Interactive comment on "Concerted measurements of lipids in seawater and on submicron aerosol particles at the Cape Verde Islands: biogenic sources, selective transfer and high enrichments" by Nadja Triesch et al.

Anonymous Referee #1

The manuscript presents a very interesting dataset on lipids, investigated in seawater, sea-surface microlayer and submicron aerosol particles at the CVAO – Cape Verde Atmospheric Observatory. Both dissolved and particulate lipids were studied, showing different degrees of enrichment and the partitioning into different classes among the three compartments studied. This is very interesting, and as the authors point out, the lipid composition in seawater, sea-surface microlayer and aerosols highlights that not only autotrophic sources may be responsible for the organic composition of submicron aerosols, but that bacterial activities and further oxidation and photodegradation pro-cesses on these atmospheric particles may be responsible for their different organic matter content. This is important to individuate the sources of these materials and possibly, their behavior once in the atmosphere.
The manuscript is well written, just some minor spelling mistakes and wording should be looked at, and it well addresses the scope of ACP. It is also novel as it presents concerted measurements on three compartments, usually studied separately in field work.
The scientific approach and methodology is sound and well described, accompanied with an extensive sub-set of supplementary information.
Overall I recommend the publication of the paper, but I suggest some minor issues to be taken into account prior to this. I think the authors shall include some more information on the importance of this study in the field. I found the manuscript technically correct, but in my opinion it lacks a bit of background information and broader outlook.

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 now revised manuscript (without track changes).

I have these comments in particular:

R#1-1 a) What is the importance of PM1 aerosols with respect to other size-distributions?

Submicron aerosol particles (PM_1) are in a size range most important for cloud processes, e.g. play a critical role in the formation of cloud condensation nuclei (Quinn and Bates, 2011) and have an atmospheric lifetime of several days (Madry et al., 2011). Moreover, marine aerosol particles contain a large quantity of organic material (e.g. Quinn and Bates (2011) and references therein). The enrichment of organic matter increases with particle size (O'Dowd et al., 2004), hence, the submicrometer aerosol particles are often dominated by organic matter (OM) (Quinn and Bates, 2011).

R#1-1b) How would you expect lipid classes be different in other size-fractions of marine aerosols?

Investigations of lipids on marine aerosol particles, especially in different size ranges, are still sparse.

In a laboratory mesocosm experiment, Cochran et al. (2016) investigated the fatty acid composition in sub- and supermicron aerosol particles and reported that about 75% of the submicron aerosol particles showed strong signals for the presence of long-chain fatty acids, whereas supermicron sea spray aerosol particles were dominated (up to 88%) by oxygen-rich species. The study of Cochran et al. (2016) shows the large varying composition of lipids in (size-resolved) aerosol particles generated in the lab. Here we aimed to contribute the composition and concentrations of lipids in ambient marine aerosol particles and discuss their relations and we choose PM_1 aerosol particles as explained above.
These aspects regarding the importance of PM_1 aerosol particles have briefly been discussed in the Introduction of the manuscript.

In the revised version we added on page 3, line 31 - page 4, line 2: ”Specific lipid classes such as long chain fatty acids and cholesterol as constituents of aerosol particles are already regarded as important factors for the activation of aerosol particles to cloud condensation nuclei (CCN) (Barati et al., 2019) or ice nucleation particles (INP) (Nguyen et al., 2017;DeMott et al., 2018). Cochran et al. (2016b) investigated the fatty acid composition in sub- and supermicron sea spray aerosol particles and reported that about 75 % of the submicron aerosol particles showed strong signals for the presence of long-chain fatty acids. In contrast, supermicrometer sea spray aerosol particles were dominated (up to 88 %) by oxygen-rich species (Cochran et al., 2016b).”

R#1-2) Why did you chose the glass plate for SML sampling compared to other devices, and can you estimate (if any), biases of the glass-plate method on lipids concentration with respect to other components of this layer?

The glass-plate technique in general:
A strong advantage of using the glass plate technique is that a thin SML sample (usually 20-150 µm thickness) is collected and the biological composition of the SML is more representative (Cunliffe, 2014). Another advantage is the simple way of sampling and the easy-to-use-format (important in field studies). A disadvantage of this sampling method is the time consuming sampling (~45 min to collect 1 L sample)(Cunliffe, 2014). Altogether, the glass plate method for collecting SML is an established sampling technique that has often been used in previous studies (e.g. Reinthaler et al. (2008);Wurl and Holmes (2008);Engel and Galgani (2016);Zäncker et al. (2018);van Pinxteren et al. (2017)).

The glass-plate technique regarding lipids:
During this study, we exclusively used the glass-plate technique and cannot compare the sampling efficiency of this technique towards others for lipids. Early papers have speculated that the glass-plate might not be very effective for hydrophobic lipids, as glass itself has a hydrophobic surface (e.g. van Vleet and Williams (1980)). However, more recent work shows that the glass-plate technique is very well suited to collect highly hydrophobic dissolved organic substances such as lipids and amino acids, e.g. Cunliffe (2014), Stolle et al. (2019). Therefore, we have no reason to believe that the glass-plate technique is more prone to biases than others. We carefully tests contamination and carry over problems by taking blanks as described in section 2.2.1.

In the revised version of the manuscript we have added the following (page 5, line 2-4): “The SML samples (n=6) were collected using the manual glass-plate technique, a standard SML sampling method whose correct application and specification are described in detail in the ‘Guide to best practices to study the ocean’s surface’ by Cunliffe (2014).”

R#1-3) Line 32 page 5: It is not clear to me why did you analyze Na+ and why you used it to calculate EFaer. Is it related to seawater salts?

The Na^+ concentration in both, seawater and aerosol particles, are necessary to calculate the EF_{aer} that is a quantitative metric for the comparison of compounds in the ocean and in the atmosphere. It considers the analyte concentration in the different matrices (seawater, aerosol particles) in relation to the Na^+ concentration in both matrices.

In the revised version we added a more detailed explanation of the EF_{aer} in section 2.2.4 'Enrichment factors', which reads as follows (page 7, line 22-26): "The EF_{aer} is a quantitative metric for the comparison of compounds in the ocean and in the atmosphere. The EF_{aer} concept is mainly applied to closed systems (Quinn et al. (2015) and references therein, Rastelli et al. (2017)) since formation or degradation pathways on aerosol particles including biological or photochemical atmospheric reactions and possible transports from other than marine sources are excluded for this parameter. However, for comparison purposes it is useful to calculate the EF_{aer} also for open systems, as in the studies of e.g. Russell et al. (2010) or van Pinxteren et al. (2017)."

R#1-4) In the figures (e.g. figure 1), maybe you can specify in the caption that where there is no _SML you refer to ULW, I suppose.

We have now more clearly distinguished between SML and ULW samples in the figures of the seawater samples in the revised version. The SML samples are specially highlighted in the figures, e.g. 20/09/2017_SML, while the ULW samples are only described as sampling date (e.g. 20/09/2017). For easier differentiation between ULW and SML samples, we have improved the labelling of the figures (Fig. 1 and Fig. 2).

The caption of Fig. 1 reads now as follows (Manuscript, page 8): "Figure 1: Concentration of individual particulate lipid classes in the ULW (sampling date) and the SML (sampling date_SML) samples along the campaign and as an averaged value in µg L^{-1}."

R#1-5) Lines 7-11, page 11: it is not very clear to me whether in the SML PL were enriched, or DL, as in page 18, line 32, you state that PL are more degraded in the SML, and more stable in the DL and PL in the ULW. This sounds a bit confusing. If PL are enriched in the SML, I would expect them to be more stable then, and less degraded.

These statements refer to the results achieved from a) the EF of PL and DL groups in the SML and b) the LI. The EF describes the enrichment/depletion of the entire DL or PL group in the SML and the LI is the ratio between the metabolites (ALC, FFA, MG, DG) and intact lipids (TG, WE, glycolipids as MGDG, DGDG, SQDG and phospholipids as PG, PE, PC) as described in equation 1 (Manuscript, page 6). As these two parameters regard different compound classes/ratios, it is no contradiction that in the SML compounds are enriched, but at the same time degradation can be interpreted from the ratio of metabolites and intact lipids, the LI.

Taking this comment into account, we have carefully rewritten the interpretations of the Lipolysis Index as follows in the revised manuscript:
In section '2.2.3 Lipid ratios' it now reads as follows: "Higher LI values are characteristic for enhanced OM degradation and metabolite release, while lower LI values indicate that the appearing lipid classes are more fresh or resistant to degradation." (page 7, line 5-7)
In section 3.1.3 it now reads: "However, on specific days, the LI_{SML} of PL was ≥ 0.5 (Table S5), indicating a slightly increased OM/lipid degradation and metabolite release in the SML compared to the ULW." (page 10, line 17/18)
and "The LI of DL (Table S5) varied between 0.13-0.53 in the ULW and between 0.20-0.48 in the SML samples, suggesting that the dissolved lipid classes were somewhat more resistant to degradation." (page 10, line 20 - page 11, line 2)

and in the Conclusion: “Although the lipids are reported as fast reactive compounds, our results suggest that the DL are somewhat more resistant to degradation.” (page 19, line 30-31)

R#1-6) Line 23, page 11: is it possible that the lower enrichment of lipids compared to other OM classes like amino acids is due to biases in the glass plate method?

The glass-plate technique is not known to be more prone to biases compared to other SML sampling techniques. We also measures amino acid samples with the same technique at the same location and found higher enrichment factors for them (Triesch et al., 2020). In this context, we would like to refer to the reviewer's comment R#1-2 regarding the SML sampling technique using the glass-plate method and its advantages and disadvantages.

R#1-7) Line 3 page 12: it is also possible that phytoplankton activity is lower in the SML because of high radiation, thus cells stay preferentially below the SML. I expect that at the Cape Verde Islands solar radiation was quite high. Are there any measurements on this parameter? It would be interesting to see how it can influence the different lipid composition in seawater, SML and PM1. Do you have any data on this? Did you run some tests?

The solar radiation during the campaign was measured with a ‘Pyranometer SKS 1110’ (Skye Instruments Ltd, Powys, United Kingdom) installed on the 10 m high tower of the Cape Verde Atmospheric Observatory (CVAO).
The table shown here shows the averaged solar radiation data (243.3 – 676.2 W m^{-2}) over the sampling period of the SML samples. Although a variance of the solar radiation data could be observed, no statistically relevant correlation/trend between the solar radiation data and the SML lipid concentrations or composition could be found, which was probably due to the small number (#5) of corresponding sample numbers.

Sampling time local time	Average solar radiation [W m^{-2}] during the sampling time
25/09/2017 9:45-10:48	676.2
27/09/2017 8:50-10:03	581.7
06/10/2017 8:04-9:47	371.2
07/10/2017 09:22-10:35	551.4
10/10/2017 8:30-9:30	243.3

The SML samples were always collected in the morning between 8:04 and 10:35 local time (UTC-1) on different days (for more details, see van Pinxteren et al. (2020)). Due to the limited sampling possibilities in Cape Verde (SML sampling from a small fishing boat), it was not possible to carry out seawater sampling at other times of the day, e.g. in the evening/night period or even investigate diurnal cycles. The aerosol particle samples are 24 h samples, hence both day and nighttime influences on aerosol lipid composition (e.g. solar radiation), the sampling periods would have to be adjusted. We will take this interesting aspect of solar radiation into future campaign.

In the revised supporting information, we included we solar radiation measurements in Table S8.

R#1-8 a) How do you relate the lipid composition of submicron aerosols, that have presumably been in the atmosphere for a longer residence time, to the ambient seawater composition both in ULW and SML, that may rapidly change even during diel cycles?

In our approach of concerted measurements, we compared PM_1 aerosol particles, sampled for 24 h with spot samples taken in the ocean (ULW, SML) within the aerosol sampling period. To allow a comparison of these two matrices, we strongly considered several additional measurements, such as backward-trajectories, the concentrations of inorganic ions and mineral dust tracers on the aerosol particles measured during the campaign. These parameters were discussed in detail in the overview paper of the campaign (van Pinxteren et al., 2020) and in a separate paper measuring amino acids within this campaign and influences (Triesch et al., 2020).

We have added these considerations in a new subchapter '3.2.1 The comparability of the different marine matrices (seawater and aerosol particles)' of section '3.2 Transfer of lipids from the Oceans'. It reads now as follows (page 12, line 6-11): "The concerted measurements performed here included spot samplings in the ocean (ULW, SML) during the sampling period of PM1 aerosol particles at the CVAO (24h). The air masses arriving at the CVAO often followed the water current (Peña-Izquierdo et al., 2012;van Pinxteren et al., 2017) and suggest an enhanced link between the upper ocean and the aerosol particles, as mainly winds drive the ocean currents in the upper 100 m of the ocean. The backward trajectories as well as the concentrations of inorganic ions and mineral dust tracers on the aerosol particles measured during the campaign, suggested a predominantly marine origin with low to medium dust influences (Triesch et al., 2020;van Pinxteren et al., 2020)."

We could not investigate diel cycles and would like to refer to the reviewer comment R#1-7.

R#1-8b) I don't know if it makes sense, but would it be possible to estimate an EFaer based on ULW properties instead of SML components?

The referee rightly stated that the EF_{aer} can also be calculated based on the ULW concentrations. This has already been done in a previous study on amino acids by Triesch et al. (2020). Since the lipid concentrations in ULW and SML were quite similar and this is reflected in only comparatively small enrichments (EF_{SML}: 1.0-1.7), the calculated EF_{aer} (based on ULW and based on SML) are also very similar. The EF_{aer} based on SML concentrations is on average $2.6{\cdot}10^5$ and the EF_{aer} based on ULW is on average $3.4{\cdot}10^5$ and therefore agree well. Thus, the calculation of the EF_{aer} based on ULW does not provide any new insights compared to the EF_{aer} based on SML and therefore we would prefer not to elaborate on this in the manuscript.

R#1-9) Just as a curiosity, would bigger aerosol particles show a more straightforward relation to seawater properties, considering that they may have resided in the atmosphere for a shorter time and travelled over shorter distances?

This is an interesting thought; however, probably complex (selective) transfer processes of lipids travelling from the ocean to the atmosphere and subsequent reactions determine the lipid composition of ambient aerosol particles in the sub- and supermicron range.
In a recent study from the same location, we could show that amino acids showed a higher diversity in submicrometer aerosol particles compared to supermicron particles. However, the composition of the amino acids in the submicron aerosol particles was more similar to that of seawater than to the supermicron aerosol particles (Triesch et al., 2020).

In the manuscript, we reported similarities between the composition of lipids in seawater and on the aerosol particles (e.g. section '3.2.3 Transfer of lipid classes from the ocean to the aerosol particles'). However, as we solely performed measurements of submicron aerosol particles it remains speculative, whether the lipid composition of the supermicron aerosol particles is more similar to that of seawater. This is certainly an interesting though to be addressed in future campaigns.

R#1-10) The PM1 lipid fraction resembled more the DL fraction of seawater, in composition. Would it be possible that by sampling larger aerosols, the lipid composition would have resembled more the PL fraction of seawater instead? If so, could this be because of molecular size?

Since we have only examined PM_1 aerosol particles, a statement about the lipid composition of larger aerosol particles is highly speculative. We would like to point out the sample preparation for lipid analysis in seawater and on the aerosol particles: The seawater was divided into the dissolved fraction (<0.7 µm) and the particulate fraction (0.7-200 µm). The aerosol particles (<1 µm) were collected as PM_1 aerosol particles. Furthermore, it must be considered that in the bubble bursting process, the formed droplets are water drops, which gradually dries up and finally leads to the formation of the aerosol particles. Therefore, the size separation in seawater is not transferable 1:1 to the aerosol particles.

Please see also our replies to R#1-1 and R#1-9.

R#1-11) What are the implications of lipid composition for marine aerosols? Could the different lipid fractions lead to different cloud forming capacities, or aerosol properties concerning optical thickness and radiative effects? Are these properties relevant for the study region, or other marine regions? I think it would be a good addition to the paper to discuss these aspects and broader implications in the conclusion section.

Lipid classes can serve as specific markers for the identification of OM sources, also with regard to possible biogenic sources and relations to (micro)organisms (see manuscript: page 2, line 26 - page 3, line 3 and page 19, line 31-34). Moreover, an important aspect of lipid composition for marine aerosol particles is the fact that lipid classes such as long-chain fatty acids can act as important factors for the activation of aerosol particles to CCN or INP as described in the manuscript (page 3, line 31-33). We would like to point out that the correlations found between lipids and ice nucleation potential relate to investigations in seawater as discussed in detail in reviewer comment R#2-25. It is difficult to extrapolate a transfer into aerosol particles with respect to organic compounds and ice nucleation potential, since other possible aerosol particles sources must also be considered when considering aerosol particles with respect to INP activity.
Statements regarding lipid fractions and various cloud forming capacities or aerosol properties such as optical thickness and radiative effects would be purely speculative, since no measurements on these properties of aerosol particles have been made that could be referred to. Due to these facts, we would like to limit our conclusions to the results that we were able to show and interpret by measurements in this study.

Additional changes performed by the authors

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 21, line 4-6)

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.921832." (page 20, line 27/28)

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

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