

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., 2021).”*

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.

Cited literature in this letter:

Triesch, N., van Pinxteren, M., Engel, A., and Herrmann, H.: Concerted measurements of free amino acids at the Cape Verde Islands: High enrichments in submicron sea spray aerosol particles and cloud droplets, *Atmos. Chem. Phys.*, 21, 163–181, 2021.