particles

were rather uniformly affected and depleted, likely by cloud processes, while the supermicron particles were influenced by clouds, and potentially other sources, in a non-uniform way. Nevertheless, the abundance of the marine tracers (sodium, MSA), together with the presence of FAA in the aerosol particles (which mainly had a similar composition compared to the oceanic and ground-based particulate FAA) indicated an oceanic contribution to the aerosol particles at cloud level.

5

### 3.3 Cloud water samples

The concentration of FAA in cloud water (Fig. 3, Table S12) was, although varying, always significantly higher than the aerosol particles (Table S8) and several orders of magnitude above the LOQs (Table S1). The individual atmospheric concentration of FAA in cloud water was calculated based on the measured liquid water content (LWC) (section 2.2.3 and Table S12). The  $\Sigma$ FAA concentrations varied strongly between 11.2 and 489.9  $\text{ng m}^{-3}$  as shown in Fig. 3.

10

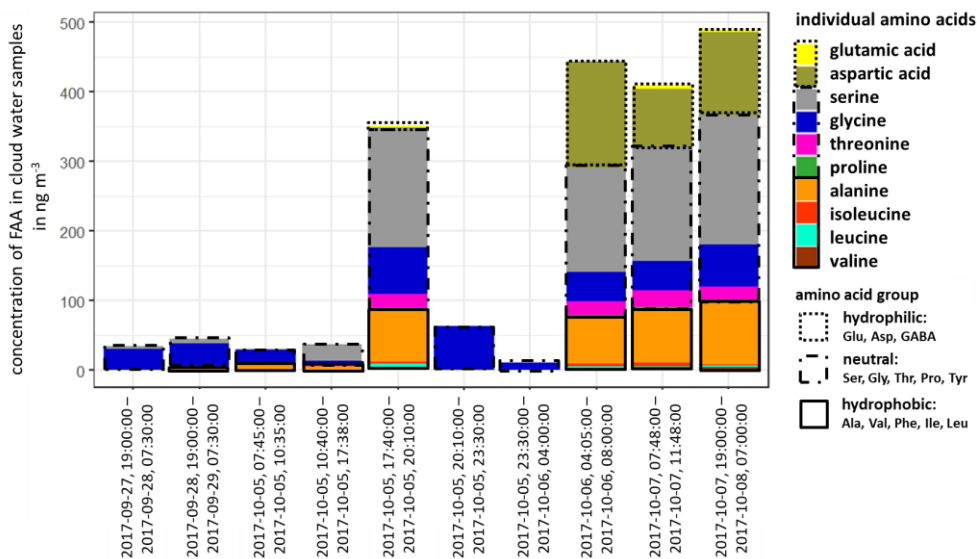


Figure 3: Concentration of individual FAA in cloud water samples at the MV station in  $\text{ng m}^{-3}$ . The time represents the local start and end time of the cloud water sampling

15

Because of the limited number of studies dealing with cloud water in the marine environment and its comparison with aerosol 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. The inorganic marine tracers in cloud water ( $\text{Na}^+$ :  $5.7 \mu\text{g m}^{-3}$ , MSA:  $25.1 \text{ ng m}^{-3}$ , Table S12) were also present in higher concentrations compared to the aerosol particle samples at the CVAO (submicron:  $\text{Na}^+$ :  $72.3 \text{ ng m}^{-3}$ , MSA:  $6.0 \text{ ng m}^{-3}$ ) and the MV (submicron:  $\text{Na}^+$ :  $17.0 \text{ ng m}^{-3}$ , MSA:  $1.8 \text{ ng m}^{-3}$ , Table S11). The concentrations of cloud water sulfate (average:  $2.9 \mu\text{g m}^{-3}$ , Table S12) and sodium were higher than in cloud water samples, collected at East Peak in Puerto Rico, which can be seen in Gioda et al. (2009). Our observed carbon concentration of FAA in cloud water at the MV station was between  $17\text{-}757 \mu\text{g C L}^{-1}$  and 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 ( $211 \pm 19 \mu\text{g C L}^{-1}$ , Bianco et al. (2016)), but showed a higher variance. Besides the concentration, the composition of FAA in cloud water also showed a high variability in the study presented here. In cloud water samples with  $\Sigma\text{FAA} < 65 \text{ ng m}^{-3}$ , Gly was usually dominant, followed by Ser. However, cloud water samples with  $\Sigma\text{FAA} > 290 \text{ ng m}^{-3}$  showed a higher complexity in FAA composition, including the concentrations of Asp and Ala. Other abundant FAA were Thr, Leu and Ile. In terms of the hydropathy classification, the first part of the campaign (27/09/2017-5/10/2017) was dominated by neutral FAAs, whereas a sudden increase of the hydrophilic FAAs was observed in its second part (06/10/2017-08/10/2017). Comparative studies on the FAA composition of cloud water in the marine environment are lacking, but especially in the second part of the campaign, it pointed to a local marine (biogenic) influence. The high concentrations of Asp might be related to diatoms and zooplankton in seawater (Hammer and Kattner, 1986). Scalabrin et al. (2012) reported local marine sources for Ile, Leu and Thr detected in aerosol particles, whereas Mashayekhy Rad et al. (2019) suggested coastal and marine phytoplankton and bacteria as possible sources for these amino acids. Therefore, the FAA composition might be related to an oceanic transfer via bubble bursting and/or microbial in-situ production. Interestingly, GABA, which was highly abundant on the aerosol particles, maybe due to biogenic production, was not present in the cloud water samples. The presence of the marine tracers (sodium, MSA) in cloud water supports a coupling to oceanic sources. In addition, the majority of low-level clouds were formed over the ocean and ocean-derived components are expected to have some influence on cloud formation (van Pinxteren et al., 2020). Nevertheless, contributions from the desert and other non-marine sources cannot be excluded.

The reason for the high concentrations of FAA in cloud water (compared to the oceanic and aerosol particle concentrations) remain speculative to date and will be subject of further studies. Altogether, the in-situ formation of FAA in cloud water by chemical processes in the cloud or by atmospheric biogenic formation or enzymatic degradation of proteins, as proposed by Malfatti et al. (2019), as well as by selective enrichment processes and pH dependent chemical reactions might be potential sources.

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

Only a few studies concerning which concern 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

Formatted: Font: +Body (Times New Roman), English (United States)

Formatted: Font color: Red

Formatted: Font: Not Bold

transfer of ~~organic-matter~~OM (sum parameter for lipids, carbohydrates and proteins) from the ocean surface into ~~the~~ marine aerosol ~~particles under controlled conditions~~ using a bubble-bursting experimental system ~~under controlled conditions~~.

Within the here presented study, a 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; and 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 ~~overabove~~ water and the mass concentration of trace ~~metal~~metals and inorganic marine ~~trace~~tracers (sodium, MSA) ~~concentration~~ (Table S8) strongly suggest a dominant marine origin of ~~the air masses and therefore no significant contributions from~~. Sources other than marine (dust or continental sources) are, by contrast, of minor importance during this sampling period. The averaged values of these sampling days represent a case study to combine and compare the ~~FAAFAAs~~ in all matrices to investigate a possible transfer of ~~FAAFAAs~~ from the ocean into the atmosphere and a possible transport of FAA inside FAAs within 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. ~~S1S2~~.

The averaged FAA composition of this case study in all marine compartments is ~~presented~~shown in Fig. 4-4. The high complexity of FAA observed in seawater was also found in the aerosol particles as well as in cloud water, and generally shows a high similarity between FAA in the different compartments. All marine compartments contained Gly, Ser, Glu and Ala as dominant species, i.e. representatives of the hydrophilic, neutral and hydrophobic groups. However, the percentage contribution of the individual FAAs to the  $\Sigma$ FAA varies within the different compartments.

Representatives of the hydrophilic, neutral, 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. For a better comparison of the individual amino acids, the ~~reactivity~~mean life time  $\tau$  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~~S13~~. The mean life time  $\tau$  of the hydrophilic, neutral and hydrophobic and aromatic individual amino acids are discussed below with respect to their distribution within depends on the pH-dependent rate constant  $k$  and the OH radical concentration of the different ~~marine matrices and with regard to a potential transfer~~ atmospheric scenarios (SI, Eq. (3)).

#### 3.4.1. ~~Hydrophlic~~Hydrophilic amino acids

The hydrophilic amino acids (Asp, Glu, GABA) ~~were found~~comprised a significant fraction in the seawater (Asp, Glu), ~~ULW and the SML, as well as in the (submicron) aerosol particles at the CVAO (Asp, Glu, GABA), in 1.2-3.5  $\mu$ m (B4) aerosol particles at the MV (Asp, Glu) and in the and in cloud water sample (Asp, Glu) (Fig. 4a-d). Glutamic acid was present in the seawater and in~~ They were not detected in the supermicron aerosol particles. A conspicuous finding is the high concentration of GABA, which is present exclusively in the submicron aerosol particles at the CVAO indicating that Glu might preferably be transferred from the ocean into the atmosphere possibly via bubble bursting. In addition, the presence of Glu in aerosol particle samples (1.2-3.5  $\mu$ m) at the MV (B1) and in cloud water samples suggests that Glu was not only transferred from the

Formatted: English (United States)

Formatted: Font: Times New Roman

Formatted: English (United States)

Formatted: Font: Times New Roman

Formatted: English (United Kingdom)

Formatted: English (United Kingdom)

ocean, but also transported (upwards) in the marine environment. The mean lifetime  $\tau_{B2}$ : 0.05-0.42  $\mu\text{m}$ ) at the CVAO. Despite the relatively high LOQ of Glu (remote aerosol case: 0.02 d, remote cloud case: 3.3 d, GABA in seawater (Table S12), showed a comparatively low atmospheric reactivity indicating that S1), a transfer process from the ocean into the atmosphere and a vertical transport without transformation reactions major abundance of Glu is likely. Similar to Glu, the amino acid aspartic acid could be detected in all investigated compartments (Fig. GABA in seawater would be detectable, 4a-d). Since correlations 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, which has been detected in all marine compartments. Furthermore, it can be produced by microorganisms (Dhakal et al., 2012) and is considered as an indicator for the microbiological decomposition of organic matter OM (Dauwe et al., 1999; Engel et al., 2018). The presence abundance of GABA on the submicron aerosol particles pointed out suggests that (marine) microorganisms were present on the aerosol particles and likely produced GABA via microbiological decarboxylation of Glu.

Formatted: English (United Kingdom)



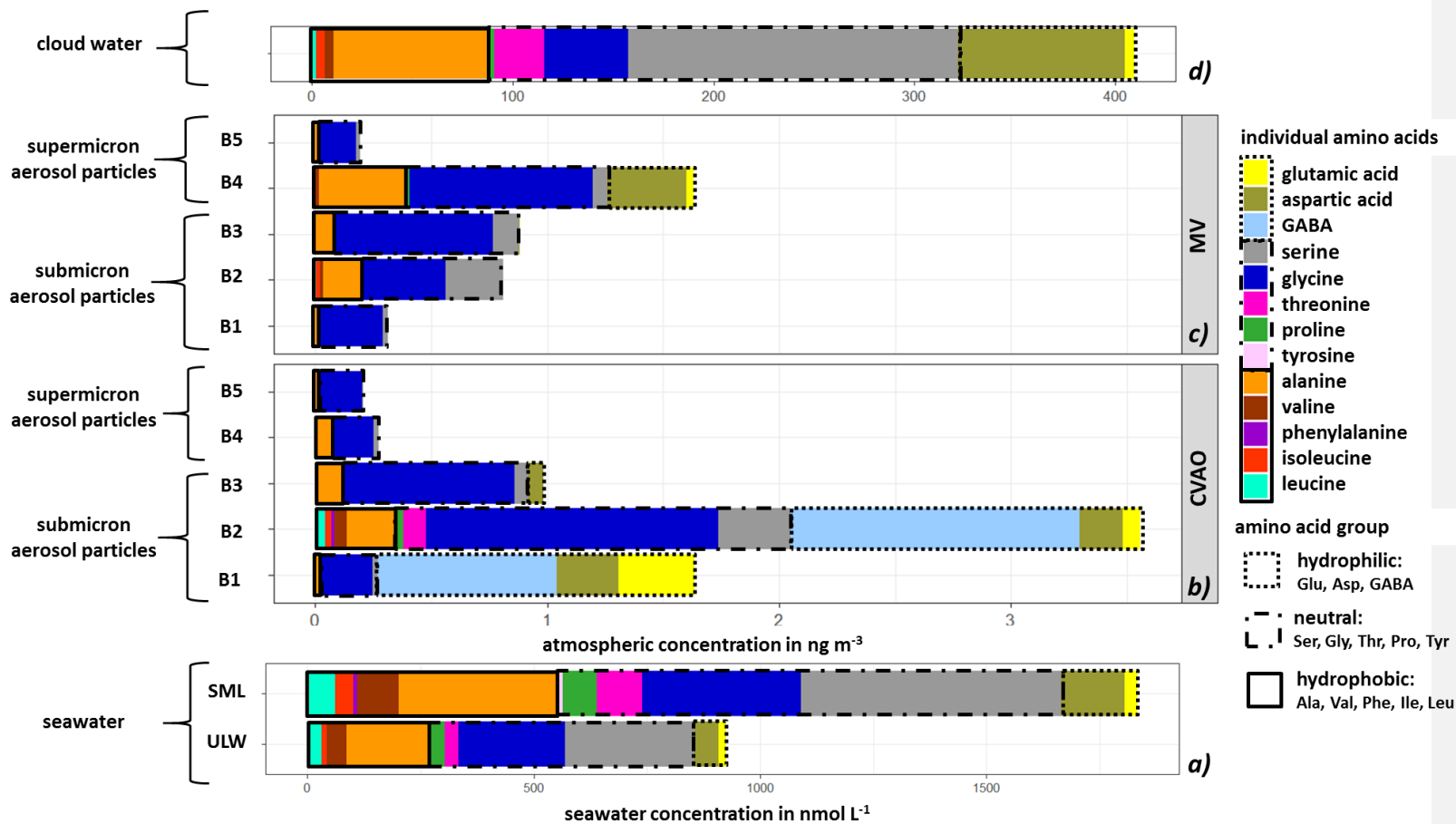
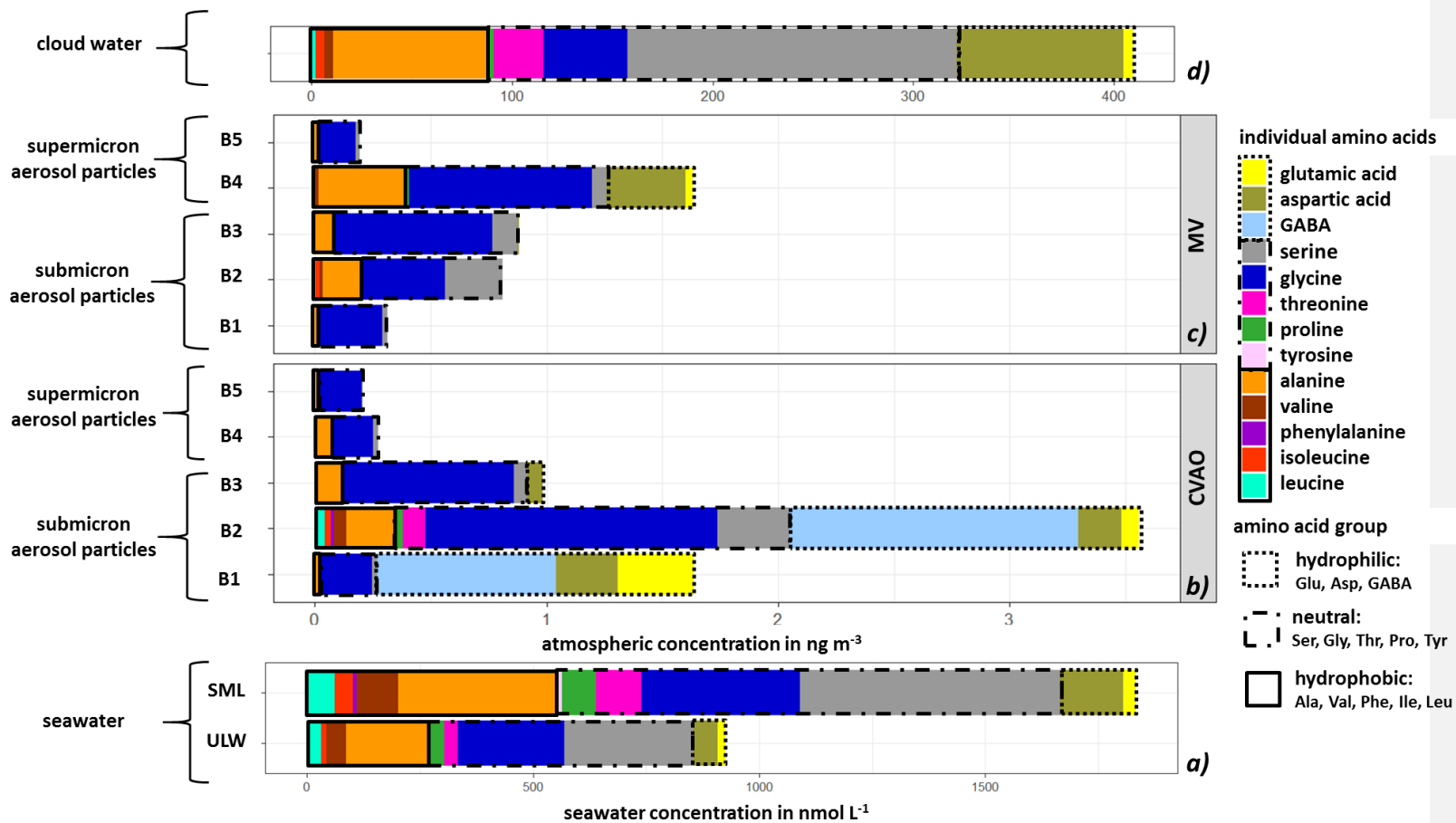


Figure 4: Case study: individual FAA concentration in a) seawater samples (ULW, SML)  $\text{nmol L}^{-1}$ , in b) size-segregated aerosol particle samples at the CVAO and c) at the MV station (size range:  $0-4 \text{ ng m}^{-3}$ ) and in d) cloud water sample (size range:  $0-400 \text{ ng m}^{-3}$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

Microbial processes on marine particles have recently been reported by Malfatti et al. (2019). The authors observed a diverse array of microbial enzymes transferred from the ocean into the atmosphere with an even higher activity on the particles compared to seawater. On this basis, they hypothesized that active enzymes can dynamically influence the composition of marine aerosol particles after ejecting from the ocean. The high GABA concentrations on the aerosol particles reported here are well in line with this hypothesis. Interestingly, GABA was not detected in



~~GABA was not detected in~~ cloud water samples, although bacteria were found ~~in cloud water~~ during the ~~MarParCloud~~ campaign ~~in cloud water~~ (van Pinxteren et al., ~~2019a~~2020) and the ~~whose~~ presence of ~~bacteria in cloud waters~~ has been reported in the literature (~~Jiaxian et al., 2019~~). ~~Whether GABA was~~ (Jardine, 2009; Vaitilingom et al., 2013; Jiaxian et al., 2019). ~~It remains speculative whether GABA was~~ degraded in cloud water despite its rather long lifetime (remote cloud case: ~~1.2~~ ~~428.8 h~~, Table ~~S12~~S13) or whether ~~GABA~~it was not produced by the bacteria in cloud water. ~~Asp has been detected in all~~ marine compartments and showed high cloud water concentrations. ~~Correlations between Asp with diatoms and zooplankton~~ have been reported for the marine environment (Hammer and Kattner, 1986).



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

~~remains speculative.~~

Hence, the occurrence of Asp in the marine environment can be attributed to a biogenic origin, whilst the high concentrations of Asp in cloud water (Fig. 3 & 4d) might be related to an oceanic source. In the Antarctic, Barbaro et al. (2015) attributed the hydrophilic amino acid fraction mainly to locally produced aerosol particles. According to the biogenic sources of the

5 hydrophilic acids and their characteristics observed here, a local marine source for Asp and Glu, together with the biogenic formation of GABA on the aerosol particles the Cape Verde islands could be prevalent.

#### 3.4.2 Neutral and hydrophobic amino acids

Neutral amino acids were generally the amino acid group with the highest concentration in all investigated marine

10 compartments, accounting for more than 50% of the FAA total (Fig. 4a-d). Neutral amino acids were generally the amino acid group with highest concentration in all investigated marine compartments (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 via bubble bursting. A further explanation

15 approach for the appearance 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 Ser and Gly were the dominant representatives of this group. Compared to other amino acids, Gly and Ser

20 have a very low atmospheric reactivity (McGregor and Anastasio, 2001) and therefore a higher mean lifetime  $\tau$  (Gly: 0.48 h, Ser: 0.24 h; remote aerosol case, Table S13). Due to its atmospheric stability, Gly is proposed as an indicator for long-range transport (Barbaro et al. (2015) and references therein) and has a very low atmospheric reactivity (McGregor and Anastasio, 2001). Gly and Ser have a higher mean lifetime  $\tau$  (Gly: 0.02 d, Ser: 0.01 d; remote aerosol case, Table S12) compared to other

25 investigated amino acids (usually  $\tau \leq 0.01$  d, Table S12). The neutral amino acid proline However, our results clearly show that Gly and Ser are also present in seawater to a high extend, likely resulting from the siliceous exoskeleton of diatom cell walls (e.g. Hecky et al. (1973)). Hence, besides long-range transport, a transfer from the ocean via bubble bursting might be an

additional likely source of the stable, long-lived FAA in the atmosphere. The neutral amino acid Pro 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.~~

30 ~~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.~~

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, and might thus be used as a tracer for an oceanic source. The presence of Pro in all marine compartments suggests a transfer from the ocean into the atmosphere up to cloud level. This is supported by the comparatively low atmospheric reactivity of Pro (remote aerosol case: 0.24 h, Table S13). Finally, the hydrophobic FAAs Ile, Leu and Thr were found in all marine compartments in low concentrations. They are classified as relatively reactive amino acids and their abundance has been attributed to local or medium local sources consequently (e.g. Mashayekhy Rad et al. (2019)). Their low but constant abundance in all marine matrices again indicates a bubble-bursting transfer.

### 3.4.3 Aromatic amino acids

Aromatic FAAFAAs as phenylalaninePhe and tyrosineTyr were present in seawater, but not on the aerosol particles and, neither in cloud water samples. It could be assumed that these aromatic FAAFAAs were either not transferred from the ocean into the atmosphere, or they reacted already reacted after their transfer because of due to chemical transformation reactions, or they were not detected because of their low atmospheric concentration. The mean lifetime  $\tau$  of Phe (0.0006 d014 h) and Tyr (0.0003 d007 h) (Table S12S13) showed that both FAAFAAs had a comparatively high atmospheric reactivity ( $\tau < 1$  min) at remote aerosol case conditions. Hence, a fast rapid chemical reaction of these compounds is most likely. Moreover, previous studies reported low atmospheric concentrations of Tyr and Phe on aerosol particles. Barbaro et al. (2011) found Phe (0.5 ng m<sup>-3</sup>) and Tyr (0.3 ng m<sup>-3</sup>) with a contribution < 1 % to  $\Sigma$ FAA ( $\Sigma$ FAA: 42.5 ng m<sup>-3</sup>) on TSP samples in urban background (Venice, Italy). In our study at the CVAO, the mean value of  $\Sigma$ FAA in PM<sub>10</sub> aerosol particles was 3.8 ng m<sup>-3</sup> (section 3.2). Assuming that Phe and Tyr were contributing to  $\Sigma$ FAA in a very small fraction as reported in Barbaro et al. (2011), their concentrations were would be below the detection limit; and could thus probably not be detected. It can therefore be concluded that the aromatic FAAFAAs could either not transferred from the ocean into the be quantified on aerosol particles due to the sensitivity of the analytical method used here, or they react very fast quickly in the atmosphere and could therefore not be detected.

### 3.4.4 Transfer of amino acids from the ocean into the atmosphere

The high similarity concerning the main FAA species within the different compartments, together with the high concentration of ocean-derived compounds (Na<sup>+</sup>, MSA) in size-segregated the aerosol particles. The EF<sub>aer</sub>, calculated using Eq. (2), is often included and cloud waters, suggest a coupling between the FAA in the ocean- and the atmosphere transfer considerations as a quantitative metric for comparing compounds in the ocean and in the atmosphere is the EF<sub>aer</sub> (Eq. (2)). The concept is mainly applied to closed systems (e.g. RussellQuinn et al. (20102015), van Pinxteren et al. (2017)). For the calculated EF<sub>aer</sub>, it should be noted that no further Rastelli et al. (2017)) because FAA formation or degradation pathways on the aerosol particles are considered, including biological or photochemical atmospheric reactions, or

Formatted: Font: +Body (Times New Roman)

Formatted: Font: +Body (Times New Roman)

Formatted: Font: Not Bold

Formatted: Font: Not Bold

and possible transport from other than marine sources is included are excluded in this parameter. The  $EF_{aer}$  However, for comparison purposes, it might be useful to calculate the  $EF_{aer}$  also from open systems as done e.g. by Russell et al. (2010) or van Pinxteren et al. (2017). The averaged  $EF_{aer}$  of  $\Sigma$ 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 based on SML and ULW concentrations are presented shown

5 in Fig. 5. The  $EF_{aer}$  of  $\Sigma$ FAA

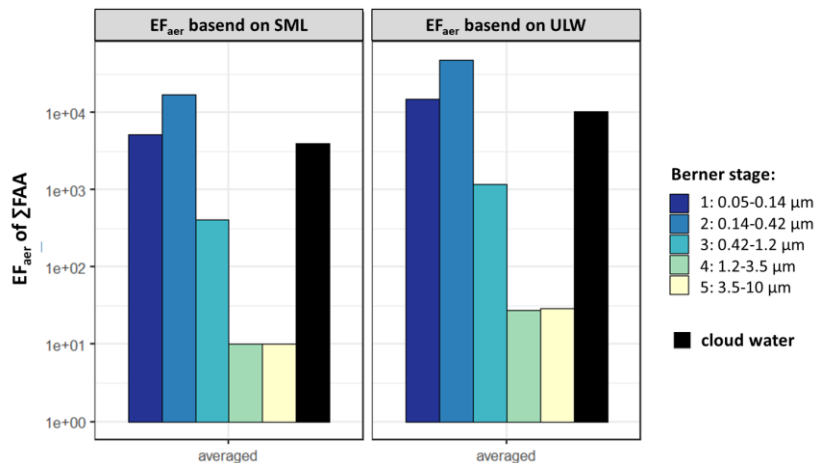


Figure 5: The averaged aerosol enrichment factor ( $EF_{aer}$ ) of  $\Sigma$ FAA in the size-segregated aerosol particle samples (Berner stage 1-5) at the CVAO and the cloud water enrichment factor ( $EF_{cw}$  in black) based on SML (left) and on ULW (right) calculation (Eq. (2))

10 The  $EF_{aer}$  of  $\Sigma$ FAA, based on SML, were 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 (range  $4 \cdot 10^2$  (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.

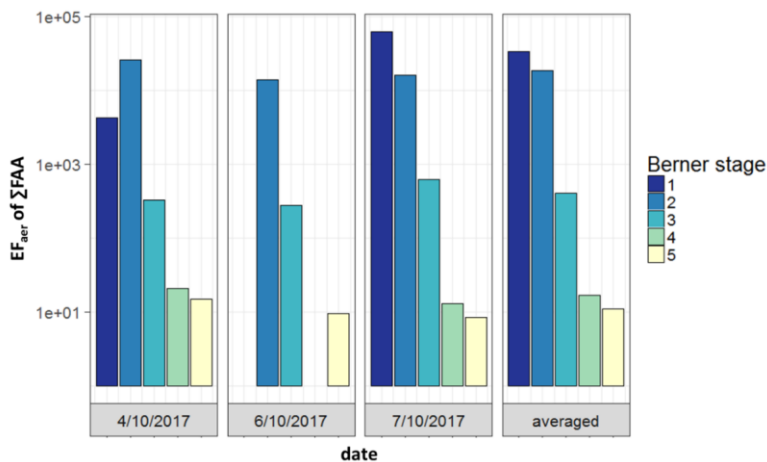


Figure 5: Enrichment factor aerosol ( $EF_{aer}$ ) of  $\Sigma$ FAA in the size-segregated aerosol particle samples (Bernier stage 1-5) at the CVAO on sampling days of the case study (4/10/2017, 6/10/2017, 7/10/2017) and as an averaged  $EF_{aer}$

van Pinxteren et al. (2017)  $5 \cdot 10^3$  (B1). Furthermore, the calculated  $EF_{aer}$ , based on ULW, was up to one order of magnitude higher in the aerosol particles than the  $EF_{aer}$ , based on the SML. This is due to the different FAA concentrations in seawater (section 3.1), as the sodium values were very similar with  $12.45 \text{ g L}^{-1}$  in the ULW and  $12.53 \text{ g L}^{-1}$  in the SML. van Pinxteren et al. (2017) showed that the  $EF_{aer}$  of OC the WSOC in the submicron marine ambient aerosols were aerosol particles at the Cape Verde ranged between  $10^3$  up to and  $10^5$ . The averaged  $EF_{aer}$  of the WSOC during our campaign in the submicron size range was between  $2 \cdot 10^3$  and  $1 \cdot 10^4$  and between  $3 \cdot 10^2$  and  $4 \cdot 10^2$  in the supermicron size-range (Table S13S14) and in good agreement with van Pinxteren et al. (2017). Comparing the  $EF_{aer}$  of  $\Sigma$ FAA ( $1 \cdot 10^1$ - $62 \cdot 10^4$ ) with the  $EF_{aer}$  of WSOC ( $1 \cdot 10^1$ - $2 \cdot 10^4$ ) in the submicron size-range, both  $EF_{aer}$  are in the same order of magnitude and showed high enrichments compared to the SML. Furthermore, Moreover, similar percentages of  $\Sigma$ FAA were observed for the DOC in the SML (up to 7.6%) (section 3.1) and for the WSOC on the submicron aerosol particles (up to 5.3%) (section 3.2) were observed.

Previous studies showed have shown that organic material OM ejected into the atmosphere during bubble bursting, resulting results in the formation of sea spray aerosol particles containing OM 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 within OM and are suggested to transfer OM from the SML to onto submicron aerosol particles (Wilson et al., 2015). The supermicron aerosol particles rather tend to form from the larger jet droplets and therefore thus represent the ULW composition (Blanchard, 1975; Wilson et al., 2015). From the ambient measurements performed here, we We cannot derive mechanistic transfer characterizations. However from the ambient measurements performed here. Nevertheless, 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 which transfer OM from the ULW) also have the potential to contribute significantly to the formation of submicron sea spray aerosol particles therefore, so, jet droplets can also contribute to FAA formation as well.

### 5 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 the aerosol particles (Table S8) with  $\Sigma$ FAA concentrations between 11.2 and 489.9 ng m<sup>-3</sup>. The inorganic marine tracers in cloud water (Na<sup>+</sup>: 5.7  $\mu$ g m<sup>-3</sup>, MSA: 25.1 ng m<sup>-3</sup>, Table S11) were also present in higher concentrations compared to the aerosol particle samples at the CVAO (submicron: Na<sup>+</sup>: 72.3 ng m<sup>-3</sup>, MSA: 6.0 ng m<sup>-3</sup>) and at the MV (submicron: Na<sup>+</sup>: 17.0 ng m<sup>-3</sup>, MSA: 1.8 ng m<sup>-3</sup>, Table S10), indicating an enrichment in cloud water. This enrichment was even stronger visible when comparing  $\Sigma$ FAA in cloud water and in the SML resulting in an enrichment factor of  $\Sigma$ FAA in cloud water ( $EF_{CW}$ ; Eq. (2)), with  $EF_{CW(\Sigma FAA)} = 4 \cdot 10^3$ . 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 to biogenic formation or enzymatic degradation of proteins, selective enrichment processes as well as pH dependent chemical reactions might be potential sources.

20

Applying the concept of the enrichment factor to cloud water and calculating the  $EF_{CW}$  (Eq. (2)), the  $EF_{CW(\Sigma FAA)} = 4 \cdot 10^3$  (based on SML) and  $1 \cdot 10^4$  (based on ULW) could be determined. As mentioned in section 3.3, several atmospheric processing (aging), oceanic transfer and biogenic-driven processes might contribute to this high enrichment and need to be addressed in future studies. The high FAA concentrations and enrichments might have implications on OM processing through clouds and are worth further studying.

25

## 4 Conclusion and Outlook

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 stations allowed to investigate FAAFAAs on a molecular level that, which 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 certain FAA contribution of FAA, especially of, in particular the hydrophilic amino acids Asp and Glu in the submicron aerosol particles at the CVAO, was probably resulted from local caused by sea spray. For the non-hydrophilic and might be transferred up to

30

cloud level. The neutral and hydrophobic amino acids, additional sources, such were also present in all marine compartments, suggesting some interconnections. Stable amino acids like Gly are often reported as long-range transport and chemical transformation can be important and aromatic tracers, but their abundance in seawater and marine air masses prevailing during the sampling period suggest an (additional) oceanic source. The oceanic link is supported by a high atmospheric concentration of ocean-derived compounds (sodium, MSA), a high fractional residence time of the air masses above water and a low-to-medium impact of other non-marine sources (based e.g. on the mass concentration of trace metals). In addition, some indications for the biological production of amino acids on the aerosol particles (GABA) were observed, supporting the recent finding of a high active enzymatic activity on marine aerosol particles. Aromatic amino acids are either not transferred from the ocean into the atmosphere or react very fast-quickly; in any case, they are present only in small concentrations close to the LOQ. By distinguishing between the submicron and the supermicron aerosol particles, differences in the chemical composition of these aerosol particle size classes could be elaborated (section 3.2). FAA identified, which show a much higher complexity of the FAA composition in the submicron aerosol particles. FAAs were present in the size range for aerosol particles connected to associated with CCN activity and cloud water, and might be connected to CCN activity due to their hygroscopicity and soluble character, however but this effect was not investigated here. Altogether, the here presented measurements suggest that several amino acids were transported. In a simplified approach, considering only a possible transfer 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  $\Sigma$ FAA was found to be between  $1 \cdot 10^4$ - $2 \cdot 10^4$  (supermicron) and  $2 \cdot 10^2$ - $6 \cdot 10^4$  (submicron size range). The similar composition together with the significant enrichment of  $\Sigma$ 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 and cloud water exhibited very high concentrations of FAA, enriched by a (neglecting e.g. atmospheric processing), the aerosol enrichment factor of  $4 \cdot 10^3$  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 was calculated. A high FAA enrichment processes or pH dependent chemical reactions are subject to future work. Altogether, the presence of in the submicron aerosol particles of  $EF_{aer(\Sigma$ FAA):  $2 \cdot 10^1$ - $6 \cdot 10^3$  and a medium enrichment on supermicron aerosol particles  $EF_{aer(\Sigma$ FAA):  $1 \cdot 10^1$ - $3 \cdot 10^1$  were observed. Applying the same concept to cloud water, an enrichment of  $4 \cdot 10^3$ - $1 \cdot 10^4$  was obtained. The high FAA concentrations ( $11.2$ - $489.9$  ng m<sup>-3</sup>) and enrichments in cloud water were reported here for the first time. Their composition, together with the 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 (sodium, MSA), indicate at least to some extent an oceanic sources on the local clouds transfer and biogenic formation that remains subject to future work. Altogether, the varying composition of FAAs in the different matrices shows that their abundance and their enrichments in the SML and their atmospheric transfer are not determined by single environmental drivers (e.g. wind speed) and/or simple physico-chemical

Formatted: English (United Kingdom)

Formatted: English (United Kingdom)

Formatted: English (United Kingdom)

parameters (e.g. surface activity). The ocean-atmosphere transfer of FAAs is influenced by biotic and abiotic formation and degradation processes. Further studies are required to unravel their drivers and understand their complex composition that, finally, have to be considered in OM transfer models. To the best of our knowledge, this study was the first to analyse FAA that simultaneously analyzed the FAA in all marine compartments - seawater including the ULW and the SML, size-segregated aerosol particles and cloud water – in such detail to obtain indications on their sources and interconnections.

Formatted: English (United Kingdom)

*Data availability.* ~~Data can be made~~The data are available ~~by through~~ the authors upon request. World Data Centre PANGAEA under the following link: <https://doi.pangaea.de/10.1594/PANGAEA.914220>.

#### 10 *Special issue statement.*

*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. We further acknowledge the professional support provided by the Ocean Science Centre Mindelo (OSCM) and the Instituto do Mar (IMar).

Formatted: English (United Kingdom)

Formatted: Font: Not Italic

*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.

Formatted: Space After: 6 pt

#### *References*

30 ~~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, 10.2216/10031-8884-30-1-1.1, 1991.

35 Barbaro, E., Zangrando, R., Moret, I., Barbante, C., Cescon, P., and Gambaro, A.: Free amino acids in atmospheric particulate matter of 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 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.
- 10 ~~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.~~
- 15 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., 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., Pöhler, 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.
- 20 Chan, M. N., Choi, M. Y., Ng, N. L., and Chan, C. K.: Hygroscopicity of ~~Water-Soluble Organic Compounds~~~~water-soluble organic compounds~~ in ~~Atmospheric Aerosols: Amino Acids~~~~atmospheric aerosols: amino acids~~ and ~~Biomass Burning Derived Organic Species~~~~biomass burning derived organic species~~, *Environ. Sci. Technol.*, 39, 1555-1562, 10.1021/es0495841, 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.
- 25 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.
- 30 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.
- 35 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.
- 40 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., Kirchgorg, 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.
- 45 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.
- 5 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.
- 10 [Gong, X., Wex, H., Voigtländer, J., Fomba, K. W., Weinhold, K., van Pinxteren, M., Henning, S., Müller, T., Herrmann, H., and Stratmann, F.: Characterization of aerosol particles at Cabo Verde close to sea level and at the cloud level – Part 1: Particle number size distribution, cloud condensation nuclei and their origins. \*Atmos. Chem. Phys.\*, 20, 1431-1449, 10.5194/acp-20-1431-2020, 2020.](#)
- 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<sub>10</sub> from Mexico City during 2000, *Chemosphere*, 61, 701-710, 10.1016/j.chemosphere.2005.03.063, 2005.
- 15 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.
- [Hecky, R. E., Mopper, K., Kilham, P., and Degens, E. T.: The amino acid and sugar composition of diatom cell-walls, \*Marine Biology\*, 19, 323-331, 10.1007/BF00348902, 1973.](#)
- 20 [Jardine, B.: Between the Beagle and the barnacle: Darwin's microscopy, 1837-1854, \*Studies in history and philosophy of science\*, 40, 382-395, 10.1016/j.shpsa.2009.10.007, 2009.](#)
- 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.
- 25 [Kanji, Z. A., Ladino, L. A., Wex, H., Boose, Y., Burkert-Kohn, M., Cziczó, D. J., and Krämer, M.: Overview of Ice Nucleating Particles, \*Meteorological Monographs\*, 58, 1.1-1.33, 10.1175/amsmonographs-d-16-0006.1, 2017.](#)
- 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.
- 30 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.
- 35 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.
- 40 [Letseher, R. T., Hansell, D. A., Carlson, C. A., Lumpkin, R., and Knapp, A. N.: Dissolved organic nitrogen in the global surface ocean: Distribution and fate, \*Global Biogeochemical Cycles\*, 27, 141-153, doi:10.1029/2012GB004449, 2013.](#)
- [M. Coggon, M., Soroshian, 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.](#)
- 45 [Mace, K. A., Duce, R. A., and Tindale, N. W.: Organic nitrogen in rain and aerosol at Cape Grim, Tasmania, Australia, \*Journal of Geophysical Research: Atmospheres\*, 108, doi:10.1029/2002JD003051, 2003.](#)

- Longhurst, A. R.: Chapter 9 - THE ATLANTIC OCEAN, in: *Ecological Geography of the Sea (Second Edition)*, edited by: Longhurst, A. R., Academic Press, Burlington, 131-273, 2007.
- Malfatti, F., Lee, C., Tinta, T., Pendergraft, M. A., Celussi, M., Zhou, Y., Sultana, C. M., Rotter, A., Axson, J. L., Collins, D. B., Santander, M. V., Anides Morales, A. L., Aluwihare, L. I., Riemer, N., Grassian, V. H., Azam, F., and Prather, K. A.: Detection of Active Microbial Enzymes in Nascent Sea Spray Aerosol: Implications for Atmospheric Chemistry and Climate, *Environmental Science & Technology Letters*, 6, 171-177, [10.1021/acs.estlett.8b00699](https://doi.org/10.1021/acs.estlett.8b00699), 2019.
- 5 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](https://doi.org/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](https://doi.org/10.1126/science.1103491), 2004.
- 10 Mashayekhy Rad, F., Zurita, J., Gilles, P., Rutgeerts, L. A. J., Nilsson, U., Ilag, L. L., and Leck, C.: Measurements of Atmospheric Proteinaceous Aerosol in the Arctic Using a Selective UHPLC/ESI-MS/MS Strategy, *J Am Soc Mass Spectrom*, 30, 161-173, [10.1007/s13361-018-2009-8](https://doi.org/10.1007/s13361-018-2009-8), 2019.
- 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](https://doi.org/10.1016/j.trac.2015.08.004), 2016.
- 15 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](https://doi.org/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 acids and alkyl amines, *Atmos. Environ.*, 35, 1091-1104, [10.1016/S1352-2310\(00\)00282-X](https://doi.org/10.1016/S1352-2310(00)00282-X), 2001.
- 20 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](https://doi.org/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-10-2709-2010](https://doi.org/10.5194/acp-10-2709-2010), 2010.
- 25 Niedermeier, N., Held, A., Müller, T., Heinold, B., Schepanski, K., Tegen, I., Kandler, K., Ebert, M., Weinbruch, S., Read, K., Lee, J., Fomba, K. W., Müller, K., Herrmann, H., and Wiedensohler, A.: Mass deposition fluxes of Saharan mineral dust to the tropical northeast Atlantic Ocean: an intercomparison of methods, *Atmos. Chem. Phys.*, 14, 2245-2266, [10.5194/acp-14-2245-2014](https://doi.org/10.5194/acp-14-2245-2014), 2014.
- Pandey, R., Usui, K., Livingstone, R. A., Fischer, S. A., Pfaendner, J., Backus, E. H. G., Nagata, Y., Fröhlich-Nowoisky, J., Schmäser, L., Mauri, S., Scheel, J. F., Knopf, D. A., Pöschl, U., Bonn, M., and Weidner, T.: Ice-nucleating bacteria control the order and dynamics of interfacial water, *Science Advances*, 2, e1501630, [10.1126/sciadv.1501630](https://doi.org/10.1126/sciadv.1501630), 2016.
- 30 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](https://doi.org/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](https://doi.org/10.1038/ngeo2092) Collins, D. B., Grassian, V. H., Prather, K. A., and Bates, T. S.: Chemistry and Related Properties of Freshly Emitted Sea Spray Aerosol, *Chem. Rev.*, 115, 4383-4399, [10.1021/cr5007139](https://doi.org/10.1021/cr5007139), 2015.
- 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](https://doi.org/10.1038/s41598-017-10563-z), 2017.
- Reinthal, T., Sintés, E., and Herndl, G. J.: Dissolved organic matter and bacterial production and respiration in the sea-surface microlayer of the open Atlantic and the western Mediterranean Sea, *Limnol. Oceanogr.*, 53, 122-136, [10.4319/lo.2008.53.1.0122](https://doi.org/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](https://doi.org/10.1002/jgrd.50417), 2013.
- 45

- 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.
- Scalabrín, 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:baaso>2.0.co;2, 1997.
- 10 [Väitilingom, M., Deguillaume, L., Vinatier, V., Sancelme, M., Amato, P., Chaumerliac, N., and Delort, A.-M.: Potential impact of microbial activity on the oxidant capacity and organic carbon budget in clouds, \*Proceedings of the National Academy of Sciences\*, 110, 559-564, 10.1073/pnas.1205743110, 2013.](#)
- [van Pinxteren, D., Brüggemann, E., Gnauk, T., Müller, K., Thiel, C., and Herrmann, H.: A GIS based approach to back trajectory analysis for the source apportionment of aerosol constituents and its first application, \*J. atmos. chem. \(Print\)\*, 67, 1-28, 2010.](#)
- 15 van Pinxteren, M., Müller, 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., Fiedler, B., van Pinxteren, D., Iinuma, Y., Körtzinger, A., and Herrmann, H.: Chemical characterization of sub-micrometer aerosol particles in the tropical Atlantic Ocean: marine and biomass burning influences, \*J. Atmos. Chem.\*, 72, 105-125, 10.1007/s10874-015-9307-3, 2015.](#)
- 20 [van Pinxteren, M., Barthel, S., Fomba, K. W., Müller, K., von Tümpling, 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. Anthropol.\*, 5, 21, 10.1525/elementa.225, 2017.](#)
- [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, 2019.](#)
- 25 [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., 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 – Anislands – an~~ introduction and overview to the MarParCloud campaign, \*Atmos. Chem. Phys. Discuss.\*, 2019, 1-63, 20. 6921-6951, 10.5194/acp-2019-997, 2019a20-6921-2020, 2020.](#)
- [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.](#)
- 35 [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, 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.
- 40 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., Judd, C., Kılıthau, 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.
- 45 [Wolber, P., and Warren, G.: Bacterial-ice-nucleation proteins, \*Trends in Biochemical Sciences\*, 14, 179-182, 10.1016/0968-0004\(89\)90270-3, 1989.](#)

[Wurl, O., Ekau, W., Landing, W. M., and Zappa, C. J.: Sea surface microlayer in a changing ocean - A perspective, \*Elementa-Sci. Anthrop.\*, 5, 11, 10.1525/elementa.228, 2017.](#)

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

5