

Referee 1: Review of van Pinxteren et al. 2023:

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

General comments:

This manuscript describes the measurement of relatively labile biogenic organic compounds of three major classes (amines, carbohydrates, and lipids) in three natural media relevant to the air-sea exchange of organic compounds: bulk surface seawater, the sea surface microlayer, and submicron aerosol. The measurements were made at or near the Cape Verde Atmospheric Observatory, a coastal site surrounded by oligotrophic waters. Roughly half of the organic carbon in the aerosols was quantified, and a major result is that the bulk of this material was lipids.

These measurements are certainly of value to the community of air-sea-exchange and marine aerosol composition researchers, and I hope this work can ultimately be published in ACP. Measuring the relevant compounds at a location from bulk seawater through SML to aerosol is a powerful approach that is worth pursuing.

We thank the Referee for the evaluation and the constructive comments. Replies to the specific Referee's comments are provided below in red and new parts included in the manuscript are marked in green. Line numbers refer to the revised (clean) version.

R1-C1: I have one main concern about the results, and that is the potential role of gas phase adsorption onto (and potentially revolatilization from) the aerosol filters in the high-volume sampler. This is of particular concern given the apparent importance of lipids in the sampled aerosol. The major contributors include hydrocarbons and free fatty acids. Both n-alkanes and fatty acids appear to be subject to gas-surface partitioning effects in ambient aerosol filter samplers (Kavouras et al., 1999; Lawler et al., 2020). The authors need to raise this issue in the manuscript, explain any steps they took to mitigate these effects, and characterize as best as possible what errors (if any) they expect may be associated with this issue. In general there needs to be more description of the sampling methods (see below).

The referee raised a very important issue that is sampling artefacts via gas phase adsorption and re-volatilization of (semi-)volatile compounds from filters. In the mentioned reference of Kavouras et al. (1999), a self-constructed system consisting of diffusion denuders prior to collecting particles on filters has been applied to account for volatilization losses of notably low molecular weight alkanes. The authors could correct for re-volatilisation effects.

However, the authors also pointed out that finding an appropriate denuder coating for organic non-polar analytes is very challenging (Kavouras et al., 1999). Each introduction of a new system enlarges the risk of sample contamination and losses of the target analytes and require therefore comprehensive tests. Such denuder devices as applied in Kavouras et al., 1999 are not easily compatible with the standard high volume filter samplers, usually applied in aerosol sampling studies. Furthermore, low sampling rates are required when applying a denuder system because of the low diffusion coefficient of semi-volatile organic molecules. For trace analysis of organic compounds in remote regions as performed here, however, a high flow rate is needed to sample enough material of trace compounds in remote environments.

The other reference, Lawler et al., (2020), found that “the field blank ... were comparable in magnitude to the samples. This likely indicates a major gas phase contribution or revolatilization and subsequent deposition on the following filter.” To this end, they could not determine accurate concentrations of these compounds.

Regarding our lipid analysis, we addressed this issue by the usage of field blanks (similar to Lawler et al. 2020), as previously described by Triesch et al. (2021b). The field blanks were prepared using pre-baked quartz fiber filters without an active sampling and treated according to the same procedure as the field samples. The concentrations of the lipid classes were calculated by external calibration. Each sample was measured twice with a relative standard deviation < 10 %, and field blanks, which were always below 20% of the real aerosol particle sample, were subtracted. All presented values were corrected for the field blank. Hence, our results were different to the issues found by Lawler et al., (2020) and less affected by gas phase absorption as described by Lawler et al., (2020). This could be related to different concentrations, sampling times, filter material etc. To this end, we think that the analysed particulate concentrations are robust, however we fully agree that the values include a certain level of uncertainty and added a description of field blank handling and remaining issues this in the revised manuscript in the new chapter 2.2.3 (Detection limits and blank handling). Finally, we want to underline that no aerosol sampling system is without artefact problems. We are suggesting the following text (line 186 ff):

“Regarding the aerosol sampling system, it needs to be underlined that artefact problems and overestimations due to gas phase absorption and underestimations due to re-volatilisations of the analytes from the filters cannot be accounted for and represent a certain level of uncertainty.”

As well as (line 304 ff):

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

R1-C2: The grammar and phrasing are by and large OK, but sometimes awkward enough that the meaning is unclear. The work would benefit from a going-over by a native English speaker.

Following this suggestion, a native English speaker has carefully revised the language. To this end, expression and grammar were improved.

R1-C3: To summarize, these results are certainly relevant to the problem of understanding sea spray aerosol composition. Some further description and likely analysis are needed to either show that the aerosol lipid concentrations and enrichment factors should be taken at face value, or what the approximate error may be. If the authors are able to address this satisfactorily, I would recommend this for final publication in ACP.

We thank the referee for this positive comment and have addressed the issues for artefacts and the resulting calculations of the enrichment factors. In addition and related to the comments from the other referee, we have performed several changes that clarify the calculation of the enrichment factor and finally added some statistical interpretation on the results.

Specific comments:

R1-C4: L48: “The same compounds studied in the seawater...” Sentence unclear. Reword, make 2 sentences?

We agree and rephrased as follows (line 47 ff):

“In contrast, the amino acids exhibited a higher enrichment in the SML with an average EF_{SML} of 2.3 ± 0.4 although they are less surface-active than lipids”.

R1-C5: L53: relative composition of the single organic compounds. Maybe relative “abundances” of the organic compounds?

We agree and changed it accordingly.

R1-C6: L79 awkward sentence.

We agree and changed it as follows (line 79 ff):

“Marine aerosol particles, their composition, sources and connection to the upper ocean are not yet fully understood, however important, as they impacts the carbon cycle and radiative properties of aerosol particles.”

R1-C7: L175: Please describe the aerosol sampling setup in more detail. Was there any attempt to remove gas phase species from the sampler, e.g. a denuder? Is there any way to assess breakthrough of compounds revolatilized from the filter? What is the timescale/frequency of the sampling? What are the handling procedures for the aerosol filters? Are there blank filters of any kind to correct for backgrounds? I realize some of this info is in Triesch et al. 2021b, but please include more info here and cite that paper for the rest.

As recommended, we added further information about the aerosol sampling. We addressed the blank issue as pointed in our reply out above. We added Table S1 with a detailed schematic on the sampling, sample handling and analysis. In addition, we included further information of the aerosol sampling as follows (line 182 ff):

“Submicron aerosol particles were sampled on preheated 150 mm quartz fiber filters (Munktell, MK 360) at a flow rate of about 700 L min^{-1} with a high volume PM_{10} aerosol sampler (Digitel, Riemer, Germany) installed on the 30 m height tower at the coastline. The sampling times were usually set to 24 h and are listed in Tab. S4 and S5, as well as in Triesch et al., 2021b and in van Pinxteren et al., 2020).”

R1-C8: L178: for a boat “to motor” is probably better than “to drive”

According to the suggestions of the English native speaker we changed the expression to “go out on the open ocean”.

R1-C9: L306 Please explain the difference between DAA and FAA in this and the Triesch study. It’s not clear to what extent those are to be considered the same or different.

We agree and added (line 363 ff):

*“The high variability of the DAA concentrations agreed well with the FAA **that comprise the sum of unbound individual amino acids i.e. not bound in a peptide or protein** and were measured at this location during the MarParCloud campaign (Triesch et al., 2021a).”*

R1-C10: L727 Seems to state too much. Maybe it’s “reasonably representative” of most of the ocean surface? I agree it’s at least better than coastal sites with upwelling e.g. It may be worth mentioning that this extrapolation to the globe also neglects any potential seasonal changes.

We agree and added “**reasonably** representative” as well as (line 817 ff): *“However, this approach only includes the bubble-bursting-mediated transfer of the respective compounds, **neglects any potential seasonal changes** and neglects additional sources and formation processes.”*

R1-C11: L759 “with respect to sea salt” maybe is meant?

We agree and changed it accordingly.

R1-C12: Table S5: Please make it clear in the caption that these relative mol fractions are relative to the total of each type (DAA, DCHO, and DL) analyzed.

We added in the Caption of Figure 2: *“Mol% were calculated from the molar masses of the respective analytes. For the lipid groups, the molar masses of the surrogate standard (sec. 2.2.2 and Tab. S8) are applied. The relative mol fractions are relative to the total of each type (DAA, DCHO, and DL) analysed.”*

References:

Kavouras, I. G., Lawrence, J., Koutrakis, P., Stephanou, E. G. and Oyola, P.: Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile: Source reconciliation and evaluation of sampling artifacts, *Atmos. Environ.*, 33(30), 4977–4986, doi:10.1016/S1352-2310(99)00281-2, 1999.

Lawler, M. J., Lewis, S., Russell, L. M., Quinn, P. K., Bates, T. S., Coffman, D. J., Upchurch, L. and Saltzman, E. S.: North Atlantic marine organic aerosol characterized by novel offline thermal desorption mass spectrometry: Polysaccharides, recalcitrant material, and secondary organics, *Atmos. Chem. Phys.*, 20(24), 16007–16022, doi:10.5194/acp-2020-562, 2020.

Referee 2: Review of the paper:

“Amino acids, carbohydrates and lipids in the tropical oligotrophic Atlantic Ocean: Sea-to-air transfer and atmospheric in situ formation” from M. van Pinxteren and co-authors.

This paper presents a very interesting work on the sources of organic compounds in the atmosphere from marine surfaces that are still badly characterized. The authors investigated the sea-to-air transfer by measuring a selection of organic compounds both in the surface sea water and in submicron aerosol particles collected at a coastal site (Cape Verde Atmospheric Observatory). Those classes of biogenic compounds are amino acids, carbohydrates, and lipids; they are strongly related to the marine biological activity. The enrichment of those compounds between the 3 sampled natural media (bulk sea water, sea surface microlayer, submicron aerosol) are evaluated in this study.

These measurements are original and provide to the community very important information on the potential mechanisms leading to the generation of organic aerosols in the atmosphere: enrichment of the surface microlayer by biotic and abiotic processes, selection of compounds according to their physical properties (hydrophobicity), etc.

We thank the Referee for the evaluation and the constructive comments. Replies to the specific Referee’s comments are provided below in red and new parts included in the manuscript are marked in green. Line numbers refer to the revised (clean) version.

R2-C1: My major concern is relative to the fact that the various samples that have been analysed have not been collected at the same period. The conclusions of the article are based on average values analysed over the period of the field campaign.

The referee is right, in the present work, we did not have the respective day to day measurements for comparisons available. However, we don’t think this is necessarily needed, as our focus was not on showing trends of the particular compounds over the campaign (this was done in (Triesch et al., 2021a;Triesch et al., 2021b) but rather on comparing the three different groups with each other. Therefore, the usage of average values (with min and max values as explained in chapter 2.3) is justified. We underlined this more clearly in the revised version and added (line 337 ff):

“It should be noted that EF_{SML} and EF_{aer} comparisons include samples from the same campaign but not necessarily from the same exact date (details in Tab.1 and Tab S2-S5). However, as our focus was not on showing trends within the campaign (this was covered by Triesch et al., 2021a,b) but rather on comparing the three different OC groups with each other, the usage of average values is justified.”

R2-C2: Moreover, the “link” between the two sites allowing the collection of sea water and atmospheric particles is not analyzed in this study. The authors need to mention the limits of their approach more explicitly concerning these two points.

The referee raised an important point that is the comparability between seawater and atmosphere (i.e. the “link”).

We addressed this link between seawater and aerosol by calculating the aerosol enrichment factor ($EF_{aer.}$) that combines the seawater and aerosol compartment with each other (as described in chapter 2.3) and is a commonly applied method (e.g. (Sander et al., 2003)).

Regarding the calculation of the $EF_{aer.}$: As processes in the water and the air happen on different timescales a day-to-day comparisons of aerosol and SML samples (meaning that aerosol concentrations, typically sampled at a 24-hour interval are combined with SML concentrations (spot samples) collected in the middle of the aerosol sampling period) may not be the most robust way to account for this. In recent studies, we started to average the organic matter concentration in the seawater and in the aerosol (over the whole campaign) and related the values to each other, e.g. for TEP and carbohydrates in (van Pinxteren et al., 2022;Zeppenfeld et al., 2021) as it was done other by other authors as well (Russell et al., 2010) In this way we are confident to achieve a general better robustness. In order to address the $EF_{aer.}$ variance, in the revised version, we added the min-max values of the $EF_{aer.}$ in Tab.1. This information was added in chapter 2.3 as follows (line 665 ff):

“it needs to be considered that processes in the ocean and the atmosphere happen on different timescales and to achieve a better robustness, we applied the average concentration values of the respective compound group in the seawater and on aerosol particles as done in (Zeppenfeld et al., 2021;van Pinxteren et al., 2022).” “To investigate the variability of the $EF_{aer.}$, the minimum ratio of $c_{(analyte)aer.} / c_{(Na+)aer.}$ vs. the maximum ratio of $c_{(analyte)seawater} / c_{(Na+)seawater}$ was applied and vice versa. “

To further underline the link between the ocean and the atmosphere, in the revised version, we added the backward trajectory from this campaign in the SI, Fig. S2 (related to a later comment by the referee) to underline the similar origin of the air and ocean current. We added in the chapter 3.2.3. (line 674 ff):

*“The backward trajectories **during the time of the campaign** (Fig. S2) as well as the mass concentrations of inorganic ions and mineral dust tracers on the aerosol particles measured during the campaign suggested a predominant marine origin with low to medium dust influences (van Pinxteren et al., 2020). Moreover, dust generally influences the supermicron particles to a larger extent than the submicron particles analysed here (Fomba et al., 2013). Hence, although different factors certainly affect the aerosol composition, it is reasonable to assume a strong oceanic contribution.*

In addition, we addressed the limitations of the study due to the limited sampling number and added (line 396 ff):

“However, it is important to mention that the number of samples that have been analysed is different and limited (Tab. 1 and Fig. 1) and samples from partly different dates of the campaign have been analysed and compared.”

By these modifications and clarifications, we are confident that we addresses the link between ocean and atmosphere and stated the limitation in a better way. These topics were raised again in the minor referee’ comments below and answered comprehensively.

R2-C3: However, the main conclusions of this work are relevant for the scientific community working on the chemical composition of sea spray aerosol that clearly play a role on the climate system (radiative aerosol properties and formation of cloud droplets and ice crystals). If the authors take into consideration these main points and consider the more minor comments listed below, I recommend accepting this article to ACP.

We thank the referee for this positive comment.

1 Introduction

R2-C4: - Lines 79-81: please rephrase this sentence.

Done. The new sentence reads (line 79 ff):

“Marine aerosol particles, their composition, sources and connection to the upper ocean are not yet fully understood, however important as they impacts the carbon cycle and radiative properties of aerosol particles.”

R2-C5: - Lines 82-84: could you add more information on the role of marine chemical composition on aerosol-cloud interaction (i.e., climatic effect).

As the referee suggested, we included some more information as follows (line 82 ff):

“Furthermore, the function of (marine) aerosol particles as cloud condensation nuclei (CCN) and ice-nucleating particles (INP), i.e. marine aerosol-cloud interaction is still elusive. Important information about marine CCN is still missing (e.g. (Bertram et al., 2018). Ocean-derived INPs have been suggested to play a dominant role in determining INP concentrations in near-surface air over remote areas such as the Southern Ocean, but their source strength in other oceanic regions and knowledge of what physicochemical properties determine INP efficiency remain largely unknown (Burrows et al., 2013;McCluskey et al., 2018a;McCluskey et al., 2018b).”

R2-C6: - Line 149: You write “atmospheric in situ formation”. I think this is more “atmospheric in situ transformation”. Could you confirm?

Yes, we confirm and changed it accordingly.

R2-C7: - At the end of this section, you should better describe your methodology. You followed the concentrations and speciation of OC from the sea to the atmospheric particles; this helps to evaluate the evaluate the enrichment factors of the various targeted compounds between the compartments. By this way, you can better assess, as you mentioned, “the coupling of marine aerosol particles to the sea surface biological and chemical properties”.

We thank the referee for this suggestion and added the following sentence to this paragraph (line 161 ff):

“Specifically, we followed the concentrations and speciation of OC from the sea to the atmospheric particles, which helps to evaluate the enrichment factors of the various targeted compounds between the compartments”.

2 M&M

2.1 Sampling strategy

R2-C8: - You describe in this section your sampling strategy.

It could be helpful for the reader to have a table where you indicate for all your samples:

- The type of samples: SML, ULW, AERO...
- The sampling period
- Meteorological information when available
- The sampling procedure (short description)
- Which kind of analysis has been performed for these samples: AA, CHO, Lipids, DOC/WSOC, IC, EC/OC, ...
- The analytical procedure (filtration, chemical treatment, analytical instrument...) (short description)

This table could be implemented in the manuscript or in the SI, as you prefer.

As suggested, we included a Table with additional information about the metadata in the SI. In addition, we referred to the fact that further information can be found in the overview paper of the campaign (van Pinxteren et al., 2020) and in Triesch et al., (2021a,b).

R2-C9: - Line 188: You mention that your glass plate and bottles were rinsed several times. How do you evaluate possible contaminations? Was it possible to do some blanks (or not!)?

The rinsing of the glass plate and sampling bottles is common practice in the SML sampling community (pers. communication from Prof. A. Engel). In addition, to avoid contamination, all material was pre-cleaned with 10% HCL as mentioned in the manuscript. Finally, we took field blanks and the handling of field blanks was added to the revised version in the new chapter 2.2.3 as follows (line 300 ff):

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

R2-C10: - Does several SML and bulk water samples have been performed at the same time? And analyzed in the lab?

Yes, SML and bulk water sampling have usually been performed at the same time and details of the sampling date can be found in the Tables S2 and S3 and in the new Figure S1.

R2-C11: - What are the storage conditions before the analysis?

After the sampling, the samples were stored frozen at -20 °C and transported in a reefer at -20 °C to the TROPOS laboratories where they were stored frozen until analysis. We added this in chapter 2.1 (line 203 ff):

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

R2-C12: - It could be interesting for the readers to give information on the backward trajectories of the air masses that have been sampled during the PM1 collection (see my comment below). If you add this in the SI, please give the relative information for these calculations (backward traj.) in section 2.1.

The backward trajectories for this campaign had been calculated and described in the overview paper by Pinxteren et al., (2020). We extracted the relevant periods and added the Figures in the SI and included some information in the revised version as follows (line 674 ff):

*“The backward trajectories **during the time of the campaign (Fig. S2)** as well as the mass concentrations of inorganic ions and mineral dust tracers on the aerosol particles measured during the campaign suggested a predominant marine origin with low to medium dust influences (van Pinxteren et al., 2020).”*

SI: Caption of Fig 2: *“96 hour back trajectories calculated on an hourly basis within the intervals of the aerosol particle filter sampling at the CVAO for selected time periods, using the NOAA HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, <http://www.arl.noaa.gov/ready/hysplit4.html>, 26.07.19) in the ensemble mode at an arrival height of 500 m ± 200 m (van Pinxteren et al., 2010), adopted from van Pinxteren et al., (2020).”*

2.2 Chemical analysis

R2-C13: - Line 199: “DOC is the fraction of OC that passes through a filter of 0.2–0.7 µm pore size”. I don’t understand here... What does it mean? In my opinion, DOC is measured by filtration via a 0.7 µm pore-sized filter only?

The referee is right; according to the Practical Guidelines for the Analysis of Seawater (Wurl, 2009) GF-F filters with a pore size of 0.7 µm is used for DOC analysis. However, due to requirements of analytical systems (e.g. HPLC, IC) filtrations with pore sizes of 0.45 or 0.2 µm are recommended and applied in several studies. In general pore size between 0.2 µm and 1.2 µm are applied (e.g. (Romankevich, 1984;Zäncker et al., 2017)).

We changed this in the revised version (line 213 ff):

“DOC is the fraction of OC that passes through a GF-F filter of 0.7 µm pore size (Wurl, 2009) however, filter pore sizes between 0.2 and 1.2 µm are often applied e.g. due to requirements of the analytical system (e.g. (Romankevich, 1984;Zäncker et al., 2017)).”

R2-C14: - Does the analysis been performed several times (triplicates)?

Samples were measured in duplicate and, as recommended by the other referee; we added a more comprehensive description of the measurements, the blank handling and artefacts as follows (line 186 ff):

“Regarding the aerosol sampling system, it needs to be underlined that artefact problems and overestimations due to gas phase absorption and underestimations due to re-volatilisations of the analytes from the filters cannot be accounted for and represent a certain level of uncertainty.”

And (line 306 ff):

“Each sample was measured twice with a relative standard deviation of typically < 10 %, and field blanks, which were for most compounds negligible and for the lipid classes always below 20% of the real aerosol particle sample, were subtracted. All presented values are corrected for the field blank.”

R2-C15: - Could you add some information regarding the LOD (limit of detection) and LOQ (limit of quantification) from your analytical procedures?

As suggested, the LOD/LOQ values were included in the revised version in the new chapter 2.2.3.

R2-C16: - Line 234: Leucine and Isoleucine are isomers. How do you distinguish these two compounds?

Despite Leucine and Isoleucine are isomers, they can be separated in the here use analytical system. The retention times are 8.46 and 8.61 min (Isoleucine and Leucine) and therefore different enough to be evaluated individually. The methodology is in detail described in Triesch et al, (2021a) and referred to in the paper.

R2-C17: - Line 225: could you explain more why the addition of ascorbic acid can avoid “the oxidation of the obtained AAs”?

The addition of ascorbic acid to avoid oxidation of the amino acids is a commonly applied procedure. Mandalakis et al., (2010) and reference therein describe that under the strongly acidic hydrolysis conditions, nitrates are converted to nitric acid, which in turn reacts with amino acids and cause their nitration or their oxidative degradation. The severity of these reactions depends on the concentration levels of nitrate and it has been shown to induce very low yields of combined amino acids in seawater. The addition of an excess of ascorbic acid or other antioxidants before hydrolysis has been suggested as an effective means to prevent degradation and achieve higher recoveries of amino acids. In their study, they found that ascorbic acid was found to be the most effective reagent for preventing the oxidative destruction of CAA during the hydrolysis process (Mandalakis et al. 2010). Hence, in other studies (e.g. Triesch et al., 2021c) as well as in the present study we applied ascorbic acid to address this potential oxidation problem. In the revised version, we added that this procedure was: “

“suggested in Mandalakis et al., (2010)”.

R2-C18: - Line 239: change “Seawater” to “seawater”.

done

2.3 Evaluation of the enrichments

R2-C19: - Here, one important information is the thickness of the sampled SML; it can be surely calculated as the quotient between the sampled volume of the SML and the sampling area of the glass plate. You indicate page 10, line 351 that the thickness is around 100 μm . Maybe you can add in this section how it is evaluated?

The referee is right, in principal the SML thickness can be calculated from the size of the glass plate, the number of dips and the sampled volume. However, during the campaign, the dips were not counted and therefore we cannot really calculate the actual sampled SML thickness but only refer to values from the same location but at an earlier sampling campaign (van Pinxteren et al., 2017). In the revised version we clarify that previously at this location the sampled SML was of about 100 μm thickness. The text reads as follows (line 417 ff):

“With the glass plate technique, an SML thickness of about 100 μm has been sampled and reported for the CVAO area (van Pinxteren et al., 2017).”

R2-C20: - Those factors are calculated based on the concentrations of the analytes in the different compartments that present uncertainties. You can mention here how these uncertainties are taking into account in the final calculations of EF_{SML} and EF_{Aero} ?

It is true that the EF present uncertainties and in the revised version, we explain these calculations in more detail. For the SML we related SML and bulk water sample directly to each other (e.g. sum of analytes in the SML vs. sum of analytes in the bulk water). The standard variation refers to the difference between the average value and the respective enrichment values of the single pairs. The same procedure was applied e.g. in Triesch et al., (2021 a,b). For DAA this was however, not possible, as the SML and bulk water were not always from the same day. For one day (10.10. 2017) we could directly calculate the EF SML (value 2.5) and the other values we averaged the SML concentration vs. bulk water concentration (EF value: 1.98). In Table 1, we present the average value between these two groups.

We added this information in the header of Tables S2 and S3 as follows:

S3: “For the calculation of the EF_{SML} ($EF_{\text{SML}} = c_{\text{SML}} / c_{\text{bulkwater}}$) the SML sample was related to the bulk water sample from the same day.”

S4: “For the calculation of the EF_{SML} ($EF_{\text{SML}} = c_{\text{SML}} / c_{\text{bulkwater}}$) two groups were constructed. The sum of amino acids from SML 16 and ULW 16 were related to each other (group 1), all other SML values were summed up and averaged and divided by all other (summed up and averaged) bulk water values. The final EF SML was calculated as the average between these two values.”

For the EF_{aer} calculations we applied average SML and bulk water concentrations from Table 1 for each compound groups and related it to the average aerosol concentration for each group. To address the variance, in the revised version, we added the min-max values of the EF_{aer} in Tab. 1.

To account for this, we added the following in the revised version:

Chapter 2.3 “Enrichment factors” (line 665 ff): *“it needs to be considered that processes in the ocean and the atmosphere happen on different timescales and to achieve a better robustness, we applied the average concentration values of the respective compound group in the seawater and on aerosol particles as done in (Zeppenfeld et al., 2021;van Pinxteren et al., 2022). To investigate the variability of the $EF_{aer.}$ the minimum ratio of $c_{(analyte)aer.} / c_{(Na+)aer.}$ vs. the maximum ratio of $c_{(analyte)seawater} / c_{(Na+)seawater}$ was applied and vice versa. ”*

and in the header of Tab. 1:

“To investigate the variability of the $EF_{aer.}$ the minimum ratio of $c_{(analyte)aer.} / c_{(Na+)aer.}$ vs. the maximum ratio of $c_{(analyte)seawater} / c_{(Na+)seawater}$ was applied (and vice versa) and the range of EF_{aer} is given in brackets.”

3 Results

R2-C21: - Line 294: “bulk water” instead of “Bulk water”.

done

3.1.1 SML and bulk Water

R2-C22: - It is essential here to refer to the number of samples that have been analyzed and to mention that the pool of samples for the various analysis (AA vs CHO vs Lipids) are different. Please indicate on Figure 1 the number of samples that have been analyzed allowing to create each boxplot.

As the referee suggested, we included the number of samples in the boxplots of Figure 1. We also added this information in the revised version (line 396 ff):

“However, it is important to mention that the number of samples that have been analysed is different and limited (Tab. 1 and Fig. 1) and samples from partly different dates of the campaign have been analysed and compared.”

And in the conclusion (line 833 ff):

*“Although conclusions on the detailed processes that lead to the varying DAA concentrations and the high SML enrichments cannot be resolved here **and the sample number is limited**, the results **suggest** (instead of: “clearly show”) that processes leading to changes in the organic matter composition within the upper 100 μm oceanic layer are more pronounced for the group of amino acids...”*

R2-C23: If the DOC in SML and BW have been measured (I’m not sur because nothing is indicated in section 2.2.2), please add this information on Figure 1 and comment this regarding the different classes (AA vs CHO vs Lipids).

We did not include the DOC measurements here.

R2-C24: - Only two samples (03/10/2017 and 07/10/2017) present a full chemical characterization (AA, CHO and Lipids) if I'm right. During these two days, you also observed a higher enrichment factor of DAA in comparison with other classes of compounds? You should mention this in the text.

Yes, this is correct. We added this information as follows (line 413 ff):

“Nevertheless, the enrichment of the DL in the SML was significantly lower compared to the carbohydrates and amino acids. This was obvious from a comparison of the averaged values as well as from single samples obtained at the same date (03.10.2017 and 07.10.2017, values in Tab. S2, S3, and Triesch et al. 2021b).”

R2-C25: - If it is possible, some statistical analysis must be performed; this will help to give more robust conclusion on the difference between groups (i.e., between the class of compounds). For example, Mann-Whitney nonparametric tests allow to validate significant differences between two groups.

We agree and performed some statistical significance tests among the groups within the seawater and the aerosol particles.

In the “material and methods” part, we added (line 345): *“Statistical significance was evaluated using the analysis of variance (ANOVA).”*

The results were added as follows:

1. Seawater (line 356 ff):

“However, despite the variability of the DAA in the SML, they are not statistically different to the other two compound groups (DL and DCHO) as well as to the DAA in the bulk water (Anova one way, $p > 0.5$ at the 0.5 level) that is different in the case of free amino acids (FAA). In total, no significant difference is present between the compound groups within the SML and the ULW (Anova one way, $p > 0.5$ at the 0.5 level).”

“However, the FAA in the SML were significantly higher compared to the FAA in the bulk water (Triesch et al., 2021a).”

2. Aerosol particles (line 526 ff):

“The concentrations of AA_{aer} and CHO_{aer} were $2.4 \pm 1.1 \text{ ng m}^{-3}$ and $1.0 \pm 1.1 \text{ ng m}^{-3}$, respectively (Fig. 3, Tab. 1) and not significantly different ULW (Anova one way, $p > 0.5$ at the 0.5 level).”

Line 561 ff: *“The $Lipid_{aer}$ were significantly higher than the AA_{aer} ($p = 6.6E-13$) and the CHO_{aer} ($p = 1.6E-7$) (Anova one way, at the 0.5 level). One possible reason for the higher $Lipid_{aer}$ concentration could lay in the difference in the extraction procedure (chapter 2.2) as AA_{aer} and CHO_{aer} were extracted in water, while the $Lipid_{aer}$ were extracted in an organic solvent.”*

R2-C26: - Figure 2. You have drawn the relative compositions of the various classes of compounds in %mol. The concentrations in the aqueous phase are in $\mu\text{g L}^{-1}$ (of water) and concentration in PM1 are in $\mu\text{g m}^{-3}$ (of air). Please explain your calculation in the SI, this will help the reader.

To address this comment, first we added an explanation of how we determined the atmospheric concentrations in 2.2.2 (line 268 ff):

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

Further, we added in the Caption of Figure 2: *“Mol% were calculated from the molar masses of the respective analytes. For the lipid groups, the molar masses of the surrogate standard (sec. 2.2.2 and Tab. S8) are applied. The relative mol fractions are relative to the total of each type (DAA, DCHO, and DL) analysed.”*

R2-C27: - Table 1. EF are presented in this table. For comparison, you mentioned the work of Rastelli et al. (2017) for EF_{aero} . Could you add other references in this table for EF_{SML} (but maybe there is no previous works looking at your targeted classes of compounds)?

Unfortunately, we did not find previous work looking at these targeted compounds or compound groups in a similar way.

R2-C28: - Line 306: You compare DAA with FAA. Do not forget to explain in the manuscript the difference.

We agree and added (line 363 ff):

*“The high variability of the DAA concentrations agreed well with the FAA **that comprise the sum of unbound individual amino acids i.e. not bound in a peptide or protein** and were measured at this location during the MarParCloud campaign (Triesch et al., 2021a).”*

In addition, the definition of DAA is given in the experimental part.

R2-C29: - Lines 333-335: Your conclusions should be made with more caution. The number of samples is rather limited, and a statistical analysis could help to conclude.

We agree and, as mentioned above, added the following (line 396 ff):

“However, it is important to mention that the number of samples that have been analysed is different and limited (Tab. 1 and Fig. 1) and samples from partly different dates of the campaign have been analysed and compared.”

3.1.2 Discussion on the SML

R2-C30: - 362-363: You mean that you cannot specifically sampled the first nano-layer on the very top of the surface? Therefore, you dilute the lipids that could be highly concentrated in this nano-layer? Could you her rephrase please to be more precise?

Yes, that's exactly what we mean and we changed the sentence as follows (line 428): *"The nanolayer, however, cannot be probed with currently applied bulk SML sampling methods."*

R2-C31: - 373-388: You explain that "non-surface active and soluble compounds" can be more concentrated due to co-adsorption some surfactants (lipids) leading to their enrichment. In the title, you mention also "complexation". You mean what? Complexation with some specific compounds? Could you add information about this point?

Thanks for pointing this out. Here we refer to the process of co-adsorption (only) and the related papers of (Burrows et al., 2016;Burrows et al., 2014) as well as (Schill et al., 2018) and not to "complexation".

Therefore, we changed the title to *"Co-adsorption"*.

R2-C32: - Line 399: you mention that Glu can be produced by biotic and abiotic mechanisms, and you refer to Jaber et al. (2021). However, this paper deals with the incubation of AAs with bacteria isolated from cloud water and representative of this kind of environment. This is different from the SML.

It is correct that Jaber et al., (2021) performed incubation experiments of cloud water. However, the transfer of bacteria from the ocean to the atmosphere has been shown before (Rastelli et al., 2017;Uetake et al., 2020) and bacteria in cloud water were also measured during the MarParCloud campaign (van Pinxteren et al., 2020). Hence, there is a potential link of bacteria and bacteria-related processes within the ocean and the atmosphere.

To clarify we changed the text as follows (line 464 ff):

"In incubated cloud water as another marine compartment, Glu has shown to be produced via biotic and abiotic mechanisms, e.g. via the oxidation of proline (Jaber et al., 2021 and refs. therein) and such processes may be relevant in the ocean surface as well."

R2-C33: - Line 402: Which stressors can modify the microflora metabolic activity?

We referred to a study from Kuznetsova and Lee (2002) who suggested that stressed microorganisms, rich in dissolved and combined amino acids, may be leached and released them, which in turn affects the pools of both these compounds in seawater. Probably the presence of water, UV radiation and temperature are influencing factors. However, details on the stressors were not given in the respective paper and are beyond the scope of our study.

R2-C34: - Lines 424-426: You indicate that cyanobacteria can generate amino acids. Do you have biological data regarding those bacterial strains during the MarParCloud campaign that could link biological activity with the AA enrichment?

Unfortunately we don't have such kind of measurements from the MarParCloud campaign. We could show that cyanobacteria were dominant during the MarParCloud campaign (as

mentioned in the text with the reference to (van Pinxteren et al., 2020)). However, beyond that we did not have information of bacterial strains. We highlight that this suggestion is rather speculative that further studies are needed to investigate if nitrogen fixation and biosynthesis via cyanobacteria might establish a considerable route for amino acid formation and enrichment in the SML from the atmospheric side.

3.2 Aerosol particles

R2-C35: - Please add on the boxplots (Figure 3) the number of samples that have been analyzed for each class of compounds.

Done.

R2-C36: - Lines 470-473: please re-phrase this sentence that is unclear.

We agree and re-phrased the sentence to (line 545 ff):

“Comparing the data obtained here with those from analytical techniques that use functional group information (FT-IR) has shown that the latter techniques often attribute a large fraction of alcohol (hydroxyl) functional groups on the marine aerosol particles to carbohydrates...”

R2-C37: - Lines 461-469: This seems strange to me why you focused your comparison specifically on polar regions. Carbohydrates, amino acids have been investigated in many other studies at sites characterized by different environmental conditions (marine, rural, urban, polar)... You should restrict your comparison to marine sites or to sites under marine influence(?)

See the review from Matos et al. (2016) and the supplementary information given in Renard et al. (2022) for AAs; see also for example the paper from Samaké et al. (2021) and Zhu et al. (2022) for sugars.

Matos, J. T. V., Duarte, R. M. B. O., and Duarte, A. C.: Challenges in the identification and characterization of free amino acids and proteinaceous compounds in atmospheric aerosols: A critical review, *TrAC-Trend. Anal. Chem.*, 75, 97–107, 2016.

Renard, P., Brissy, M., Rossi, F., Lereboure, M., Jaber, S., Baray, J.-L., Bianco, A., Delort, A.-M., and Deguillaume, L.: Free amino acid quantification in cloud water at the Puy de Dôme station (France), *Atmos. Chem. Phys.*, 22, 2467–2486, <https://doi.org/10.5194/acp-22-2467-2022>, 2022.

Samaké, A., Jaffrezo, J.-L., Favez, O., Weber, S., Jacob, V., Albinet, A., Riffault, V., Perdrix, E., Waked, A., Golly, B., Salameh, D., Chevrier, F., Oliveira, D. M., Bonnaire, N., Besombes, J.-L., Martins, J. M. F., Conil, S., Guillaud, G., Mesbah, B., Rocq, B., Robic, P.-Y., Hulin, A., Le Meur, S., Descheemaeker, M., Chretien, E., Marchand, N., and Uzu, G.: Polyols and glucose particulate species as tracers of primary biogenic organic aerosols at 28 French sites, *Atmos. Chem. Phys.*, 19, 3357–3374, <https://doi.org/10.5194/acp-19-3357-2019>, 2019.

Zhu, R.-G., Xiao, H.-Y., Cheng, L., Zhu, H., Xiao, H., and Gong, Y.: Measurement report: Characterization of sugars and amino acids in atmospheric fine particulates and their

relationship to local primary sources, *Atmos. Chem. Phys.*, 22, 14019–14036, <https://doi.org/10.5194/acp-22-14019-2022>, 2022.

We thank the referee for pointing out these additional references. We checked them and included them in the discussion. For the sugars we realized, that the sugar spectrum looks quite different when including continental biological sources (e.g. strong contribution of sugar alcohols) and general concentration and composition are very different. To this end we think it is also important to focus our comparison on remote marine areas (as the Arctic), also because very similar analytical techniques have been applied and allow a good comparison. The new references are included as follows (line 538 ff):

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

R2-C38: - Lines 470-526: I was wondering if FT-ICR-MS analysis were also performed on marine aerosol. Using van Krevelen diagrams, you can have access to the proportion of some classes of compounds (lipids, proteins, carbohydrates, amino-sugars...). This could be included in your discussion here.

That is a very interesting idea. However, data products from FT-ICR-MS and our studies are partly different. FT-ICR-MS results provide several thousand molecular formulas (Bao et al., 2018) that show the general composition but are difficult to pinpoint to single exact compounds. (Schmitt-Kopplin et al., 2012) found that typical chemical fingerprints of compounds enriched in the aerosol phase were CHO and CHOS molecular series, and comprise smaller molecules of higher aliphaticity and lower oxygen content, and are typical surfactants. These authors further demonstrated that these molecules corresponded to homologous series of oxo-, hydroxy-, methoxy-, branched fatty acids and mono-, di and tri carboxylic acids as well as monoterpenes and sugars. However, this relates to all three compound classes (without differentiation) investigated in our study. The van Krevelen plots compare to H/C and the O/C ratios of the compound, this is however difficult to bring together with the here performed molecular studies.

However, we found one study that could attribute the molecular formulas in Arctic aerosols measured with FT-ICR-MS to similar compound classes as investigated in our study (Choi et al., 2019). The authors found that large peak numbers were assigned to proteins and lignins (phenolic macromolecules) followed by carbohydrates and lipids in aerosol originating from the ocean (vs. non-ocean aerosol). Moreover, protein and carbohydrate intensities were correlated to the increase in air mass exposure to oceanic chlorophyll (compared to non-oceanic air masses). Altogether, this emphasized the importance of biogenic organics in the ocean as a source of primary aerosol over the ocean, being in agreement with the results from our study. Nevertheless, it needs to be considered that FT-ICR-MS data are generally not quantitative. In the study of Choi et al., (2019) the number of observed assigned molecules and the sum of intensities were interpreted as semi-quantitative.

We included the results in the revised version (line 575 ff):

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

And in the conclusion (line 871 ff):

“Nevertheless, the results obtained here show that even in such an oligotrophic region, at least half of the OC on the aerosol particles consists of rather short-lived biogenic material, likely from the surface ocean, as (qualitatively) suggested by other studies (Choi et al., 2019; Schmitt-Kopplin et al., 2012).”

R2-C39: With this technique, the recent paper from Renard et al. (2022) analyzed the organic matter in cloud waters under marine influence. These authors indicated that “Lipids are correlated with the sea surface for air masses transported within the free troposphere, confirming the long-range transport of marine biogenic sources.”. Their conclusions confirm your results concerning the predominance of lipids.

We thank the referee for this comment. However, in the paper of Renard et al., (2022) we found information about free amino acids measured in cloud water but no information about lipids. We included important findings of the Renard et al., (2022) paper regarding atmospheric aging of the amino acids and biotic and abiotic (mainly oxidation) processing in the discussion of the amino acid composition in seawater and atmosphere. In addition, the Renard et al., (2022) reference was inserted for comparisons of the amino acid values (see comment above).

R2-C40: - Lines 583-598: this paragraph highlights the limitations of the comparison between seawater and aerosol samplings. You mention the sampling periods that are different but also the link between CVAO and the sea water site. Some previous works are indicated in this section to validate the possible link between the upper ocean and the aerosol particles.

Several parts of the paragraph are directly related to data from the here presented MarParCloud campaign (e.g. concentration of MSA...). We mentioned this already regarding the backward trajectories and clarified this in the revised version as follows (line 674 ff):

*“The backward trajectories **during the time of the campaign (Fig. S2)** as well as the mass concentrations of inorganic ions and mineral dust tracers on the aerosol particles measured during the campaign suggested a predominant marine origin with low to medium dust influences (van Pinxteren et al., 2020). ...”*

R2-C41: You analyzed in this study specific days of sampling during the field campaign. Is it possible to add in the SI information about for example backward trajectories, meteorological information during this specific period?

As mentioned above, we extracted the backward trajectories for the here relevant periods and added them together in the SI and discussed them in the revised manuscript.

Regarding the meteorological conditions, we added in the SI: *“The meteorological conditions observed during the campaign were typical for this site with strong north-easterly wind (30 to 60 °) and are reported in van Pinxteren et al., (2020). “*

3.4 Contribution to OC

R2-C42: - I think that organic carboxylic acids other than oxalic acid have been also quantified (?); what are their contributions to the OC?

With our analytical methods (ion chromatography) we are able to measure other dicarboxylic acids, however oxalic acid was always the most pronounced one and the other dicarboxylic acids were mostly below the detection limit. We added this information with an asterisk in the Table S7:

*“*Oxalic acid was the dominant dicarboxylic acid and all other dicarboxylic acids were below LOD.”*

4 Conclusions

R2-C43: - Line 778-779: Dominutti et al. (2022) have also shown that AAs detected in cloud waters sampled at a tropical site under strong marine influence contribute to a small % of the DOC. Sugars were more significantly present than in the present study.

Dominutti, P. A., Renard, P., Väitilingom, M., Bianco, A., Baray, J.-L., Borbon, A., Bourianne, T., Burnet, F., Colomb, A., Delort, A.-M., Duflot, V., Houdier, S., Jaffrezo, J.-L., Joly, M., Lereboure, M., Metzger, J.-M., Pichon, J.-M., Ribeiro, M., Rocco, M., Tulet, P., Vella, A., Leriche, M., and Deguillaume, L.: Insights into tropical cloud chemistry in Réunion (Indian Ocean): results from the BIO-MAÏDO campaign, *Atmos. Chem. Phys.*, 22, 505–533, <https://doi.org/10.5194/acp-22-505-2022>, 2022.

We thank the referee for mentioning this reference. Dominutti et al., (2022) published a very interesting study that investigated cloud-terrestrial vegetation exchange of a broad range of organic compounds that are, however partly different to those investigated in the present study. Their measurements took place in a different region with probably other influencing factors. Hence, a proper comparison of the results achieved here with the study of Dominutti et al., (2022) would require a more comprehensive approach. In the revised version, we included the study of Dominutti et al., (2022) in the comparison of the atmospheric data in chapter 3.2.1, as mentioned above.

Citation: <https://doi.org/10.5194/acp-2022-832-RC2>

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