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

References

Cochran, R. E., Laskina, O., Jayarathne, T., Laskin, A., Laskin, J., Lin, P., Sultana, C., Lee, C., Moore, K. A., Cappa, C. D., Bertram, T. H., Prather, K. A., Grassian, V. H., and Stone, E. A.: Analysis of Organic Anionic Surfactants in Fine and Coarse Fractions of Freshly Emitted Sea Spray Aerosol, Environ. Sci. Technol., 50, 2477-2486, 10.1021/acs.est.5b04053, 2016.

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.

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.

Madry, W. L., Toon, O. B., and O'Dowd, C. D.: Modeled optical thickness of sea-salt aerosol, Journal of Geophysical Research: Atmospheres, 116, https://doi.org/10.1029/2010JD014691, 2011.

O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y. J., and Putaud, J. P.: Biogenically driven organic contribution to marine aerosol, Nature, 431, 676-680, 10.1038/nature02959, 2004.

Quinn, P. K., and Bates, T. S.: The case against climate regulation via oceanic phytoplankton sulphur emissions, Nature, 480, 51, 10.1038/nature10580, 2011.

Reinthaler, T., Sintes, 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, 2008.

Stolle, C., Ribas-Ribas, M., Badewien, T. H., Barnes, J., Carpenter, L. J., Chance, R., Damgaard, L. R., Quesada, A. M. D., Engel, A., Frka, S., Galgani, L., Gašparović, B., Gerriets, M., Mustaffa, N. I. H., Herrmann, H., Kallajoki, L., Pereira, R., Radach, F., Revsbech, N. P., Rickard, P., Saint, A., Salter, M., Striebel, M., Triesch, N., Uher, G., Upstill-Goddard, R. C., Pinxteren, M. v., Zäncker, B., Zieger, P., and Wurl, O.: The MILAN campaign: Studying diel light effects on the air-sea interface, Bull. Amer. Meteorol. Soc., null, 10.1175/bams-d-17-0329.1, 2019.

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. Discuss., 2020, 1-24, 10.5194/acp-2019-976, 2020.

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

van Pinxteren, M., Fomba, K. W., Triesch, N., Stolle, C., Wurl, O., Bahlmann, E., Gong, X., Voigtländer, J., Wex, H., Robinson, T. B., Barthel, S., Zeppenfeld, S., Hoffmann, E. H., Roveretto, M., Li, C., Grosselin, B., Daële, V., Senf, F., van Pinxteren, D., Manzi, M., Zabalegui, N., Frka, S., Gašparović, B., Pereira, R., Li, T., Wen, L., Li, J., Zhu, C., Chen, H., Chen, J., Fiedler, B., von Tümpling, W., Read, K. A., Punjabi, S., C. Lewis, A. C., Hopkins, J. R., Carpenter, L. J., Peeken, I., Rixen, T., Schulz-Bull, D., Monge, M. E., Mellouki, A., George, C., Stratmann, F., and Herrmann, H.: Marine organic matter in the remote environment of

the Cape Verde Islands - An introduction and overview to the MarParCloud campaign, Atmos. Chem. Phys. Discuss., 2019, 1-63, 10.5194/acp-2019-997, 2019.

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 Vleet, E. S., and Williams, P. M.: Sampling sea surface films: A laboratory evaluation of techniques and collecting materials, Limnol. Oceanogr., 25, 764-770, 10.4319/lo.1980.25.4.0764, 1980.

Wurl, O., and Holmes, M.: The gelatinous nature of the sea-surface microlayer, Mar. Chem., 110, 89-97, 10.1016/j.marchem.2008.02.009, 2008.

Zäncker, B., Cunliffe, M., and Engel, A.: Bacterial Community Composition in the Sea Surface Microlayer Off the Peruvian Coast, Front Microbiol, 9, 2699-2699, 10.3389/fmicb.2018.02699, 2018.

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 #2

General comments

The authors of the manuscript 'Concerted measurements of lipids in seawater and on submicron aerosol particles at the Cape Verde Islands: biogenic sources, selective transfer and high enrichments' present a valuable data set. The concerted measurement of a broad range of lipid classes in seawater, in the sea surface microlayer and on submicron aerosols is novel and benefits the scientific community as an inventory. This data bridges oceanic and atmospheric research by applying a common method and thus enabling a direct comparison between organic matter present in each realm. This is a clear step forward into required interdisciplinarity within the field and fits the scope of ACP. Overall, I recommend to publish this paper.

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 revised manuscript (without track changes).

R#2-1) However, several major improvements on representing and discussing this dataset can be made.
R#2-1 a) In the introduction, a brief outline of the study area, i.e. the Tropical Atlantic, in terms of phytoplankton bloom dynamics, relevance for aerosol formation and ice nucleation activity should be given.

We thank the reviewer for the suggestions for improvement. In order to describe and to better motivate the study area, the tropical Atlantic, we have carefully revised section 2.1 'Study area and sampling sites'.
In the revised version we have stronger specified the marine region according to Longhurst (2007). The region investigated here, the 'North Atlantic Tropical Gyral Province (NATR)' region around the Cape Verde Islands, is an interesting but rarely studied oligotrophic region. The region often experiences clean marine air and low anthropogenic influences. Regarding the phytoplankton bloom dynamics, the NATR regions is described as an oligotrophic region with the lowest surface concentrations of chlorophyll in the North Atlantic and greater annual variability than seasonality (Longhurst, 2007).
Regarding the topic of aerosol formation and ice nucleation activity, we included the finding that high marine INP concentrations were predicted in oceanic regions surrounding the Cape Verde Islands, in fact they were higher than in the rest of the North Atlantic (Wilson et al., 2015).

We added the information on the relevance of this region in terms of aerosol formation and ice nucleation activity in more detail in section 2.1 and it reads now as follows (page 4, line 24-29): "The ocean around the Cape Verde Islands belongs to the region 'North Atlantic Tropical Gyral Province (NATR)' according to the classification of Longhurst (2007), a region with the lowest surface chlorophyll in the North Atlantic and with a greater annual variability than seasonality. Wilson et al. (2015)

reported that high concentrations of marine INPs can occur in the North Atlantic and comparatively high surface-level marine (INP_{15}) and OC concentrations have been predicted by models in this region around the Cape Verde Islands."

R#2-1b) It is not completely conclusive how the work ultimately relates to Chl-a as a proxy for in general phytoplankton biomass (?) or org. matter enrichment in aerosols, although discussed over some lines. The authors should formulate a clearer statement.

In most parameterizations the transfer of OM from the ocean into the atmosphere and the prediction of the OM content on marine aerosol particles, is based on chl-*a* seawater concentrations that are used as a broad indicator of biological productivity (Gantt et al., 2011;Rinaldi et al., 2013). However, chl-*a* concentration alone does not adequately describe the complete spectrum of biological activity (Quinn et al., 2014) and especially in oligotrophic regions other parameters besides wind speed and chl-*a* must be taken into consideration for a good prediction of OM on marine aerosol particles (van Pinxteren et al., 2017). Moreover, different groups of OM, such as lipids, carbohydrates and proteins show different characteristics in terms of their sea-air transfer (Burrows et al., 2014). In a new approach by Burrows et al. (2014) the parameterization/ OM prediction for marine aerosol particles is based on important compound classes of OM, e.g. lipids, carbohydrates, proteins, humic-like compounds, instead of chl-*a* concentrations in seawater. To apply and further develop such OM parameterizations/ predictions, distinct measurements of these specific organic compound groups on molecular level in different oceanic regions are urgently needed. To this end, concerted measurements such as those we have performed in this study are essential. With studies like ours, simultaneous measurements of e.g. lipid classes in both marine compartments (seawater and aerosol particles) are obtained, and such data can finally be used to improve organic matter transfer models.

In the revised manuscript, we summarized the current state of knowledge regarding chl-*a* and OM parameterizations now more clearly (page 3, line 22-30): "Most parameterizations, the transfer of OM and the prediction of the OM content on marine aerosol particles, is based on chl-*a* seawater concentrations that are used as a broad indicator of biological productivity (Gantt et al., 2011;Rinaldi et al., 2013). However, especially in oligotrophic regions additional parameters besides wind speed and chl-*a* must be taken into consideration for accurately prediction of OM on marine aerosol particles (van Pinxteren et al., 2017). In a new approach by Burrows et al. (2014) the parameterization/ OM prediction for marine aerosol particles is based on important compound classes of OM, e.g. lipids, carbohydrates, proteins, with different physico-chemical properties instead of chl-a concentrations of the seawater. This new approach requires information of distinct OM groups in both marine matrices (seawater and aerosol particles) such as the lipid concentrations performed in the present study."

R#2-2) In general, it is crucial to discuss location of sampling and the temporal succession of sample events since enrichment factors for aerosols are calculated and, more importantly, conclusions on processes leading to the observed enrichment are drawn.
Marine sources of the aerosols sampled at CVAO most likely do not match the location where they have sampled the SML and ULW, nor did sampling of aerosols (over the course of 24 hours) matches the specific time slots of seawater sampling.

The reviewer addressed a very important point: the comparability of aerosol particle measurements and seawater measurements. In our approach of concerted measurements, we combined PM_1 aerosol particle samples (sampled for 24 h) with spot samples taken in the ocean (ULW, SML) during the aerosol sampling period. To allow a comparison of these two matrices, we strongly considered several additional parameters, 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 and in a paper regarding amino acid measurements within this campaign and show that aerosol particles were predominantly of marine origin with low to medium dust influences (Triesch et al., 2020;van Pinxteren et al., 2020). In this context a possible transport of the aerosol particles is also discussed.

We have addressed this briefly 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 PM_1 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)."

R#2-3) The authors further compared the enrichments of lipid classes in the SML and aerosols to a defined theoretical 'surface activity' characterized by certain criteria i.e. density, partitioning coefficient between octanol and water (Kow) and topological polar surface area (TPSA). It should be kept in mind, that the solute is water and thus surface enrichment of lipids may be rather dictated by amphiphilic behavior i.e. an increase in TPSA and lower Kow.

We thank the reviewer for his comment. The 'surface activity` is a parameter regarding the enrichment of lipid classes in the SML and on the aerosol particles (e.g. Burrows et al. (2014)). To estimate and describe this surface activity for lipids we used different physico-chemical parameters (K_{OW}, TPSA and density) as described and discussed in detail in the SI (page 26/27) in section "surfactant activity of investigated individual lipid classes".
We agree with the reviewer that the amphiphilic structure of lipids in water is not negligible. Due to hydrophilic and hydrophobic components within the lipid structures, it is likely that not only one distinct parameter, but e.g. a combination of physico-chemical parameters might explain the observed enrichment of lipid classes on the aerosol particles. As suggested by the reviewer, we therefore performed a multilinear regression of the parameters EF_{aer}, TPSA and K_{OW} as shown in the Figure R1 below. The statistical parameters of this regression ($f(EF_{aer})=k1+k2*TPSA+k3*K_{OW}$) are the following: $R^2=0.45$ and n=11 but p=0.0875, which can therefore not be described as statistically significant, but only as a trend.

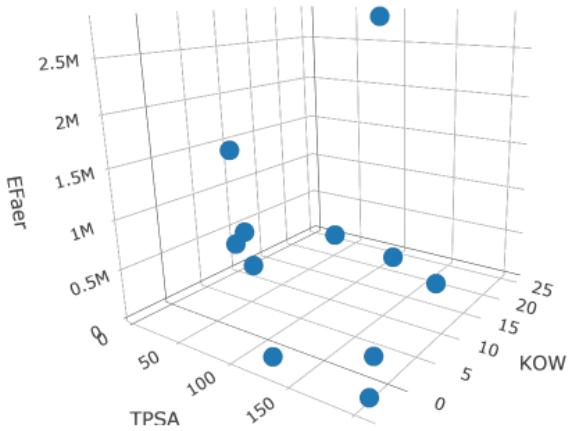

Figure R1: Plot of KOW, TPSA and the EF_{aer} of the individual lipid classes

Therefore, this approach unfortunately does not contribute any clear added value to the explanation of EF_{aer} by these two physico-chemical parameters and we think it is not meaningful to include it in the manuscript.

R#2-4) Also, it should be discussed how the two models of 'surface activity' compare (the authors also calculate adsorption coefficients based on concentrations and saturation vapor pressure as proxy for enrichment in the bubble-water-interface). I am not yet completely convinced that these approaches actually help to understand surface dynamics of enriched substances in the marine realm.

The idea of the adsorption coefficient is based on the study of Kelly et al. (2004). In this study, they regarded the atmospheric distribution and enrichment of oxidized organic compounds in the aerosol particle from the gas phase to the aqueous phase. Assuming equilibrium state, we made the assumption that such a distribution and enrichment is also possible from the aqueous (seawater) phase to the gas phase. By considering these two distribution possibilities between gas and aqueous phase, we want to discuss the distribution of analytes in the seawater with respect to air bubbles in connection with the formation of primary aerosol particles by the bubble bursting process.
This is a new theoretical approach, where the observed differences in selective transfer of lipids (different EF_{aer} for the different lipid classes) are described by the adsorption coefficients K_a and K_{aq}, based on the individual physical parameters of the lipid classes (Henry's law constant (H) and saturation vapor pressure (p)). These constants are used to describe the physical-dynamic effects of the analytes in the liquid medium. By calculating the adsorption coefficient in air (K_a), for example, it is possible to determine from which analyte concentration the partial pressure of the analyte is exceeded. If this happens the analyte then condenses on existing surfaces. The adsorption coefficient in water (K_{aq}) expresses the maximum amount of the analyte that can be dissolved. If this value is exceeded ($K_a>K_{aq}$), enrichment takes place in this medium. As we have explained in the main text, with this theoretical approach the distribution of the analyte can be estimated:
"When $K_{aq}>>K_a$ (Fig. S17a), the analyte should be preferred distributed (from water) to air (inside the bubble). When $K_a>>K_{aq}$ (Fig. S17b) in turn, the analyte should be preferably distributed (from air) into water while the analyte should be preferred distributed within the bubble interface when $K_{aq}\sim K_a$ (Fig. S17c)." (Manuscript: page 17, line 14-15)
We agree that this theoretical approach needs to be further investigated in future studies (e.g. tank/laboratory studies), because of the low number of available data points. Still, we could show in this study that this theoretical approach has the potential be used to explain the variance of the EF_{aer} for lipid classes.

In order to explain the adsorption coefficients and their significance more clearly, we have added the following statements to section 'Adsorption of the individual lipid classes at bubble air-water interface' on page 31 in the SI. It now reads as follows: "K_a expresses the maximum gas-phase concentration of the analyte before condensation on surfaces occurs." (SI, page 31, line 16/17) and "K_{aq} expresses the maximum amount of analyte that can be dissolved. If this value is exceeded ($K_a>K_{aq}$), enrichment takes place in this medium." (SI, page 31, line 19/20).

#2-5) In the end, I advise that the authors should focus on the biological context since all lipid classes seem to relate to the marine realm, degradation indices are derived, pigment analysis and basic abundances of microorganisms were measured and INP analysis ultimately shows that a strong biological component controls activity and aim to better link their findings.

We agree that the biological link is very important in this study. We have emphasized this at several parts throughout the manuscript.

Starting with the introduction, we have mentioned that the information of lipid classes "can be used as specific markers for the identification of OM sources and biogeochemical cycles in the marine environment (Parrish et al., 1988;Frka et al., 2011)." (page 2, line 26/27)
Furthermore, we discuss which lipid classes have been reported in context to (micro)organisms (page 2, line 27- page 3, line 3). We have phrased one of the main objectives of this study as follows: „The present work aimed at investigating lipids at the Cape Verde Atmospheric Observatory (CVAO) as species representative for different lipid classes in the marine environment of the tropical Atlantic Ocean, to study their abundance, (biogenic) sources and selective transfer into the marine atmosphere. The lipid data set obtained for samples from different marine compartments at the CVAO is discussed with regard to its biological origin and its ice nucleation potential." (page 4, line 10-14)
In section 3.1.4 (manuscript page 11) not only the general biological results are introduced and discussed, but also associated in detail with individual lipid classes through statistical correlation analyses. Moreover, we concluded that "it is most likely that bacteria have influenced the lipid pool which is consistent with the results obtained from the lipid composition" (page 12, line 1-2).
The relationship between chemical, physical and biological measurement data was also considered and discussed as follows in section 3.3 (page 19, line 17-20): "The relationships presented here between the lipids in general and in particular the lipid classes with assigned biological context (PE, FFA) and INP activity at higher temperatures (-10 °C, -15 °C) in the ambient SML indicating that lipids in the tropical North Atlantic Ocean have the potential to contribute to (biogenic) INP activity when transferred to the atmosphere."
Finally, in the conclusion (page 19/20) we summarized our findings with a strong focus on biological lipid connections.
To this end, we believe that the connection between lipids and biological sources from the introduction through the results section to the conclusion is outlined through the manuscript, thus illustrating the connection between chemical and biological processes regarding lipids in the marine environment.

Specific comments

#2-6) Page 2 Line 24-26 Clarify: Marine dissolved lipids are produced either by dissolution from the particulate fraction, or 'by' primary production: : : living cells are also part of the particulate pool. Maybe better distinguish between abiotic and biotic processes and include the microbial loop?

We agree with the reviewer's comment and clarified this sentence. Now it reads as follows (page 2, line 23/24): "Marine lipids can be produced by abiotic and biotic processes and play an important role as energy sources in the aquatic ecosystem (Parrish, 2013)."

#2-7) Page3 Line 3 Consider quoting Becker et al. 2018 on TG's as storage compounds in phytoplankton.

We thank the reviewer for this comment and quoted the interesting paper you mentioned. This now reads as follows in the manuscript (page 2, line 32 - page 3, line 1): "Triacylglycerols (TG) indicate metabolic reserves (Frka et al., 2011) and are reported as storage compounds in phytoplankton (Becker et al., 2018)."

#2-8) Line 8-9 'However, Chl-a (concentration?) is also found to be a poor descriptor of autotrophs (biomass, cell abundance?), especially in oligotrophic regions (Quinn et al., 2014).' The authors should clarify this, since Quinn et al. concluded that Chl-a concentration is only a poor proxy for organic matter enrichment in aerosols.

We agree with the reviewer's comment and removed this sentence. For a more detailed discussion and description of chl-*a* in seawater as a proxy for the prediction of OM on aerosol particles we would like to refer to the review comment R#2-1b).

#2-9) Line 27-30 ': : :TG lipid class serves as an indication that the aerosol particles consist to a certain extent of freshly emitted sea spray: : :' Additional literature or an explanation would be very helpful, since Schiffer et al. 2018 concluded that on SSA surfaces the 'reduction in activity could essentially reduce the processing (by BC Lipase) of triacylglycerols into fatty aicds' i.e. if TG is present in SSA, it is not necessarily an indicator of freshly emittance. Also relevant on page 13, line 8

We thank the reviewer for this comment and agree that the transfer of TG lipase from the sea to the atmosphere mentioned in Schiffer et al. (2018) and their statement that lipases have the potential to change the composition of SSA (described in the study of Schiffer et al. (2018) as "Triacylglycerol lipases have recently been shown to be transferred from the ocean to the atmosphere in atmospheric sea spray aerosol (SSA). Lipases have the potential to alter the composition of SSA…") are not sufficient to make a statement about the freshness of the aerosol particles. Only under the assumption that the triacylglyercol lipase enzyme a) has been transferred to the aerosols and b) is actively present there, it is possible to say that TG can be degraded to FFA. However, these enzymatic investigations were not performed in this study. Therefore, we have removed these statements from the revised manuscript.

#2-10) Line 29 'In laboratory studies by the authors Schiffer et al. (2018), lipase enzymes have shown to be transferred from the ocean into the atmosphere: : :' Again, additional literature and explanations are needed. Schiffer et al. 2018 conducted a laboratory experiment on surface behavior of lipase and lipids in a Langmuir trough and conducted molecular dynamics simulations to judge on the activity of enzymes on SSA.

We would like to refer to the previous reviewer comment R#2-9.

#2-11) Page 4 Line 19 A map illustrating seawater sampling stations and CVAO location including distances and height of tower (!) would be helpful. Also, wind directions over the sampling period seem crucial to your study.

We agree with the reviewer's comment. We added a map illustrating the seawater sampling station and the CVAO including the distance between both stations and the height of the tower at the CVAO. Moreover, we added the prevailing wind direction during the sampling period in this map. The map is listed as Figure S1 in the Supporting Information (page 2).

#2-12) Page 5 Line 25-28 The authors should mention that the analysis was conducted by Flow Cytometry. It is not completely clear, if the analysis of eukaryotic (based on autofluorescence?) and prokaryotic cells (based on staining with SYBR green?) was conducted simultaneously and if autotrophic prokaryotes were excluded from prokaryotic cell numbers?

According to the reviewer's suggestion, we provide more details about microbial cell counting via flow cytometry in the revised manuscript (page 6, line 7-14), which reads now as follows: "Microbial cell numbers were counted via flow cytometry after seawater samples were fixed, flash-frozen in liquid-nitrogen, and stored at -20 °C. For prokaryotic cells counts, all samples were stained with SYBR Green solution. Counting was performed after addition of latex beads serving as an internal standard. Further

details can be found in Robinson et al. (2019). Small autotrophic cells were counted in a separate measurement after addition of red fluorescent latex beads (Polysciences, Eppelheim, Germany). Cells were detected by their signature in a plot of red (FL3) vs. orange (FL2) fluorescence, and red fluorescence vs. side scatter (SSC). This approach allows discrimination between different groups of prokaryotic and eukaryotic autotrophs (Marie et al., 2010), which in our case were size classes defined as *Synechococcus-like* cells and *Nanoeucaryotes*."
As assumed by the reviewer, prokaryotic and eukaryotic counts were performed in two separate measurements, based on SYBR-green-staining and autofluorescence signals, respectively. Prokaryotic cell numbers (i.e. TCN) include autotrophic prokaryotes. We decided not to correct TCN for autotrophic prokaryotes, as the latter were 2 orders of magnitude less in abundance, and thus, their numbers had only negligible impact on TCN numbers and dynamics. Moreover, the correction of TCN would have needed proper discrimination of *Prochlorococcus-like* cells as well, which we dich not perform in the present study. In order to avoid confusion, we have deleted the wording 'heterotroph' for TCN (page 11, line 21), and added the above mentioned fact to page 11, line 32/33: "Due to the low abundance of *Synechococcus-like* cells, we assume that most bacteria counted as TCN are heterotrophic and could have taken up the 'metabolites'."

#2-13) Page 6 Line 21 ': : : while lower LI values indicate that the appearing lipid classes are very fresh or resistant to degradation: : :' In my opinion, this is somehow critical and should be explained in more detail, since degradation products are themselves defined by their resistance to further degradation. This influences also concluding remarks later on, e.g. Page 10, line 2 ': : :suggesting that the dissolved lipid classes were quite resistant to degradation: : :' How can the authors decide whether lower LI's indicates fresh production or resistance to degradation as introduced in the experimental section?

Goutx et al. (2003) proposed to use this lipolysis index (LI) as a new tool which characterizes the degradation stage of labile organic matter in natural seawater samples. A dominance of ALC, FFA, MG, DG counterparts, i.e. lipids present in the living plankton, over lipid degradation product indicate lipid freshness. Therefore, higher LI means the lipids are more degraded and vice versa. We rewrote the sentence on page 7, line 5-7 and it reads now as: "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."
Further, we would like to underline that lipid degradation indices (ALC, FFA, MG, DG), which can be detected by thin layer chromatography, are only first step in lipid degradation. They are subject to further degradation, whether to smaller molecules that are not any more soluble in organic solvents or converted to CO_2.

Moreover, we rewrote also the sentence on page 10, line 20 - page 11, line 2, which reads now as follow: "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."

Overall, we may assume that lipids that are found in the dissolved fraction were composed of more saturated compounds. It is known that saturated compounds are generally less reactive than unsaturated (e.g. Sun and Wakeham (1994).

#2-14) Line 13 'However, these differences between bacterial and phytoplankton sources are not reflected in the total observed (particulate) lipid pool, because degradation products like FFA also contribute strongly.' Since FFA are present in the particulate fraction they apparently had to be enclosed within intact cells or other larger particles (>0.7_m). To my understanding, FFA would be part of the dissolved fraction otherwise. Thus, I am

not so sure if FFA can serve as an indicator of degradation when encountered within the particulate pool. Is the LI defined as a proxy for degradation in the dissolved and particulate phase likewise (Goutx et al. 2003)?

Lipids that are found in the dissolved fraction are part of non-living OM, and from free living bacteria. Those bacteria represent small part of all bacteria in the seawater. Therefore, we may assume that lipids from the dissolved fraction are of non-living origin. Moreover, FFA represent small fraction of total cell lipids, from low detection limit to 10% (Jónasdóttir, 2019). So, we take that it is reasonable to take FFA as and degradation product.
Concerning the LI: Besides Goutx et al. (2003), who suggested to use this lipolysis index (LI) as a new tool which characterizes the degradation stage of labile organic matter in natural sea water samples, the LI was also used by Parrish et al. (1995), who evaluated LI in the particulate fraction. Based on these previous studies, the LI can therefore be considered as a proxy for the degradation of OM in both the dissolved and the particulate fraction.

#2-15) Page 9 Line 15-16 The authors should quote, which lipid class they refer to when talking about 'chlorophyll degradation products'.

In the manuscript we have now defined that 'chlorophyll degradation products' are the pigments (PIG) determined by the TLC-FID method.

This is now read as follows (page 10, line 15-17): "This coincides well with the low concentrations of chlorophyll degradation products (PIG), suggesting that only moderate grazing took place and the (pigment-containing) organisms were fresh and in healthy condition (van Pinxteren et al., 2020)."

#2-16) Line 18-19 Please clarify to what exactly you are referring to. Does 'This observation' relates to enhanced degradation in the SML or simply high LI values in the East Atlantic Ocean?

We clarified this sentence and it now reads as follows (page 10, line 18-20): "A higher LI in the SML was also observed by Gašparović et al. (2014) in the East Atlantic Ocean and can be attributed to both bacterial and photochemical abiotic degradation (Christodoulou et al., 2009)."

#2-17) Page 10 Line 33 Since the authors judge on ': : :Chl-a as a proxy for bioproduction, may not sufficiently explain the variability of lipid classes: : :' They should introduce their results regarding Chl-a in greater detail instead of referring to a table in the supplementary material. Also, I do not recall an introduced scientific discussion concerning the reliability of Chl-a as a proxy for lipid classes.

With regard to reviewer comment R#2-1b we want to emphasize again that chl-*a* was not used as a proxy for lipid classes. Therefore, we have removed this mentioned sentence from the manuscript. We have now included the results of the chl-*a* concentrations in the manuscript (with reference to the SI) in section 3.1.4.

This now reads as follows (page 11, line 9-11): "In addition, the chl-*a* concentration in seawater increased from 0.11 µg L^{-1} to 0.60 µg L^{-1} (Table S2) during the campaign, but was generally low compared to other subtropical/tropical regions or worldwide (Duhamel et al., 2019)."

#2-18) Page 11 Line 7-14 ': : : slightly higher enrichment of the particulate fraction: : :' I actually

do not think, this is meaningful to discuss in relation to the presented results, since variance of the dissolved EF's range within the larger variance of particulate EF's and means only very slightly.

We agree with the reviewer's comment that this variance is not meaningful for such a discussion. Therefore, we have deleted the sentences dealing with the 'very slightly enrichment of the particulate fraction compared to the dissolved fraction of lipids' from the manuscript.

#2-19) Line 12-14 'Moreover, marine dissolved lipids can be produced by dissolution from the particulate fraction and through primary production and released during the life cycle and after cell death. This(!) might lead to a slightly higher SML enrichment of the particulate lipids.' Please elucidate, I cannot follow the conclusion made. Why does a dependence of the dissolved pool from the particulate pool indicate higher enrichments? Increased degradation and abiotic photochemical reaction within the SML could likewise produce higher enrichment of the dissolved fraction: : :

With regard to the reviewer comment R#2-18, we have shortened the discussion on lipid enrichment in SML. In this context, we have removed these sentences from the manuscript.

#2-20) Page 15 32 Lead the reader towards your conclusion stating that 'a differentiation of the contribution' of the particulate versus the dissolved pool was not possible also when taking into account the size of the fractions. To my understanding it is more likely that the fraction of lipids smaller than 0.7_m (i.e. dissolved) contributed to submicron aerosols (PM1).

Within the sample preparation procedure, the seawater was divided into dissolved fraction (<0.7 µm) and particulate fraction (0.7-200 µm). Aerosol particles (<1 µm) were collected on the PM_1 aerosol particles. 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.
In our study, we calculated the EF_{aer} based on the lipid concentrations of the dissolved fraction in seawater as well as of the particulate fraction. The enrichment factors were not very different in both cases and the conclusion are not affected. We discussed this in the SI (SI: page 28, line 10-13).

To underline this fact, we added in the revised manuscript (page 14, line 17-19): "The EF_{aer} based on the particulate total lipids in SML was with an average of $2 \cdot 10^5$ very similar to the EF_{aer} of the dissolved total lipids ($3 \cdot 10^5$) as discussed in the SI, Table S8."
As all the several lipid classes were present in the dissolved and particulate fraction, an attribution to the lipid classes on the aerosol particles to a dissolved or particulate seawater origin was not possible, as stated in the manuscript (page 17, line 2-3).

#2-21) Page 15 Line 14 I actually sense it is assumed that marine bacteria transmitted into the atmosphere behave similarly in terms of production and metabolism than within the hydrosphere i.e. their natural habitat. I think, this is a hypothesis which needs to be discusses more carefully. (Also Page 4, line 4)

We apologize for this misunderstanding. We did not mean to imply that bacterial metabolism will be similar in both the 'original' aquatic habitat and in aerosols. This would be bay far too speculative and for sure we don't show any data to support this. We nevertheless think that microbial activity may

affect the composition of the OM pool of aerosol particles – either passively or actively – although the extent of either contribution is absolutely unclear.

We have rephrased this part to: "Here, besides passive contribution (i.e. providing lipids to aerosol particles upon cell disintegration), bacteria may also actively influence the OM composition of aerosols (i.e. lipid production or degradation). However, the extent of this passive and especially of potential active bacterial contribution to the lipid pool of aerosols warrants further studies." (page 16, line 19-21)

#2-22) Page 18 Line 19 ': : :samples are consistent with the results of Wilson et al. (2015) indicating that lipids in the tropical North Atlantic Ocean have: : :'. This could leave the reader under the impression that Wilson et al. 2015 have assessed lipids and concluded they contribute to the biogenic INP pool.

We agree with the reviewer's comment and rephrased this sentence to avoid misunderstandings. It now reads as follows (page 19, line 17-20): "The relationships presented here between the lipids in general and in particular the lipid classes with assigned biological context (PE, FFA) and INP activity at higher temperatures (-10 °C, -15 °C) in the ambient SML indicating that lipids in the tropical North Atlantic Ocean have the potential to contribute to (biogenic) INP activity when transferred to the atmosphere."

#2-23) Line 34 'However, concentration of Chl-a, as often used proxy for biological production via phytoplankton, is not sufficient to describe lipid concentration.' Again, Chl-a is not described as a proxy to determine lipid classes in literature.

We agree with the reviewer's comment and have deleted this ambiguously worded sentence. For a more detailed explanation of the relationship between chl-*a* concentrations in seawater and the prediction of OM on the aerosol particles we would like to refer to the comment R#2-1b).

#2-24) Supplementary Material Page 28 Table S7 'XLogP3-AA' replaces Kow, which is found in the main text, yet for the method in use to calculate this value, no literature is provided.

We have changed the designation in MS and SI and in the revised version accordingly and we continuously use (log) K_{OW}. The column in table S7 (page 26) has been renamed to log K_{OW} and an explanation of the calculation has been added as a footnote, which reads as follows: "* The calculation of the octanol-water partition coefficient (KOW) is based on the XLOGP3-AA method, which predicts the log KOW as XLogP3-AA value of compound by using the known log KOW of a reference compound as a starting point (Cheng et al., 2007). For each compound we also used the PubChem database (https://pubchem.ncbi.nlm.nih.gov/), an open chemistry database at the National Institutes of Health (NIH), to extract chemical and physical properties."

Technical comments

#2-25) Page 1 Title: 'Concerted measurements of lipids in seawater and on submicron aerosol particles at the Cape Verde Islands: biogenic sources, selective transfer and high enrichments'. The authors should overthink the title, e.g. include instead of 'high enrichment', 'ice nucleating potential' to better describe the content of the article.

We would like to point out that the correlations found between lipids and ice nucleation potential relate to seawater measurements. 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 regarding aerosol particles with respect to INP activity. For example, dust can also play an important role for ice nucleating potential in the marine environment as discussed e.g. by Burrows et al. (2013). Because of these limitations, we consider the results from section 3.3 'Connection between lipids and INP activity in seawater' not strong enough to switch the focus of the paper and its title to the 'ice nucleating potential' of lipids.
We would therefore suggest to leave the title 'Concerted measurements of lipids in seawater and on submicron aerosol particles at the Cape Verde Islands: biogenic sources, selective transfer and high enrichments' (page 1) and also section 3.3 'Connection between lipids and INP activity in seawater' (page 18/19) as it is.

#2-26) Line 16-23 Exclude 'To this end'. The set of lipid classes analyzed includes : : : and rephrase the following sentence: Introduced lipid classes have been analyzed in the dissolved and particulate fraction of seawater, while differentiating between underlying water (ULW) and the sea surface microlayer (SML), and on submicron aerosol particles (PM1) collected from the ambient (air?) at the Cape Verde Atmospheric Observatory (CVAO). Or consider other fragmentation.

We agree with the reviewer's comments and have reformulated the sentence as proposed and divided it into two sentences. It now reads as follows (page 1, line 16-24): "The set of lipid classes includes hydrocarbons (HC), fatty acid methyl esters (ME), free fatty acids (FFA), alcohols (ALC), 1,3-diacylglycerols (1,3 DG), 1,2-diacylglycerols (1,2 DG), monoacylglycerols (MG), wax esters (WE), triacylglycerols (TG), phospholipids (PP) including phosphatidylglycerols (PG), phosphatidylethanolamine (PE), phosphatidylcholines (PC), glycolipids (GL) including sulfoquinovosyldiacylglycerols (SQDG), monogalactosyl-diacylglycerols (MGDG), digalactosyldiacylglycerols (DGDG) and sterols (ST). Introduced lipid classes have been analyzed in the dissolved and particulate fraction of seawater, while differentiating between underlying water (ULW) and the sea surface microlayer (SML), and on ambient submicron aerosol particle samples (PM1) collected from the ambient at the Cape Verde Atmospheric Observatory (CVAO) applying concerted measurements."

#2-27) Line 24 Include ∑toalignstyletotherestofthetext

We made sure the character ∑ was used uniformly throughout the manuscript according to the ACP Guidelines (Times New Roman in font size 10).

#2-28) Line 32-33: For aerosols, however, the high enrichment of lipids (as a sum) on aerosols corresponds well: : : Include 's' and exclude one of the redundant 'aerososls'.

We included the 's' in aerosols and removed the redundant 'on aerosols' in this sentence. It now reads (page 1, line 32 - page 2, line 1) : "For aerosols, however, the high enrichment of lipids (as a sum) corresponds well with the consideration of their high surface activity, thus the EF_{aer} (enrichment factor on submicron aerosol particles compared to SML) ranges between $9 \cdot 10^4$-$7 \cdot 10^5$."

#2-29 a)Line 32 Separate 'physico-chemical' to align style to the rest of the text.

We used 'physico-chemical' in the whole text of the revised manuscript.

R#2-29b) Page 2 Keywords: consider to replace rather generic words such as ‘seawater’, ‘concerted measurements’, ‘transfer’ by e.g. ‘sea surface microlayer’, ‘sea spray aerosols’to characterize the work.

Following the suggestion, we have revised the keyword list and it now reads as follows (page 2, line 13/14): “Lipids, organic matter, submicron marine aerosol particles (PM1), sea surface microlayer (SML), ice nucleating particles (INP), enrichment factor, concerted measurements, Cape Verde Atmospheric Observatory (CVAO).”

#2-30) Page 4 Line 6 Rephrase and clarify this sentence ‘is discussed in terms of biological and physical (INP) parameters: : :’ E.g. is discussed in the context of its biological origin and its ice nucleation potential.

We rephrased and clarified this sentence accordingly. Now it reads (page 4, line 12/13): “The lipid data set obtained for samples from different marine compartments at the CVAO is discussed with regard to its biological origin and its ice nucleation potential.”

#2-31) Page 5 Line 33 The authors should briefly explain the unit in use: Does the unit relates to the total filter area used for the extraction of lipids in aerosols (28.27cm2)?

We briefly explained that the 28.27 cm^2 of the total filter area was used for the extraction of lipids in aerosol. It now reads as follows (page 6, line 20/21): “For the analysis of lipid classes, 28.27 cm^2 of the total PM_1 filter area were extracted and measured following the procedure for particulate lipids in seawater (see section 2.2.1).”

#2-32) Page 7 Line 14 Exclude, since this is a repetition of line 12: ‘: : :but considered a ‘trend’ to be valid: : :’.

In section ‘2.2.5 Statistical analysis’ we have discussed the statistical parameters that we used in seawater and the conditions for defining relationships statistically relevant or just as ‘trends.’ Since we have used both ULW and SML samples for the statistical analyses, but these have, for example, different sample numbers (n), which also affects the statistical parameters, we have defined both sample types individually. In order to make the selection criteria for a trend in ULW and SML (which are slightly different) easy for the reader to understand, we would therefore prefer to leave these explanations of the "trend in SML" in the manuscript.

#2-33) Page 8 Line 8 Maybe introduce the PE/PG ratio along with LI and EF’s in the experimental section.

We agree with the reviewer’s comment and introduced the PE/PG ratio together with the LI in section 2.2.3 ‘Lipid ratios’, which reads now as follows (page 7, line 9-12): “The PE/PG ratio can be used to determine the origin of the phospholipids that contribute to the OM pool in seawater (Goutx et al., 1993). Here, PG as the most important compound of the phospholipids of microalgae is an indicator for algae as potential sources, whereas PE is predominantly found in bacterial membranes and thus represents an indicator for bacterial sources (Goutx et al., 1993).”

#2-34) Line 10 Replace ‘afterwards’ with ‘towards the end’.

We took the suggestion and it now reads as follows (page 9, line 6-8): “The PE/PG ratio varied along the campaign with increasing values towards the middle of the campaign (maxima on 03/10/2017 and 04/10/2017) and decreasing values towards the end (Table S4), following the same trend as the total bacteria number (TCN, Table S3).”

#2-35) Line 11 Consider rephrasing or exclude ‘-‘: ‘This indicates a change in the lipid dominant biological contributions, with bacterial sources dominating in the first part and
especially in the middle of the campaign, whereas in the last part rather phytoplanktondominated contributions to the lipid pool.’

We rephrased this sentence accordingly. It now reads as follows (page 9, line 8-11): “This indicates a change in the lipid dominant biological contributions, with bacterial sources dominating in the first part and especially in the middle of the campaign. However, in the last part of the campaign (afterwards on 05/10/2017) contributions to the lipid pool were rather dominated by phytoplankton.”

#2-36) Page 9 Line 18 Include the articles ‘: : :release in the SML compared to the ULW: : :’.

We inserted the articles ‘the’ and it now reads as follows (page 10, line 17/18): “However, on specific days, the LI_{SML} of PL was ≥ 0.5 (Table S5), indicating increased OM/lipid degradation and metabolite release in the SML compared to the ULW.”

#2-37) Page 10 Line 32 Exclude ‘the’: ‘: : :it is most likely that the bacteria have influenced: : :’
Check for consequential mistakes.

We excluded ‘the’ and it now reads as follows (page 11, line 33 - page 12, line 2): “Although it remains unclear whether the bacteria have a passive (i.e. via membrane) or active (i.e. metabolism of the lipid ‘metabolites’) effect on the observed correlation between LI_{PL} and TCN, it is most likely that bacteria have influenced the lipid pool which is consistent with the results obtained from the lipid composition.”

#2-38) Page 11 Line 23 ‘: : :OM compound groups: : :’ I think, this is redundant, use groups or compounds instead.

We thank the reviewer for his comment and used ‘OM compounds’ in this sentence. Now it reads as (page 12, line 26-28): “A comparison of lipid enrichment with other OM compounds showed that SML enrichment of lipids seemed to be less pronounced in contrast to other organic species such as amino acids (Reinthaler et al., 2008; Triesch et al., 2020).”

#2-39) Line 28 Instead of ‘regarded’ use ‘considered’.

We agree and it now reads as follows (page 12, line 30-32): “It has to be considered that a SML described here represents a layer with a thickness of about 100 µm (van Pinxteren et al., 2017) and therefore gradients within this layer (e.g. an enhanced enrichment of surfactants only in the top layer of a few µm) cannot be considered here.”

#2-40) Page 12 Line 6 ‘: : :different diversity and different taxa: : :‘ Redundant if diversity actually

indicates the composition of species. However, it can be defined as functional etc.

We agree that this is redundant. We meant the overall community composition to differ between SML and ULW. This might imply differences in functional diversity as well and we corrected this sentence accordingly: "Besides increased abundance of microbial cells, this may also be due to a different microbial community composition between SML and ULW and thus, different functional diversity (Cunliffe et al., 2011)." (page 13, line 10-12)

#2-41) Line 8 ': : :in the particulate fraction. In the particulate fraction: : :' Try to rephrase due to repetition.

We rewrote the second sentence to avoid repetition. It reads now as follows (page 13, line 12-14): "The metabolic reserves lipids, represented by TG, showed the highest variability of enrichment in the SML along the campaign in the particulate fraction. In this fraction, $EF_{SML(TG)}$ varied between 0.3 and 4.4, resulting in an averaged enrichment of 2.3."

#2-42) Line 11 Consider rephrasing: This indicates that the lipid reserves are stored in the particulate lipids and are dissolved producing dissolved TG. For example: This indicates that lipid reserves such as TG are stored within the particulate pool and upon dissolution become part of the dissolved pool.

We rephrased this sentence as suggested. It now reads as follows (page 13, line 16/17): "This indicates that lipid reserves such as TG are stored within the particulate pool and upon dissolution become part of the dissolved pool."

#2-43) Line 13 Use 'physicochemical descriptors' instead of 'physical processes'.

We agree and it now reads as follows (page 13, line 18/19): "Altogether, our results indicate that physicochemical descriptors alone, which are related to the surface activity of the lipids, are not sufficient to describe the SML enrichment of the lipids, at least not in the top 100 µm."

#2-44) Line 28 Caption of Fig. S11 states 'dissolved' lipids in aerosols particles, which is probably a mistake.

We thank the reviewer for this comment. Regarding the reviewer's comment R#2-57, Figure S11 (percentage composition of lipids on aerosol particles) has been removed.

#2-45) Page 13 Fig. 3 Absolute concentration of lipids in aerosol particles do not fit percentage data in the supplement of Fig.S11. For example, on the 29/09/2017 PE are present in Fig.3 while being completely absent in Fig. S11, the color schemes might have been confused.

We thank the reviewer for this comment. As correctly assumed, the color scheme of PG and PE was swapped in Figure S11 The uniform color scheme of the individual lipid classes in the Figures in the manuscript as well as in the Supporting Information was double-checked. PE now shows the defined red tone and PG the green tone, as is now the case throughout the paper (MS and SI). As mentioned above, regarding the reviewer's comment R#2-57, Figure S11 has been removed.

#2-46) Line 6 ‘bacteria, possibly transported from the ocean into the atmosphere, produce PE on aerosol particles’: : : Better to replace ‘produce’ by ‘contribute’.

We agree with the reviewer’s comment and replaced ‘produce’ by ‘contribute’ in this sentence. It now reads as (page 14, line 10-12): “Since heterotrophic bacteria are reported as a dominant source of PE (Michaud et al., 2018), this suggests that i) bacteria, possibly transported from the ocean into the atmosphere, contribute PE on the aerosol particles and/ or ii) PE is directly transferred from the ocean into the atmosphere, likely via bubble bursting.”

#2-47) Line 10 Replace ‘maritime samples’ by ‘of marine origin’.

This sentence was removed during the revision of the manuscript.

#2-48) Page 15 Line 9 This is misleading, better state ‘aerosol particles’ instead of ‘particle phase’.

We agree with the reviewer’s comment and used ‘aerosol particles’ instead of ‘particle phase’ to avoid any misunderstanding. It reads now as (page 16, line 10/11): “TG and ALC showed a high enrichment both in the SML and in the aerosol particles.”

#2-49) Line 30 Rephrase: ‘The finding here, that both DL and PL, contain similar classes of lipid, which are also found on the aerosol particles, suggest that both types of lipids in seawater are transferred to the aerosol particles via bubble bursting process.’

We rephrased this sentence accordingly. Now it reads as follows (page 16, line 34 - page 17, line 2): “The finding that both classes of lipids (DL and PL) are found on the aerosol particles (Fig. 5, Fig. S12) indicates that both types of lipids can be transferred from seawater to the aerosol particles, e.g. via bursting the bubbles.”

#2-50) Page 17 Figure 6 ‘interface’ is hard to read. Improve color scheme. There is also a logical mistake, since the caption states ‘Scheme of a bubble during the bubble bursting process’. During bubble bursting, the bubble actually has reached the air-water interface i.e. exhibits two surfaces oriented towards the air inside and the atmosphere outside. Otherwise, the caption should state ‘during the process of a bubble rising through the water column’: : :

We improved the color scheme as suggested. Moreover, we rephrased the caption of this Figures. It reads now: “Figure 6: Scheme of a bubble during the process of a bubble rising through the water column, distinguished between ‘air’ (inside the bubble), ‘water’ (surrounding the bubble), the ‘interface’ (bubble surface) and the distribution of the lipid classes MGDG, TG and ALC related to their K_a and K_{aq} values”. Figure 6 can be found on page 18 in the MS.

#2-51) Line 12 Rephrase ‘contain: : : abilities’.

We rephrased this sentence and it now reads as follows (page 18, line 12/13): “One main feature of biological components in general is their potential ability to contribute to ice nucleation and act as INP in the atmosphere (Šantl-Temkiv et al. (2019) and references therein).”

#2-52) Page 18 Line 11-12 Replace ‘by: : :’ with ‘of sea spray aerosols’.

We replaced ‘by’ with ‘of’. Now it reads (page 19, line 11/12): “DeMott et al. (2018) reported that ice nucleation by particles containing long-chain fatty acids in a crystalline phase was relevant for freezing of sea spray aerosols.”

#2-53) Line 25 Consider rephrasing: ‘At the CVAO, concerted measurements of lipids as representatives of their respective classes were performed during the MarParCloud campaign to determine their concentrations in seawater and SML (as dissolved and particulate lipids) and on submicron aerosol particles.’ For example: Concerted measurements of lipids were performed in proximity to the Cape Verde Islands to compare the concentration of specific lipid classes in submicron aerosol particles and in the dissolved and particulate phase of seawater (ULW and SML).

We rephrased this sentence as suggested. Now it reads (page 19, line 25/26): “Concerted measurements of lipids were performed in proximity to the Cape Verde Islands to compare the concentration of specific lipid classes in submicron aerosol particles and in the dissolved and particulate fraction of seawater (ULW and SML).“

#2-54) Line 27 Consider rephrasing: E.g. The analysis of lipid classes in seawater showed that, although concentrations in the particulate and dissolved phase are generally very similar, the contribution of lipids within phases differed.

We rephrased the sentence accordingly. It reads now as follows (page 19, line 27/28): “The analysis of lipid classes in seawater showed that, although concentrations in the particulate and dissolved fraction are generally very similar, the contribution of lipids within fractions differed.”

#2-55) Page 23 Line 31-35 Check format, looks like a line spacing error.

We corrected the line spacing error.

#2-56) Page 25 Line 1 Adjust the predicate ‘Van’ to the same format i.e. ‘van’.

We have now written 'van Wambeke' as well as 'van Pinxteren'.

#2-57) Supplementary Material I recommend to shorten the supplementary information provided, maybe consider excluding Fig. S7, 8, 11, S12, S13, S19.

We have carefully reviewed the supplementary information and the proposed reductions and agree that in the submitted SI version Figure S7, S8 and S11 can be removed.
Regarding the other proposed figures in the SI, we would prefer not to exclude them as S12, S13 and S19 are important information for a better understanding of the context. Figure S12, ‘Boxplot explanation related to Fig. 4’, provided more information on the shown Boxplot (Fig. 4) in the MS. Figure S13, ‘Correlation plot of the EF_{aer} and the corresponding log KOW of the individual lipid classes: HC, TG, FFA, ALC, ST, 1,2DG, MGDG, DGDG, SQDG, PG, PE’, showed the correlation and the R^2 of the relationship between the EF_{aer} and the log KOW of individual lipid classes, which are discussed in the

MS. Figure S19, 'Overview of possible distributions of the analyte between interface, water and air: a) Kaq>>Ka, analyte is preferred distributed (from water) to air; b) Ka>>Kaq, analyte is preferred distributed (from air) into water; c) Kaq~ Ka, analyte is preferred distributed at the interface' illustrates the effects of the adsorption coefficients on the possible distribution of the analytes between interface, water and air and is in our opinion an important aid for the understanding of this adsorption coefficient approach.
By omitting the figures S7, S8 and S11 (so called in the submitted SI), the SI could be tightened and in addition there is a new numbering of the figures in the revised SI and therefore also of the references in the MS.

#2-58) Equalize color scheme and figures i.e. when drawing a regression line, use the same design and report same correlation values as in the main text e.g. R versus R2

We unified the design of the regression lines accordingly. Figures S11 (SI, page 12) and S16 (SI, page 17) have been adapted to the design of the other regression lines. The regression lines are now shown in black and the corresponding R^2 is also noted in the graph. Figure S9b) and Figure S9c) (SI page 10) is still an exception. Since the regression lines for ULW and SML are shown in the same graph, the regression lines for ULW are shown in black and for SML in blue for a better visual differentiation.

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

References

Burrows, S. M., Hoose, C., Pöschl, U., and Lawrence, M. G.: Ice nuclei in marine air: biogenic particles or dust?, Atmos. Chem. Phys., 13, 245-267, 10.5194/acp-13-245-2013, 2013.

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.

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.

Goutx, M., Guigue, C., and Striby, L.: Triacylglycerol biodegradation experiment in marine environmental conditions: definition of a new lipolysis index, Organic Geochemistry, 34, 1465-1473, 10.1016/S0146-6380(03)00119-0, 2003.

Jónasdóttir, S. H.: Fatty Acid Profiles and Production in Marine Phytoplankton, Marine drugs, 17, 151, 2019.

Kelly, C. P., Cramer, C. J., and Truhlar, D. G.: Predicting Adsorption Coefficients at Air−Water Interfaces Using Universal Solvation and Surface Area Models, The Journal of Physical Chemistry B, 108, 12882-12897, 10.1021/jp037210t, 2004.

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.

Parrish, C., McKenzie, C., MacDonald, B. A., and Hatfield, E. A.: Seasonal studies of seston lipids in relation to microplankton species composition and scallop growth in South Broad Cove, Newfoundland, Marine Ecology-progress Series - MAR ECOL-PROGR SER, 129, 151-164, 10.3354/meps129151, 1995.

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

2014.

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

Schiffer, J. M., Luo, M., Dommer, A. C., Thoron, G., Pendergraft, M., Santander, M. V., Lucero, D., Pecora de Barros, E., Prather, K. A., Grassian, V. H., and Amaro, R. E.: Impacts of Lipase Enzyme on the Surface Properties of Marine Aerosols, The Journal of Physical Chemistry Letters, 9, 3839-3849, 10.1021/acs.jpclett.8b01363, 2018.

Sun, M.-Y., and Wakeham, S. G.: Molecular evidence for degradation and preservation of organic matter in the anoxic Black Sea Basin, Geochimica et Cosmochimica Acta, 58, 3395-3406, 10.1016/0016-7037(94)90094-9, 1994.

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. Discuss., 2020, 1-24, 10.5194/acp-2019-976, 2020.

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

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

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.

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

Concerted measurements of lipids in seawater and on submicron aerosol particles at the Cape Verde Islands: biogenic sources, selective transfer and high enrichments

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Abstract

Measurements of lipids as representative species for different lipid classes in the marine environment have been performed to characterize their oceanic sources and their transfer from the ocean into the atmosphere to marine aerosol particles. ~~To this end, a~~The set of lipid classes ~~(~~includes hydrocarbons (HC), fatty acid methyl esters (ME), free fatty acids (FFA), alcohols (ALC), 1,3-diacylglycerols (1,3 DG), 1,2-diacylglycerols (1,2 DG), monoacylglycerols (MG), wax esters (WE), triacylglycerols (TG), phospholipids (PP) including phosphatidylglycerols (PG), phosphatidylethanolamine (PE), phosphatidylcholines (PC), glycolipids (GL) including sulfoquinovosyldiacylglycerols (SQDG), monogalactosyl-diacylglycerols (MGDG), digalactosyldiacylglycerols (DGDG) and sterols (ST~~)) is investigated~~). Introduced lipid classes have been analyzed in ~~both~~ the dissolved and particulate fraction ~~in~~of seawater, ~~differentiated~~while differentiating between underlying water (ULW) and the sea surface microlayer (SML), and ~~in~~on ambient submicron aerosol particle samples (PM_1) collected from the ambient at the Cape Verde Atmospheric Observatory (CVAO) applying concerted measurements. The different lipids are found in all marine compartments but in different compositions. At this point, a certain variability is observed for the concentration of dissolved ($\sum DL_{ULW}$: 39.8-128.5 µg L^{-1}, $\sum DL_{SML}$: 55.7-121.5 µg L^{-1}) and particulate ($\sum PL_{ULW}$: 36.4-93.5 µg L^{-1}, $\sum PL_{SML}$: 61.0-118.1 µg L^{-1}) lipids in seawater of the tropical North Atlantic Ocean along the campaign. Only slight SML enrichments are observed for the lipids with an enrichment factor EF_{SML} of 1.1-1.4 (DL) and 1.0-1.7 (PL). On PM_1 aerosol particles, a total lipid concentration between 75.2-219.5 ng m^{-3} (averaged: 119.9 ng m^{-3}) is measured ~~with high atmospheric concentration of TG (averaged: 21.9 ng m^{-3}) as a potential indicator for freshly emitted sea spray.~~. Besides phytoplankton sources, bacteria influence the lipid concentrations in seawater and on the aerosol particles, so that the phytoplankton tracer (chlorophyll-*a*) cannot sufficiently explain the lipid abundance. The concentration and enrichment of lipids in the SML is not related to physicochemical properties describing the surface activity. For ~~aerosol~~aerosols, however,

the high enrichment of lipids (as a sum) corresponds well with the consideration of their high surface activity, thus the EF_{aer} (enrichment factor on submicron aerosol particles compared to SML) ranges between $9 \cdot 10^4$-$7 \cdot 10^5$. Regarding the single lipid groups on the aerosol particles, a weak relation between EF_{aer} and lipophilicity (expressed by the K_{OW} value) was identified, which was absent for the SML. However, overall simple physico-chemical descriptors are not sufficient to fully explain the transfer of lipids. As our findings show that additional processes such as formation and degradation influence the ocean-atmosphere transfer of both OM in general and of lipids in particular, they have to be considered in OM transfer models. Moreover, our data suggest that the extend of enrichment of lipid classes constituents on the aerosol particles might be related to the distribution of the lipid within the bubble-air-water-interface. Lipids, which are preferably arranged within the bubble interface, namely TG and ALC, are transferred to the aerosol particles to the highest extend. Finally, the connection between ice nucleation particles (INP) in seawater, which are active already at higher temperatures (-10 °C to -15 °C), and the lipid classes PE and FFA suggests that lipids formed in the ocean have the potential to contribute to (biogenic) INP activity when transferred to the atmosphere.

Keywords

Lipids, organic matter, submicron marine aerosol particles (PM_1), ~~seawater, biogenic sources,~~sea surface microlayer (SML), ice nucleating particles (INP),~~ transfer,~~ enrichment factor, concerted measurements, Cape Verde Atmospheric Observatory (CVAO)

1. Introduction

Lipids are a major biochemical class of organic matter (OM) in seawater along with carbohydrates and proteins. Their ocean concentrations are much lower, yet their surface affinity and enrichment ~~is~~are higher than for the other groups (Burrows et al., 2014). As lipids are rich in carbon and serve as energy storage compounds, they are important components of the cellular metabolisms of species, at least in the ocean (Wakeham et al., 1997). They are universally distributed in the marine environment and are involved in numerous essential biological processes of both the dissolved and particulate OM pool (Arts et al., 2001;Frka et al., 2011). As regards the particulate lipid pool, important sources are phytoplankton cells with a contribution of up to 79 % in biologically productive surface water layers, while the contribution of lipids in phytoplankton cells ranges between ≤ 1 % and 46 % of dry weight (Frka et al. (2011), and references therein). ~~Marine dissolved lipids are produced either by dissolution from the particulate fraction, or through primary production and could be released during life cycle or after cell death (Yoshimura et al., 2009;Novak et al., 2018).~~Marine lipids can be produced by abiotic and biotic processes and play an important role as energy sources in the aquatic ecosystem (Parrish, 2013). As a whole, the analysis of lipids and their classes is a useful method to study the dynamics of the global carbon cycle in the ocean (Yoshimura et al., 2009), since lipid classes can be used as specific markers for the identification of OM sources and biogeochemical cycles in the marine environment (Parrish et al., 1988;Frka et al., 2011). Phosphorus-containing lipids or phospholipids (PP), i.e.

phosphatidylglycerols (PG), phosphatidylethanolamine (PE) and phosphatidylcholines (PC), belong to the organic substances associated with living organisms (Derieux et al., 1998) since they are a major component of cell membranes providing the structure and protection of cells (Khozin-Goldberg, 2016). The most common glycolipids (GL) in plankton are mono- and di-galactosyldiacylglycerols (MGDG and DGDG) as well as sulfoquinovosyldiacylglycerol (SQDG) (Guschina and Harwood, 2009;Gašparović et al., 2013). Triacylglycerols (TG) indicate metabolic reserves (Frka et al., 2011) ~~and wax~~ and are reported as storage compounds in phytoplankton (Becker et al., 2018). Wax esters (WE) are a major group of neutral lipids of some zooplankton species (Kattner, 1989). Fatty alcohols (ALC) mainly originate from zooplankton wax esters (Frka et al., 2011). Diacylglycerides (DG), monoacylglycerides (MG) and free fatty acids (FFA) are glyceride degradation products which characterize the degradation level of lipids by means of the lipolysis index (LI) (Parrish et al., 1988;Goutx et al., 2003). Using lipids as biomarkers, estimates of marine OM sinks and sources can be made and previous OM parameterizations, based only on chl-*a* can be extended. Indeed, chl-*a* is often used as an indicator of marine biological productivity, representing the abundance of the major group of organisms, i.e. the photoautotrophs (Gantt et al., 2011;Rinaldi et al., 2013). ~~However, chl-*a* is also found to be a poor descriptor of autotrophs, especially in oligotrophic regions (Quinn et al., 2014).~~ To fully describe the biological control of the OM cycle, both autotrophic and heterotrophic organisms must be considered. The information on the abundance of the main OM classes, namely lipids, proteins and carbohydrates, contributing to the marine OM pool and reflecting the OM sources, can therefore be used for advanced modelling approaches to predict OM on marine aerosol particles depending on the chemical composition of marine OM, as e.g. described by Burrows et al. (2014). Further spatio-temporal investigations of the organic classes in different oceanic areas are important for this purpose. The study of lipids is particularly important because their reactivity and physical surface properties contribute to the formation and stabilization of the sea surface microlayer (SML) (Frka et al. (2012), and references therein). The SML represents a chemically distinct film enriched with surface active OM that accumulates at the air-water interface relative to the underlying water (ULW) (Wurl and Holmes, 2008;Wurl et al., 2011;Cunliffe et al., 2013). Furthermore, the SML, as a natural interface between ocean and atmosphere, could play an important role as OM source for aerosol particles in the marine environment (Engel et al., 2017). The presence of lipids at the air-water interface is the result of their high surface affinity, competitive adsorption and segregation from other OM constituents (Frka et al., 2012).

OM can be transferred from the ocean to the atmosphere by wind-driven processes and bubble bursting, resulting in the formation of primary marine aerosol particles. Within this process, film drops leading to the formation of submicron particles are enriched mainly with OM compared to larger jet drops (Wilson et al., 2015). ~~Long~~Most parameterizations, the transfer of OM and the prediction of the OM content on marine aerosol particles, is based on chl-*a* seawater concentrations that are used as a broad indicator of biological productivity (Gantt et al., 2011;Rinaldi et al., 2013). However, especially in oligotrophic regions additional parameters besides wind speed and chl-*a* must be taken into consideration for accurately prediction of OM on marine aerosol particles (van Pinxteren et al., 2017). In a new approach by Burrows et al. (2014) the parameterization/ OM prediction for marine aerosol particles is based on important compound classes of OM, e.g. lipids, carbohydrates, proteins, with different physico-chemical properties instead of chl-*a* concentrations of the seawater. This new approach requires

information of distinct OM groups in both marine matrices (seawater and aerosol particles) such as the lipid concentrations performed in the present study.

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). The presence of the TG lipid class serves as an indication that the aerosol particles consist to a certain extent of freshly emitted sea spray. Schiffer et al. (2018) reported that TG was broken down into fatty acids via the enzymes of triacylglycerol lipase and that these lipases therefore had the potential to alter the composition of sea spray aerosol. In laboratory studies by the authors Schiffer et al. (2018), lipase enzymes have shown to be transferred from the ocean into the atmosphere. Until now, lipids or individual lipid classes have often only been analyzed in one compartment of the ambient marine environment, i.e.. 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 fattiy acids. In contrast, supermicrometer sea spray aerosol particles were dominated (up to 88 %) by oxygen-rich species (Cochran et al., 2016b).

Until now, lipids or individual lipid classes have been often analyzed only in one compartment of the ambient marine environment, i.e. seawater or marine aerosol particles (Gagosian et al., 1982;Simoneit and Mazurek, 1982;Frka et al., 2011;Gašparović et al., 2014). The possible transfer of total lipids (determined as a sum parameter) has so far only been described under controlled conditions in laboratory studies (Rastelli et al., 2017) or for certain lipid classes such as fatty acids, *n*-alkanes, total hydrocarbons (Marty et al., 1979) or as fatty acids and their derivatives (Cochran et al., 2016b) in freshly emitted sea spray aerosol. Unfortunately, comprehensive studies on marine lipid biogeochemistry and a possible transfer of certain lipid classes into the atmosphere are missing.

The present work aimed at investigating lipids at the Cape Verde Atmospheric Observatory (CVAO) as species representative for different lipid classes in the marine environment of the tropical Atlantic Ocean, to study their abundance, (biogenic) sources and selective transfer into the marine atmosphere. The lipid data set obtained for samples from different marine compartments at the CVAO is discussed in terms ofwith regard to its biological origin and physical (INP) parametersits ice nucleation potential. Finally, the potential transfer of the lipids from seawater to aerosol particles will be investigated by relating the physico-chemical properties of individual lipid classes to their respective observed atmospheric enrichment.

2. Experimental

2.1 Study area and sampling sites

As part of the MarParCloud project (Marine biological production, organic aerosol particles and marine clouds: a Process chain) with a contribution from 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, 16°51''49'N, 24°52'02'E) from 13 September to 13 October 2017 (Triesch et al., 2020;van Pinxteren et al., 2019a2020). The CVAO, a remote marine station in the tropical Atlantic Ocean located on the northeast coast of Sao Vicente

island (16º 51' 49" N. 24º 52' 02" S), is described in more detail in Carpenter et al. (2010) and Fomba et al. (2014). The ocean around the Cape Verde Islands belongs to the region 'North Atlantic Tropical Gyral Province (NATR)' according to the classification of Longhurst (2007), a region with the lowest surface chlorophyll in the North Atlantic and with a greater annual variability than seasonality. Wilson et al. (2015) reported that high concentrations of marine INPs can occur in the North Atlantic and comparatively high surface-level marine (INP_{15}) and OC concentrations have been predicted by models in this region around the Cape Verde Islands. Concerted sampling was carried out during the campaign, including PM_1 aerosol particles at the CVAO and seawater at the ocean site (~16°~~53'30'N~~53'17'N, ~24°~~54'00''W~~54'25'E). The seawater sampling site was located upwind of the CVAO and had minimal island influence. A map illustrating the seawater sampling station and the CVAO is shown in Figure S1.

2.1.1 SML and seawater sampling

~~The SML samples (n=6) were collected using the manual glass plate technique (Cunliffe, 2014). A glass plate with a sampling area of 2000~~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). A glass plate (500x250 mm) with a sampling area of 2500 cm^2 was briefly immersed vertically in the seawater and then slowly pulled upwards. The surface film material adsorbed on the surface of the glass plate was then moved directly into pre-cleaned bottles using Teflon wipers. The ULW samples (n=13) were collected from a depth of 1 m in pre-cleaned plastic bottles, which were attached to a telescopic rod. The bottles were opened under water at the intended sampling depth in order to avoid influences by the SML. In addition, 5-6 litres of bulk surface water (at a depth between 10 and 50 cm) were collected with a plastic bottle for pigment analysis (n=11).

2.1.2 Aerosol particles sampling

At the top of a 30 m high sampling tower at the CVAO, PM_1 aerosol particles (n=13) were investigated with a high-volume Digitel sampler DHA-80 (Walter Riemer Messtechnik~~.~~, Germany) on ~~preheated (105 °C, 24 h)~~ 150 mm quartz ~~fiber~~fibre filters (~~Minktell~~Munktell, MK 360) at a flow rate of 700 L min^{-1} in 24 h. The filters used for sampling were preheated at 105 °C for 24 h to avoid contamination. The collected filters were stored in aluminium boxes at -20 °C up until analysis.

2.2 Analytics

2.2.1 Seawater samples analytics: lipids, pigments, nutrients, microorganisms, INP activity

For lipid analysis, the seawater samples (2 L) were passed through a 200 µm stainless steel screen to remove zooplankton and larger particles. ~~They~~Afterwards, they were ~~then~~ filtered through pre-combusted (350 °C for 5 h) 0.7 µm GF/F filters (Whatman®, Sigma Aldrich). After the filtration step, the internal standard 2-hexadecanone (purity ≥ 98 %, Sigma Aldrich) (10 µg) was added to each filtrate, while the corresponding filters were stored in tubes at -78 °C until analysis. Dissolved lipids

(DL) were immediately extracted from the filtrate with ~~dichlormethane~~dichloromethane (DCM; ~~dichlormethane~~dichloromethane for liquid chromatography LiChrosolv®, Merck) in four extraction steps (twice at pH 8 and twice at pH 2). The final extract was concentrated using a rotary evaporator. Particulate lipids (PL) were extracted by a modified one-phase solvent mixture of DCM-methanol-water (Bligh and Dyer, 1959)~~.~~ after the addition of 2-hexadecanone as internal standard . DL and PL classes were further analyzed by ~~latroscan~~Iatroscan thin layer chromatography-flame ionization detection (TLC- FID) (~~latroscan~~Iatroscan MK-VI, ~~latron~~Iatron, Japan) as described in Gašparović et al. (2015) and (2017). After separation on Chromarod-SIII thin layer rods, lipid classes were identified and quantified by external calibration with a standard lipid mixture. The lipid classes investigated included HC, ME, FFA, ALC, 1,3 DG, 1,2 DG, MG, WE, TG, PP (including PG, PE, PC), GL (including SQDG, MGDG, DGDG), ST and PIG. Each sample was measured in duplicate with a relative standard deviation < 10 %. Also, blank seawater samples (high purity water filled in pre-cleaned plastic bottles and handled the same as the seawater samples) were ~~analyzed.~~analysed and the blank values were always below 15 % of ambient seawater samples. All presented lipid values for SML and ULW samples were blank corrected by subtracting the field blank values from the samples.

For the pigment analysis, 5-6 L of bulk water were filtrated through GF/F filters. These were extracted in 5 mL ethanol, an aliquot (20 µL) was injected into a high performance liquid chromatograph system (HPLC) with fluorescence detection (Dionex, Sunnyvale, CA. USA). The pigments, including chl-*a*, chl-*b*, fucoxanthin, ~~phaeophorbide, phaeophytin~~pheophorbide, pheophytin a/b, zeaxanthin, diadinoxanthin, lutein, chlorophyllide, violaxanthin, β-~~carotine~~carotene, were separated under gradient elution using methanol/acetonitrile/water systems as mobile phase, as described in ~~van Pinxteren et al. (2019b).~~van Pinxteren et al. (2019). Nutrients covering nitrogen oxides (N_2O_3, NO_2, NO_3), phosphate (PO_4^{3-}) and silicates (SiO_4^{4-}) were measured colorimetrically according to Grasshoff et al. (1999) with a Seal Analytical QuAAtro constant flow analyzer. ~~Following~~Microbial cell numbers were counted via flow cytometry after seawater samples were fixed, flash-frozen in liquid-nitrogen, and stored at -20 °C. For prokaryotic cells counts, all samples were stained with SYBR Green solution. Counting was performed after addition of latex beads serving as an internal standard. Further details can be found in Robinson et al. (2019)~~, the prokaryotes were detected by characteristic signature in a side scatter plot and were presented as total prokaryotic cell numbers (TCN). In order to distinguish between prokaryotic and eukaryotic autotrophs, the approach described in van Pinxteren et al. (2019a) was used to study~~. Small autotrophic cells were counted in a separate measurement after addition of red fluorescent latex beads (Polysciences, Eppelheim, Germany). Cells were detected by their signature in a plot of red (FL3) vs. orange (FL2) fluorescence, and red fluorescence vs. side scatter (SSC). This approach allows discrimination between different groups of prokaryotic and eukaryotic autotrophs (Marie et al., 2010), which in our case were size classes defined as *Synechococcus-like cells* and *Nanoeucaryotes*. Two droplet freezing devices called LINA (Leipzig Ice Nucleation Array) and INDA (Ice Nucleation Droplet Array) were used at TROPOS to obtain information on the ice nucleation activity as described in more detail by ~~Gong et al. (2020)~~Gong et al. (2020), and references therein.

2.2.2 Aerosol particle samples analytics

The analysis of sodium (Na^+) was performed by ion chromatography (ICS3000, Dionex, Sunnyvale, CA, USA) as described in Mueller et al. (2010). For the analysis of lipid classes, 28.27 cm^2 of the total PM_1 ~~samples~~filter area were extracted and measured following the procedure for particulate lipids in seawater (see section 2.2.1). A chromatogram of the TLC-FID measurements of an aerosol particle sample and the standards is shown in Fig. S2. The field blanks (n=5) were prepared using pre-baked quartz ~~fiber~~fibre filters without active sampling and treated according to same procedure as the field samples. The concentrations of the lipid classes were calculated by external calibration. Each sample was measured in duplicate with a relative standard deviation < ~~10 % and taking field blanks into account~~ 10 % and field blanks, which were always below 20 % of real aerosol particle sample, were subtracted. All presented values are blank corrected.

2.2.3 Lipid ratios

~~2.2.3~~ The Lipolysis ~~index~~

~~The lipolysis index~~Index (LI) is an index describing the lipid degradative state and the biological degradation processes of lipids (Goutx et al., 2003). In this concept, it is proposed that the degradation process of marine acyl-lipids by the concentration ratio of free lipids/metabolites (ALC, FFA, MG, DG) to their precursors (TG, WE, glycolipids as MGDG, DGDG, SQDG and phospholipids as PG, PE, PC) could be described by equation (1).

$$LI = \frac{(ALC+FFA+MG+DG)}{(TG+WE+MGDG+DGDG+SQDG+PG+PE+PC)} \quad (1)$$

It is obvious that the concentration of precursor lipids and metabolites alone can already influence the LI and that there may be a natural variance between them. For example, metabolites can be quickly absorbed by existing microorganisms, which would lead to a reduction of the concentration and thus influence the LI. However, the LI is reported as a useful measure to characterize the degradation level of biogenic organic material (Goutx et al., 2003). Higher LI values are characteristic for enhanced OM degradation and metabolite release, while lower LI values indicate that the appearing lipid classes are ~~very~~more fresh or resistant to degradation.

The PE/PG ratio can be used to determine the origin of the phospholipids that contribute to the OM pool in seawater (Goutx et al., 1993). Here, PG as the most important compound of the phospholipids of microalgae is an indicator for algae as potential sources, whereas PE is predominantly found in bacterial membranes and thus represents an indicator for bacterial sources (Goutx et al., 1993).

2.2.4 Enrichment factors

The enrichment factor in the SML (EF_{SML}) was calculated by dividing the concentration of the respective analyte in the SML by the concentration of the analyte in the ULW using equation (2):

$$EF_{SML} = \frac{c\,(analyte)_{SML}}{c(analyte)_{ULW}} \quad (2)$$

An enrichment in the SML is defined as $EF_{SML} > 1$, a depletion with $EF_{SML} < 1$.

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).

To calculate the enrichment factor of the different analytes in aerosol particles (EF_{aer}) relative to the SML, the atmospheric concentration of the analyte relative to the sodium concentration on the PM_1 sample was divided by the analyte concentration relative to the sodium concentration in the corresponding SML sample using equation (3):

$$EF_{aer} = \frac{c\,(analyte)_{PM_1}/c\,(Na^+)_{PM_1}}{c\,(analyte)_{SML}/c\,(Na^+)_{SML}} \quad (3)$$

The EF_{aer} calculation was limited by the availability of the analyte concentration in both matrices, i.e. PM_1 and SML samples collected simultaneously.

2.2.5 Statistical analysis

To investigate possible relationships between chemical, (micro)biological and physical parameters of the seawater samples (ULW, SML), listed in Fig. ~~S1~~S3, a Pearson correlation analysis was performed. Figs. ~~S2-S5~~S4-S7 show the matrix of parameters when either ULW or SML samples of the dissolved or particulate fraction are considered. The correlation coefficient (R), number of samples examined (n) and the p-value were used to validate the significance of the correlation. In particular, the p-value as a test for statistical hypothesis in research areas must be considered when defining statistical relevance (Bhattacharya and Habtzghi, 2002;Perezgonzalez, 2015). The statistical parameters for the performed analysis of the ULW and SML samples are defined as follows. For the ULW samples, the statistical relevance of a relationship was defined if $n \geq 4$ (n_{max}=13), $R \geq 0.6$ and p-value ≤ 0.05 (Perezgonzalez, 2015). We considered a 'trend' to be valid if $n \geq 4$ (n_{max}=13), $R \geq 0.4$ and p-value ≥ 0.05. Due to the limited number of SML samples, p-values were always ≥ 0.05, so we could not define statistical relevance, but considered a 'trend' to be valid if $n \geq 4$ (n_{max}=6), $R \geq 0.4$.

3. Results and Discussion

3.1 Seawater and SML samples

3.1.1 Lipids and lipid classes in the particulate fraction

The particulate lipids showed a certain variance during the campaign, as shown in Fig. 1. For the ULW samples, the

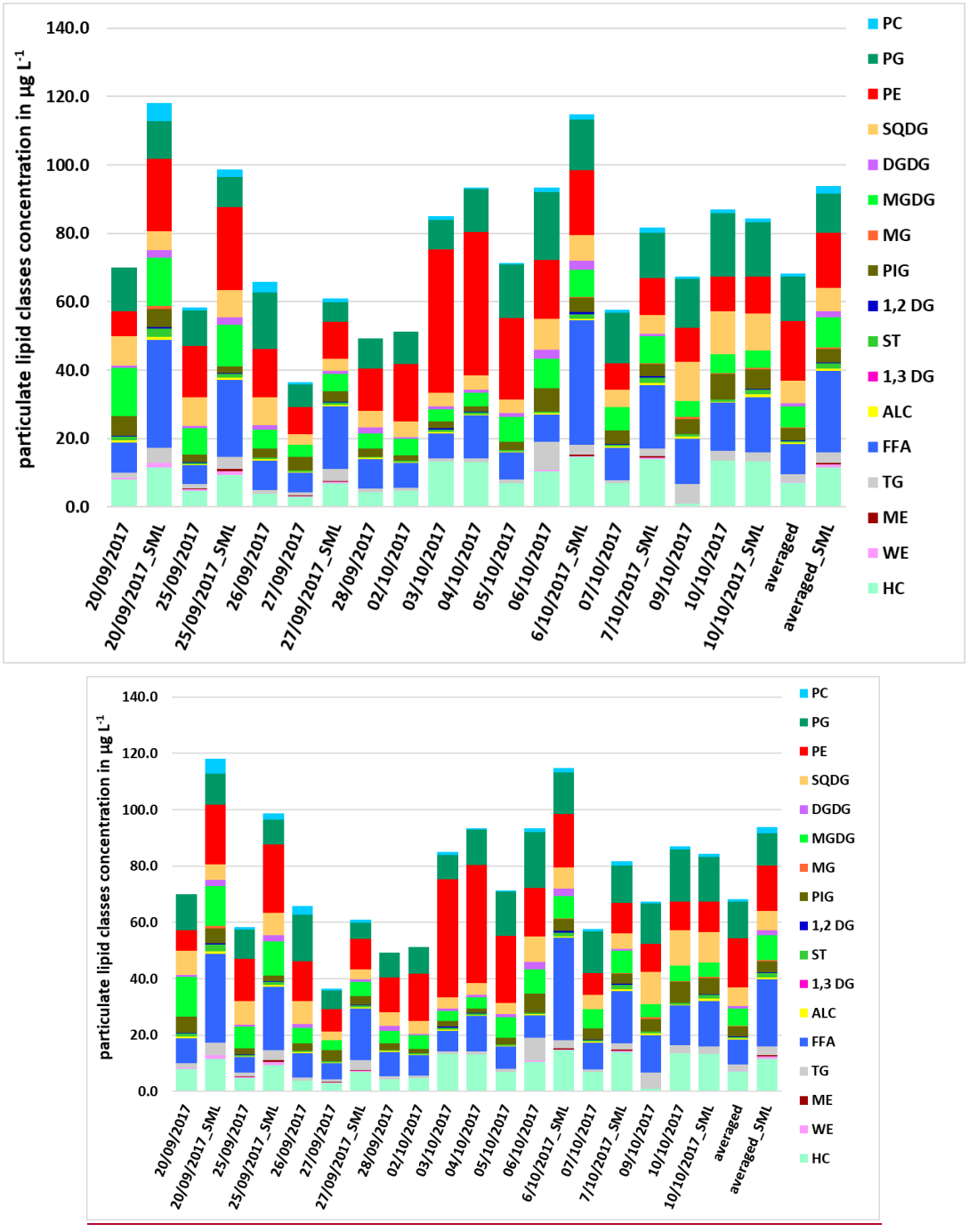

Figure 1: Concentration of individual particulate lipid classes in the ULW (sampling date) and the SML (sampling date_SML) samples along the campaign and as an averaged value in µg L^{-1}

concentration of ∑PL was between 36.4 and 93.5 µg L^{-1}, for the SML samples between 61.0 and 118.1 µg L^{-1}. The measured total lipid concentrations are within the concentration range of the previous measurement studies in different oceanic regions

(Frka et al., 2011;Gašparović et al., 2014;Stolle et al., 2019). The lipid classes FFA and phospholipids (PE, PG, PC) dominated within the PL while other lipid classes like TG, HC, ST showed not only a much lower concentration but also much less pronounced variance. Another interesting feature is the opposite abundance of the two phospholipids PE and PG. On sampling days when PE had a high concentration, PG was significantly less concentrated as found in the middle of the campaign (e.g. 3/10/2017 and 4/10/2017, see Fig. 1), whereas towards the end of the campaign (e.g. 07/10/2017 and 09/10/2017), when the concentration of PE becomes lower, the concentration of PG increased. ~~Via the PE/PG ratio the contribution of bacterial lipids to the OM pool in seawater can be retrieved (Goutx et al., 1993).~~ The PE/PG ratio varied along the campaign with increasing values towards the middle of the campaign (maxima on 03/10/2017 and 04/10/2017) and decreasing values ~~afterwards~~towards the end (Table S4), following the same trend as the total bacteria number (TCN, Table S3). This indicates a change in the lipid dominant biological contributions, with bacterial sources dominating in the first part and especially in the middle of the campaign~~, whereas~~. However, in the last part of the campaign (afterwards on 05/10/2017) ~~rather phytoplankton-dominated~~ contributions to the lipid pool were rather dominated by phytoplankton. These differences between bacterial and phytoplankton sources are not reflected in the total lipid concentrations, because degradation products like FFA also contribute strongly to the total lipids (Fig. 1~~, S6~~). For this reason, neither bacterial nor phytoplankton sources alone are the controlling drivers for the total lipid concentration, at least in the short term.

3.1.2 Lipids and lipid classes in the dissolved fraction

Compared to the particulate fraction, slightly higher concentrations of total dissolved lipids were detected, 39.8-128.5 µg L^{-1} in the ULW and 55.7-121.5 µg L^{-1} in the SML samples (Fig. 2). The concentrations reported here were slightly higher than the total dissolved lipid concentrations reported by Frka et al. (2011) in the Mediterranean semi-enclosed temperate Adriatic sea (∑DL: 7.5-92.2 µg L^{-1}).

In contrast to the particulate lipids, HC showed the highest concentration and variation within the lipids and varied between 6.6 up to 64.0 µg L^{-1} in the ULW and in the SML between 9.2-49.6 µg L^{-1} (Fig. 2). HC can have both anthropogenic and natural sources (Scholz-Böttcher et al., 2009). Shorter *n*-alkanes (as 2-nonadecane) may have additional sources as mature organic matter or petroleum contamination, but the main sources of the investigated HC surrogate (2-nonadecane) is marine phytoplankton (Scholz-Böttcher et al. (2009) and references therein).

Phospholipids, especially PE and PG, as well as FFA, which dominated in the particulate lipids, showed significantly lower concentrations within the total dissolved lipids. In contrast to the particulate fraction, both phospholipids (PE and PG) showed most similar concentrations and percentages in the dissolved fraction.

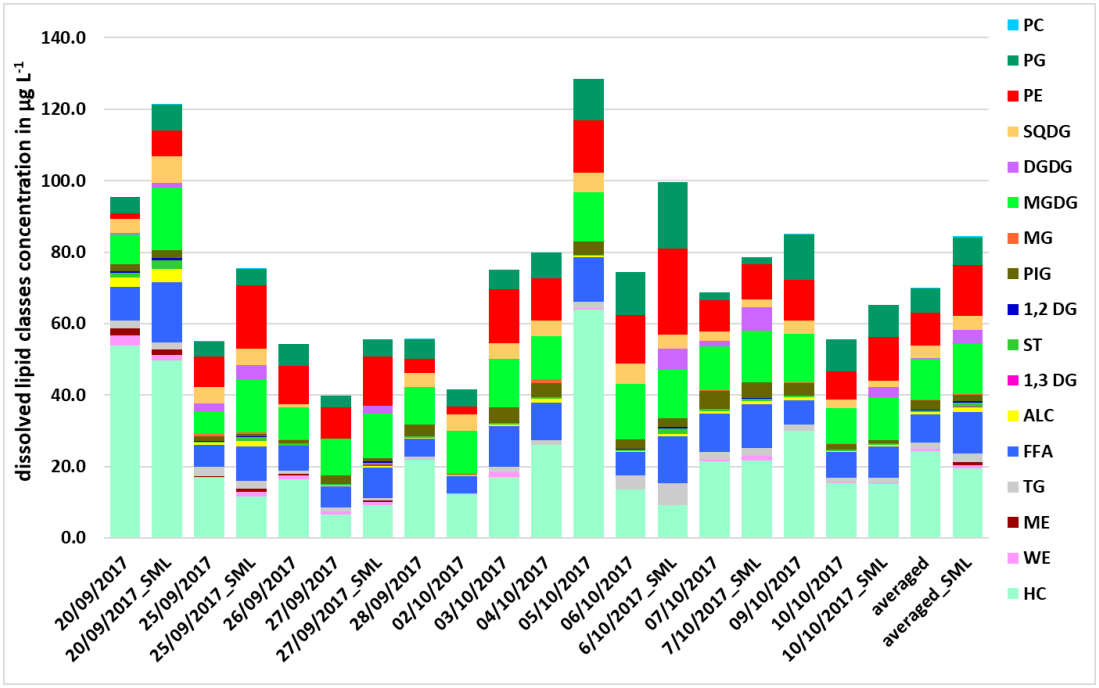

Figure 2: Concentration of individual dissolved lipid classes in the ULW (sampling date) and the SML (sampling date_SML) samples along the campaign and as an averaged value in µg L^{-1}

The percentage composition of total dissolved lipids ~~(Fig. S7)~~ is in good agreement with the literature (Goutx et al., 2009;Marić et al., 2013). Altogether, our detailed analysis of the lipid classes shows that, although the concentration of PL and DL are overall very similar ~~overall~~, the composition of the lipids to the PL and DL groups is partly different. This indicates that different production and degradation mechanisms for DL and PL contribute to the respective lipid composition.

3.1.3 Lipolysis Index

To evaluate the lipid degradative state and (bio)degradation processing, the LI (Eq. (1); Table S5) was calculated for the lipids in the seawater samples. The LI in the particulate fraction varied between 0.13-0.31 in the ULW and between 0.37-0.66 in the SML samples. ~~Van Wambeke et al. (2001)~~van Wambeke et al. (2001) reported LI values of particulate lipids (0.21-0.39) in the north-western Mediterranean Sea during the end of a phytoplankton bloom up to pre-oligotrophic conditions. In general, the LI indicated that the intact lipid classes were dominant compared to the degradation indices/metabolites for the particulate lipids and that the lipids were thus degraded only to a small extent. This coincides well with the low concentrations of chlorophyll degradation products~~,~~ (PIG), suggesting that only moderate grazing took place and the (pigment-containing) organisms were fresh and in healthy condition (van Pinxteren et al., ~~2019a~~2020). 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. ~~This observation~~A higher LI in the SML was also ~~made~~observed by Gašparović et al. (2014) in the East Atlantic Ocean and can be attributed to both bacterial and photochemical abiotic degradation (Christodoulou et al., 2009). 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 ~~quite~~somewhat more resistant to degradation.

3.1.4 Pigments, nutrients and microbiological investigations in seawater

To further elucidate the biological production and degradation state of lipids, lipid concentrations were related to a set of biological parameters, including indicators for autotrophic organisms (namely marine pigments, chl-*a*, *Nanoeucaryotes* and *Synechococcus-like cells)* and TCN as a proxy for bacterial abundance. Altogether, the concentrations of pigments and autotrophic and heterotrophic cells indicated an oligotrophic system (detailed values in Tables S2/S3, further information is given in van Pinxteren et al. (~~2019a~~2020)~~).~~). In addition, the chl-*a* concentration in seawater increased from 0.11 µg L^{-1} to 0.60 µg L^{-1} (Table S2) during the campaign, but was generally low compared to other subtropical/tropical regions or worldwide (Duhamel et al., 2019).

The pigment measurements of the bulk water indicated temporal changes in the composition of the community and an increasing trend in pigment concentration towards the end of the campaign. A correlation of total lipids with the abundances of chl-*a*, *Nanoeucaryotes and Synechococcus-like* cells was not observed. However, with regard to specific pigments beyond chl-*a*, a statistically relevant correlation between particulate PE and the pigment zeaxanthin with R=0.69 (p-value=0.03, n=10) was found in the ULW (Fig. S8a). Zeaxanthin has been reported as a proxy for chlorophytes and cyanobacteria (Grant and Louda, 2010) and for some microalgae (Galasso et al. (2017), and references therein). Furthermore, the pigment fucoxanthin, a marker for diatoms (Descy et al., 2009), showed a weak trend with particulate FFA (R=0.53, p-value=0.12, n=10) in ULW samples (Fig. S8b)**.** The observed correlations/trends of zeaxanthin and fucoxanthin with individual particulate lipid classes pointed to a contribution of chlorophytes, cyanobacteria and diatoms to the lipid pool in our study.

~~Regarding the heterotrophic parameters,~~ We observed a positive and statistically relevant correlation between PE and TCN ~~was observed~~ in the dissolved fraction of ULW samples (R=0.79, p-value=0.006, n=10, Fig. S9a). We also found a positive correlation between the particulate PE and TCN in the ULW (R=0.72, p-value=0.02, n=10), a similar trend was noticed for PE and TCN in the SML (R=0.64, p-value=0.36, n=4) (Fig. S9b). The contribution of bacteria to the PE pool most likely results from the fact, that PE is part of the bacterial membrane (Stillwell, 2016;Gašparović et al., 2018). Additional indications for bacteria influencing the lipid pool results from a negative correlation between the lipolysis index of total particulate lipids (LI_{PL}) and TCN in ULW and SML samples. In the ULW, a correlation between LI_{PL} and TCN with R= -0.73 (p-value=0.02, n=10) (Figure S9c) was observed. In the SML (Figure S9c), a similar trend was noticeable for LI_{PL} and TCN (R= -0.87, p-value=0.13, n=4). These relationships may result from the passive contribution (higher cell abundance and thus higher concentration of PE) of TCN to the phospholipids pool via PE. Phospholipids contribute to LI as part of the intact lipids (section 2.2.3, Eq. 1), which leads to a negative correlation with LI_{PL}. On the other hand, the 'metabolites' could be actively taken up by bacteria, which most likely happens when more bacteria are present. Due to the low abundance of *Synechococcus-like* cells, we assume that most bacteria counted as TCN are heterotrophic and have taken up the 'metabolites'. Although it remains unclear whether the bacteria have a passive (i.e. via membrane) or active (i.e. metabolism of the lipid 'metabolites')

effect on the observed correlation between LI_{PL} and TCN, it is most likely that ~~the~~ bacteria have influenced the lipid pool which is consistent with the results obtained from the lipid composition. ~~In addition, the results underline that chl *a*, as commonly used proxy for bioproduction, may not sufficiently explain the variability of the lipid classes in the marine region studied.~~

~~3.2~~

3.2 Transfer of lipids from the Oceans

3.2.1 ~~3.2.1~~ The comparability of the different marine matrices (seawater and aerosol particles)

The concerted measurements performed here included spot samplings in the ocean (ULW, SML) during the sampling period of PM_1 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).

~~3.2.1~~3.2.2 Enrichment in the SML

The EF_{SML} was calculated using Eq. (2) to compare the concentration of the lipid classes in the SML samples with the ULW samples. The EF_{SML} of the total lipids and of ~~the~~lipid class representatives ~~of the lipid classes~~ in the particulate and dissolved fraction is listed in Table S6. For the total lipids in the particulate fraction, the EF_{SML} varied between 1.0-1.7 (averaged $EF_{SML(\sum PL)}$: 1.4), whereas in the dissolved fraction it varied between 1.1-1.4 (averaged $EF_{SML(\sum DL)}$: 1.3). The EF_{SML} of the total lipids are therefore quite similar for PL and DL. ~~The slightly higher enrichment of the particulate fraction compared to the dissolved fraction in the SML is in good agreement with the literature (Marty et al., 1988;Gašparović et al., 1998;Kuznetsova and Lee, 2002;Kuznetsova et al., 2005;Burrows et al., 2014). The preferred enrichment of the particulate fraction is probably due to the fact that the bubbles capture larger particles more efficiently because of their larger radius and inertia (Sutherland, 1948;Weber et al., 1983;Dai et al., 1998) and that the gelatinous nature of the SML can ensure that the particulate OM is captured (Robinson et al., 2019). Moreover, marine dissolved lipids can be produced by dissolution from the particulate fraction and through primary production and released during the life cycle and after cell death (Yoshimura et al., 2009;Novak et al., 2018). They might lead to a slightly higher SML enrichment of the particulate lipids.~~

A major aspect contributing to lipid enrichment in the SML might be explained by the physico-chemical properties of the respective lipid classes, namely the surface activity (Table S7). The parameters describing this characteristic, i.e. the density, the partitioning coefficient between octanol and water (K_{ow}~~ow~~K_{OW}) and the topological polar surface area (TPSA), were compared with lipid enrichment. As shown in Table S7, the nonpolar lipids such as FFA and ALC have a higher surface ~~accumulation~~enrichment potential compared to the more polar glycolipids and phospholipids, but a correlation between enrichment of lipids and surface activity was absent. In the dissolved fraction neither such a gradation of enrichments at the surface, nor a correlation between enrichment and parameters describing surface activity were visible. As Table ~~S4~~S6 shows,

similar EF_{SML} were found in the dissolved fraction for the individual lipid classes (EF_{SML}: 1.5 (FFA), 1.7 (ALC) and 1.6 (PP)). A comparison of lipid enrichment with other OM ~~compound groups~~compounds showed that SML enrichment of lipids seemed to be less pronounced in contrast to other organic species such as amino acids (Reinthaler et al., 2008;Triesch et al., 2020). This is somehow surprising, since SML enrichment of lipids is likely to be strongest among organic groups due to their surface activity (Burrows et al. (2014), and references therein). It has to be considered that a SML described here represents a layer with a thickness of about 100 µm (van Pinxteren et al., 2017) and therefore gradients within this layer (e.g. an enhanced enrichment of surfactants only in the top layer of a few µm) cannot be ~~regarded~~considered here. The fact, that other (less surface active) compounds are stronger enriched in the SML (upper 100 µm) underlines the need to consider additional parameters to describe the SML enrichment of lipids in the ambient marine environment.

To this end, besides the physical processes leading to SML enrichment, the ~~in situ production of OM~~potential importance of OM-producers and -degraders (bacteria, phytoplankton and their released metabolites) were further investigated. Regarding the enrichment in the SML within the lipid classes or within both fractions (dissolved and particulate), stronger differences are found when looking at the individual lipid classes. The bacterial marker PE was enriched in the SML in DL and PL fractions with $EF_{SML(PE)}$ of 1.6 (PF) and with 2.1 (DF). In contrast, the phytoplankton marker PG was always depleted in the SML (EF_{SML} < 1) in the PL and mostly enriched in the DL (averaged $EF_{SML(PG)}$ of 1.3). This is consistent with the observed permanent abundance and slight enrichment of TCN and ~~indicates~~may indicate enhanced bacterial activity in SML. Furthermore, the degradation lipid class FFA showed high enrichments in the SML (averaged $EF_{SML(FFA)}$: of 3.1 (PL) and 1.5 (DL)). These high concentrations and enrichments point to an enhanced biodegradation in the SML, which is consistent with previous observations~~,~~ (Frka et al., 2011;Gašparović et al., 2018), that lipids are degraded more strongly in the SML (high LI) than in the ULW. ~~This~~Besides increased abundance of microbial cells, this may also be due to a different ~~diversity~~ microbial community composition between SML and ULW and thus, different ~~taxa of microorganisms in the SML that can differ significantly from those in the underlying water~~functional diversity (Cunliffe et al., 2011). The metabolic reserves lipids, represented by TG, showed the highest variability of enrichment in the SML along the campaign in the particulate fraction. In ~~the particulate~~this fraction, $EF_{SML(TG)}$ varied between 0.3 and 4.4, resulting in an averaged enrichment of 2.3. The enrichment in the lipid classes of the dissolved fraction was less pronounced and always showed an opposite trend to PL, i.e. if TG was highly enriched in PL, it was less enriched in DL and vice versa. This indicates that ~~the~~ lipid reserves such as TG are stored ~~in~~within the particulate ~~lipids~~pool and ~~are~~ upon dissolution become part of the dissolved ~~producing dissolved TG~~pool.

Altogether, our results indicate that ~~physical processes~~physico-chemical descriptors alone, which are related to the surface activity of the lipids, are not sufficient to describe the SML enrichment of the lipids, at least not in the top 100 µm. In-situ formation and degradation by phytoplankton and mainly bacterial processes, as shown here from the lipid classes patterns, also contribute to the abundance and SML enrichment of lipids in the ambient marine seawater.

3.2.2 Measured PM_1 aerosol particle composition

Up to now, the discussion about lipids on (marine) aerosol particles has only covered distinct classes of lipids (mostly fatty acids). Given this fact, this work firstly presents a comprehensive analysis of several lipid classes on marine aerosol particles. The atmospheric concentration of total lipids in PM_1 samples at the CVAO varied between 75.2 and 219.5 ng m^{-3} (average 119.9 ng m^{-3}), as shown in Fig. 3. The atmospheric concentration at the CVAO was 18.5 ng m^{-3} (8.7-33.9 ng m^{-3}) for FFA and 6.3 ng m^{-3} (3.4-9.8 ng m^{-3}) for ALC. This was in good agreement with Kawamura et al. (2003), who reported atmospheric concentrations between 0.19-23 ng m^{-3} (average 2.0 ng m^{-3}) for ALC and between 2.5-38 ng m^{-3} (average 14 ng m^{-3}) for FAA on marine aerosol particles from the western North Pacific. Other than that, Mochida et al. (2002) observed atmospheric concentration between 0.8-24 ng m^{-3} for saturated fatty acids (C_{14}-C_{19}) on marine aerosol particles collected overt the northern Pacific.

~~The percentage contribution of the individual lipid classes to the total lipids is shown in Fig. S1.~~ A high percentage contribution of the lipid classes TG, FFA and ALC (26.3-64.0 %, average 39.8 %) to the total lipids was observed. Especially, high percentages for TG (11.9-29.1 %, average 18.8 %) and FFA (8.4-31.2 %, average 15.4 %) were noticeable ~~(Fig. S10).~~ Compared to the seawater lipids, the atmospheric composition showed the same classes of lipids with a stronger agreement to the DL composition (high contribution of HC and lower contributions of phospholipids).

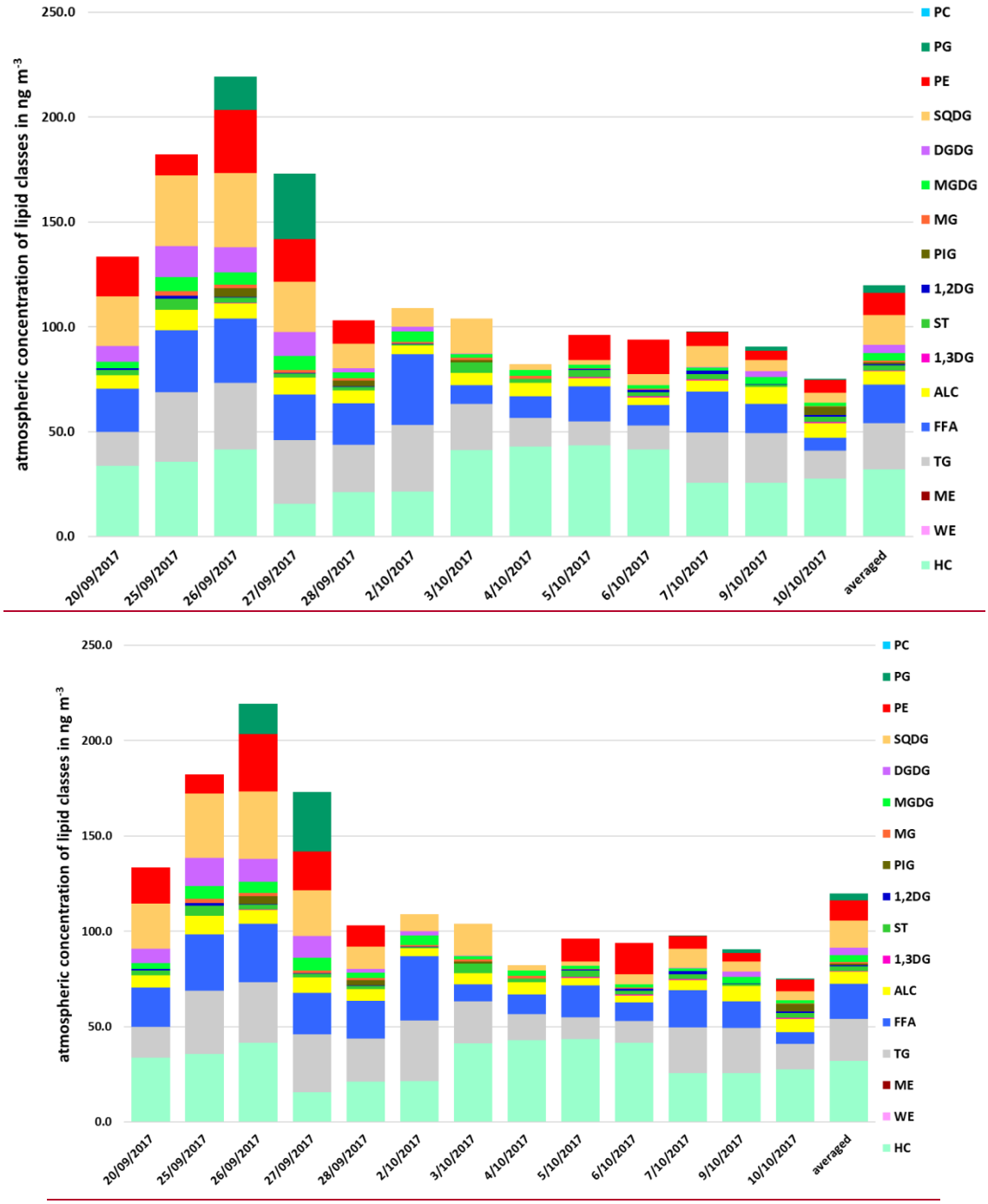

Figure 3: Atmospheric concentration of individual lipid classes in PM_1 aerosol particle samples and as an average at the CVAO in ng m^{-3}

However, although the atmospheric concentration of phospholipids was lower, it was found that PE was always higher concentrated as PG, with one exception on 27/09/2017 (Fig. 3). Since heterotrophic bacteria are reported as a dominant ~~sources~~source of PE (Michaud et al., 2018), this suggests that i) bacteria, possibly transported from the ocean into the atmosphere, ~~produce~~contribute PE on the aerosol particles and/ or ii) PE is directly transferred from the ocean into the atmosphere, likely via bubble bursting. ~~The high presence of TG on the aerosol particles (Fig. 3) strongly suggests that the aerosol particles consist to a certain extent of freshly emitted sea spray. This is consistent with the observation that the submicron aerosol particle samples at the CVAO were mainly maritime influenced during this period, based on particulate mass, and showed only minor dust or anthropogenic impacts (Triesch et al, 2020).~~

3.2.3 Transfer of lipid classes from the ocean to the aerosol particles

An often applied parameter to quantify the transfer of OM from the ocean to the atmosphere, is the EF_{aer} (e.g. Russell et al. (2010), van Pinxteren et al. (2017), ~~Triesch et al. (2020)). According to Eq. (3), the $EF_{aer(TL)}$ was calculated based on the dissolved total lipids in SML and varied between $9{\cdot}10^4$ and $7{\cdot}10^5$ with an average value of $3{\cdot}10^5$ (Fig. 4, Table S8).~~Triesch et al. (2020)). According to Eq. (3), the $EF_{aer(TL)}$ was calculated based on the dissolved total lipids in SML and varied between $9{\cdot}10^4$ and $7{\cdot}10^5$ with an average value of $3{\cdot}10^5$ (Fig. 4, Table S8). The EF_{aer} based on the particulate total lipids in SML was with an average of $2{\cdot}10^5$ very similar to the EF_{aer} of the dissolved total lipids ($3{\cdot}10^5$) as discussed in the SI, Table S8. The data reported in the literature for enrichment factors of organic carbon or groups of OM in aerosol particles often originate from laboratory experiments, e.g. using controlled artificial bubbling unit (Quinn et al. (2015), and references therein). Rastelli et al. (2017) determined the enrichment of lipids, as a sum parameter, on submicron aerosol particles compared to seawater in a bubble-bursting experimental set-up and found an EF_{aer} of $1{\cdot}10^5$. The good agreement of the $EF_{aer(TL)}$ derived from the ambient measurements reported here with the EF_{aer} derived from laboratory experiments under controlled conditions by Rastelli et al. (2017) indicates that the transfer of lipids from the SML to the aerosol phase under ambient conditions is consistent with processes described in laboratory studies.

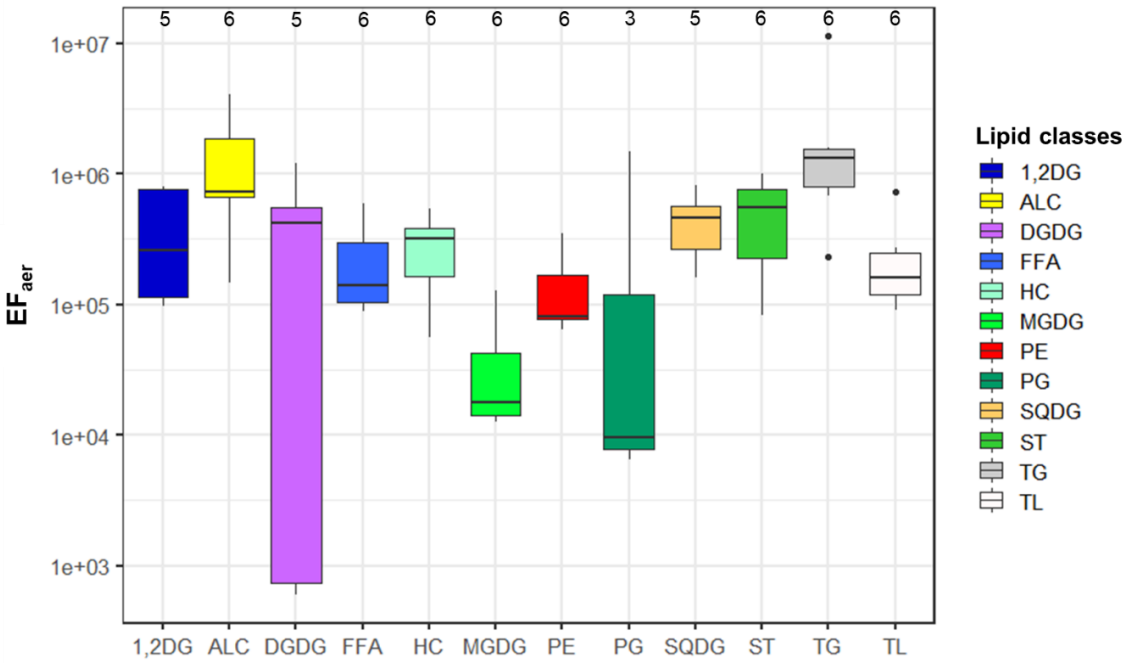

Figure 4: Boxplot of the enrichment factor aerosol (EF_{aer}) of the individual lipid classes and total lipids (TL) at the CVAO including the median, the 25th and 75th percentile; more explanation in Fig. ~~S11~~S10

The EF_{aer} of total lipids was about one to two orders of magnitude higher than the EF_{aer} of free amino acids ($4 \cdot 10^2$-$3 \cdot 10^4$) on submicron aerosol particles measured during the same campaign ~~(Triesch et al., 2020)~~(Triesch et al., 2020), underlining the preferred transfer of lipids from the ocean to the atmosphere. In contrast to SML enrichment, the higher enrichment of lipids on aerosol particles observed here corresponds well with the high surface activity of the lipids and the preferred adsorption to (bubble) surfaces resulting in a strong sea-to-air-transfer (Tervahattu et al., 2002;Facchini et al., 2008;Cochran et al., 2016a;Schmitt-Kopplin et al., 2012;Rastelli et al., 2017), and their possible association with other compounds promoting co-aerosolization processes (Quinn et al., 2015;Hoffman and Duce, 1976;Rastelli et al., 2017). Further possible transport mechanisms are discussed in section 3.2.4.

A gradient regarding EF_{aer} of the individual lipid classes was found, showing that some of them were enriched to a larger extent than others (Fig.4, Table S9). Such differences between the lipid classes have not been reported so far because the lipids were mainly measured as a sum (Rastelli et al., 2017) or only a specific lipid class (as FFA, HC) has been investigated (Cochran et al., 2016b;Marty et al., 1979). In our data set we observed that TG ($EF_{aer(TG)}$: $3 \cdot 10^6$) followed by ALC were most enriched ($EF_{aer(ALC)}$: $1 \cdot 10^6$), while MGDG showed a lower enrichment with $EF_{aer(MGDG)}$: $4 \cdot 10^4$. For the SML enrichment, the parameters describing the surface activity (density, ~~K$_{ow}$~~K_{OW} and TPSA, Table S7), were compared with lipid enrichment. Lipid classes with comparatively low surfactant activity (in relation to the TPSA value of the lipid class, Table S7) including PP and GL showed relatively lower enrichments ($EF_{aer(PP)}$: $2 \cdot 10^5$ and $EF_{aer(GL)}$: $3 \cdot 10^5$) compared to highly enriched ALC ($EF_{aer(ALC)}$: $1 \cdot 10^6$). Furthermore, a mild connection (R^2=0.~~43~~45, p=0.028) was found between the log ~~K$_{ow}$~~K_{OW} and the EF_{aer} of the individual

lipid classes (Fig. ~~S12~~S11), indicating that the compounds with higher log ~~K_{ow}~~K_{OW} and therefore stronger lipophilicity are preferably enriched on the aerosol particles. For example, TG with the highest log K_{OW} value of 25.5 (Table S7) was observed to have the highest enrichment on aerosol particles ($EF_{aer(TG)}$: $3 \cdot 10^6$). In contrast, lipid classes with lower log ~~K_{ow}~~K_{OW} values such as MGDG (log ~~K_{ow}~~$K_{OW(MGDG)}$: -3.5) were characterized by lower enrichments ($EF_{aer(MGDG)}$: $4 \cdot 10^4$). The compounds that are highly enriched in the aerosol phase only partially correspond to their respective enrichment in the SML. TG and ALC showed a high enrichment both in the SML and in the ~~particle phase.~~aerosol particles. However, FFA, that showed a pronounced SML enrichment in PL ($EF_{SML(FFA)}$:3.1), exhibited only a medium enrichment in the aerosol particles compared to other lipid groups.

It needs to be emphasized, that the calculated EF_{aer} provides the quantitative description of the transfer from the ocean to the atmosphere, but does not consider additional formation or degradation pathways of lipids on the aerosol particles, including biological or photochemical atmospheric reactions and a transport from other than marine sources. In agreement with the results of SML enrichment, these results suggest that additional processes such as biotic formation and degradation influence the lipid abundance on the aerosol particles. It has been reported that microorganisms (Rastelli et al., 2017) and especially bacteria (Michaud et al., 2018) can be transported from the ocean into the atmosphere. Bacteria can be transferred to marine aerosol particles ~~and may produce or degrade lipids.~~. Here, besides passive contribution (i.e. providing lipids to aerosol particles upon cell disintegration), bacteria may also actively influence the OM composition of aerosols (i.e. lipid production or degradation). However, the extent of this passive and especially of potential active bacterial contribution to the lipid pool of aerosols warrants further studies. In addition, photochemical oxidation processes can take place in the atmosphere, i.e. conversion of FFA to ALC (Bikkina et al., 2019).

Overall, the detailed measurements of the lipid classes within the concerted measurements together with additional parameters showed that although lipids are the highly OM species in aerosols, which is in-line with their high surface activity, additional biological processes influence the lipid composition. These need to be further studied and considered in OM transfer models. More recent models recognized that OM transfer must be modeled by including the individual OM groups (like lipids) rather than phytoplankton tracers like chl-*a* (Burrows et al., 2014). Indeed, these models describe OM transfer on the basis of their physico-chemical properties, but our data suggest that in the ambient marine environment, additional in-situ formation and degradation must also be considered in order to fully address OM abundance in general and the lipid abundance in particular.

3.2.4 Discussion of possible transfer mechanisms

The transfer of the dissolved and particulate OM from the ocean to the atmosphere probably occurs via bubble bursting, whereby bubbles rising through the water column absorb OM and, when bursting at the surface, release the OM to the aerosol particles via jet and film drops (Quinn et al. (2015), and references therein). The finding ~~here, that both DL and PL, contain similar classes of lipid, which~~lipids (DL and PL) are ~~also~~ found on the aerosol particles (Fig. ~~5), suggests~~5, Fig. S12) indicates that both types of lipids ~~in seawater are~~can be transferred from seawater to the aerosol particles, e.g. via ~~bubble~~ bursting

~~process~~the bubbles. A differentiation of the contribution of the dissolved and particulate lipid fractions in seawater to the formation of the aerosol particles was therefore not possible here.

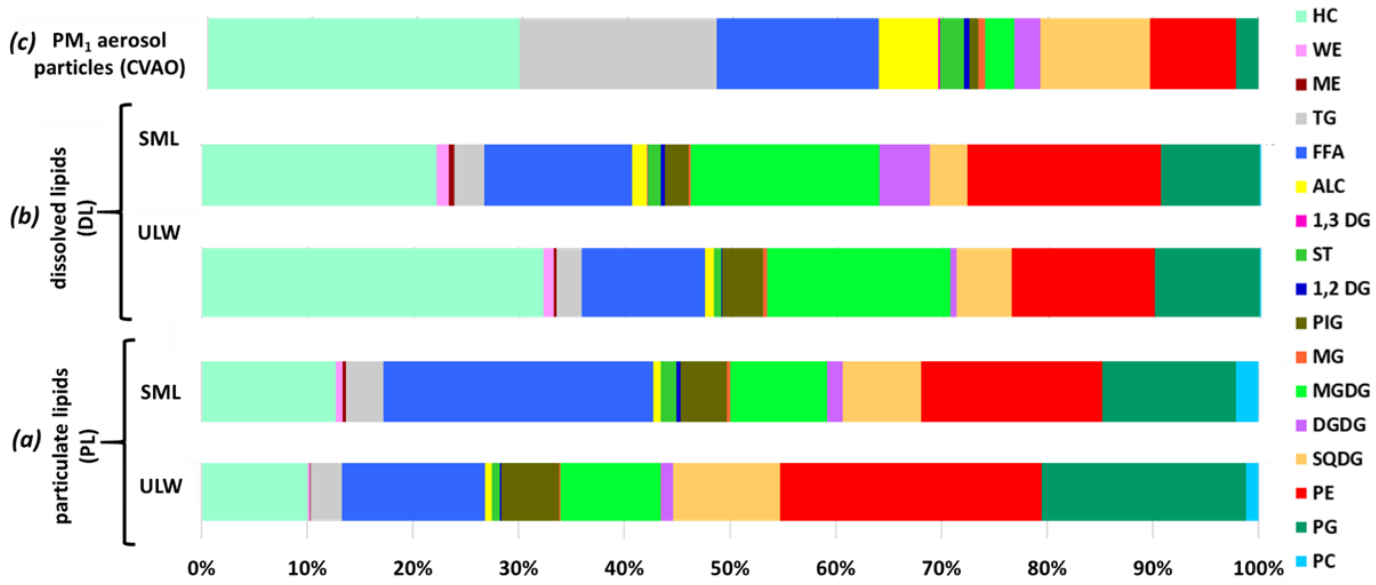

Figure 5: The percentage contribution of the individual lipid classes to the total lipids in the (a) particulate and (b) dissolved fraction in seawater (differentiation between ULW and SML) and on (c) PM_1 aerosol particles at the CVAO

However, regarding the process of OM absorption on the bubbles in more detail, the OM absorbed on the bubble can be distributed either towards the gas or aqueous phase or can preferably reside within the bubble interface. To conceptually address the distribution of the OM towards the bubble-water-interface, we calculated the adsorption coefficient related to air (K_a) after Kelly et al. (2004) and additionally an adsorption coefficient of the analytes related to water (K_{aq}). The calculation included the measured SML concentrations, Henry's Law constants and the gas-phase saturation vapor pressure as explained and discussed in detail in Table S10. The comparison of the calculated K_a and K_{aq} values can give a hint on the distribution of lipids at the bubble-air-water-interface. When K_{aq}>>K_a (Fig. ~~S18a~~S17a), the analyte should be preferred distributed (from water) to air (inside the bubble). When K_a>>K_{aq} (Fig. ~~S18b~~S17b) in turn, the analyte should be preferably distributed (from air) into water while the analyte should be preferred distributed within the bubble interface when K_{aq}~ K_a (Fig. ~~S18c~~S17c). Our data set showed that the analytes that had similar K_a and K_{aq} values (Table S10), namely TG and ALC, had highest EF_{aer} ($EF_{aer(TG)}$: $3 \cdot 10^6$ and $EF_{aer(ALC)}$: $1 \cdot 10^6$). This indicates that analytes, which are preferably distributed within the interface of the bubble, are transferred to the aerosol particles to a larger extent via the bubble bursting process, probably due to the higher stickiness to the interface (Fig. 6).

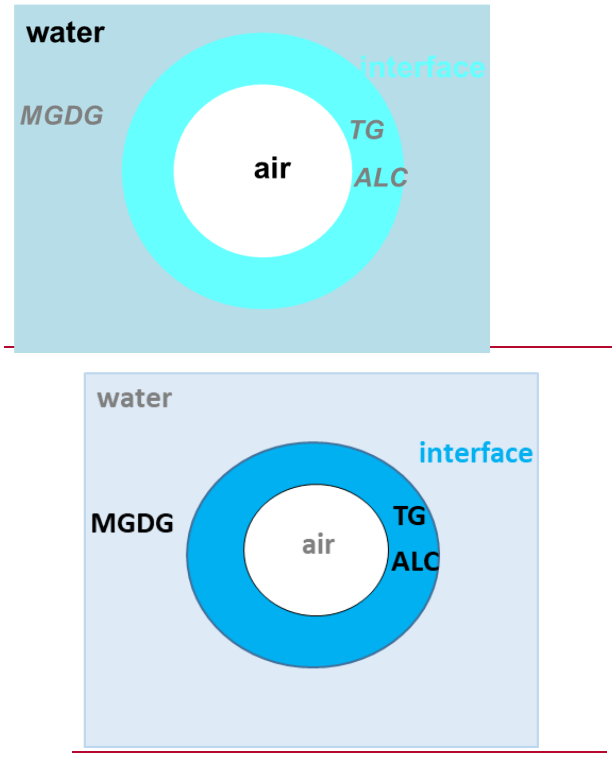

Figure 6: Scheme of a bubble during the process of a bubble ~~bursting process~~rising through the water column, distinguished between 'air' (inside the bubble), 'water' (surrounding the bubble), the 'interface' (bubble surface) and the distribution of the lipid classes MGDG, TG and ALC related to their K_a and K_{aq} values

For MGDG, the lipid class with the lowest EF_{aer} ($4 \cdot 10^4$), the observed ratio was $K_a >> K_{aq}$, meaning that MGDG was preferably distributed in water. For the other lipid classes, however, we did not find such a connection between the adsorption coefficients (K_{aq}, K_a) and the aerosol enrichment (EF_{aer}). Nevertheless, the hypothesis that the transfer and enrichment of the lipids is related to the distribution of a compounds within the bubble-air-water-interface, as observed for the lipid classes with extreme EF_{aer}, should be further investigated, preferably in controlled laboratory experiments.

3.3 Connection between lipids and INP activity in seawater

One main feature of biological components in general is their potential ability to ~~contain~~contribute to ice ~~nucleating abilities~~nucleation and act as INP in the atmosphere (Šantl-Temkiv et al. (2019) and references therein). To identify potential connections between lipid classes and INP activity in seawater, a statistical analysis was performed as described in section 2.2.5. As shown in detail in ~~Gong et al. (2020)~~Gong et al. (2020), all samples collected for the present study contained both SML and ULW INP with concentrations of ~ 200 L^{-1} at temperatures of about -10 °C (Fig. ~~S16~~S17), increasing to 10^7 L^{-1} at ~ -25 °C. The existence of INP that are already ice active at temperatures above -15 °C indicated the presence of biogenic INP (Kanji et al., 2017;Šantl-Temkiv et al., 2019).

Both lipid fractions of the SML samples showed a positive trend towards the INP concentrations measured at -10 °C (R=0.72, p-value=0.28, n=4 for the total PL and R=0.69, p-value=0.31, n=4 for the total DL, Fig. ~~S14a~~S13a/b). This connection suggests the involvement of lipids in biogenic INP. Furthermore, the lipid classes which had shown a relationship with autotrophic or heterotrophic organisms, namely PE and FFA (section 3.1.4), were investigated for their INP relationship. The relationship between PE and INP with regard to ULW cannot be discussed here, as the criteria defined in section 2.2.5 were not met (e.g. not enough matching data points were available). But a trend was found between SML particulate PE and INP measurements at -10 °C (R=0.95, p-value=0.06, n=4, Fig. ~~S14c~~S13c). Similar relations between lipids and INP activity have been reported previously (Govindarajan and Lindow, 1988;Palaiomylitou et al., 1998;DeMott et al., 2018). Palaiomylitou et al. (1998) reported that ice nucleation proteins were associated with phospholipids and showed that phospholipids, especially PE, not only contribute to increased overall activity but also to the production of ice nuclei active at higher temperatures. To further test biogenic INP activity, we analyzed the INP activity of the seawater samples before and after heating (95°C for 1 hour), since biogenic, especially proteinogenic, compounds are deactivated when heated to 100 °C (Šantl-Temkiv et al., 2019). It could be shown that a large proportion of INPs, that were active between -10 °C and -15 °C, lost their ice activity after the heating procedure (Fig. ~~S16~~S15). As mentioned above, the deactivation of the INP function by heating is often associated with proteins. However, it has been shown that ice nucleating proteins have a connection to lipids and interactions with membrane lipids, especially PE, are needed to maintain the conformational structure and functional activity of many membrane-bound proteins (Govindarajan and Lindow, 1988;Palaiomylitou et al., 1998). For this reason, the lipids might have a driving function in the INP activity of biogenic INP. In the SML samples, trends between INP measurements at -10 °C and the particulate FFA (R=0.84, p-value=0.16, n=4, Fig. ~~S15a~~S14a) and dissolved FFA (R=0.63, p-value=0.37, n=4, Fig. ~~S15b~~S14b) were observed. Moreover, a trend was found between the particulate FFA in the ULW and the INP measurements at -15 °C (R=0.64, p-value=0.025, n=12, Fig. ~~S15c~~S14c). DeMott et al. (2018) reported that ice nucleation by particles containing long-chain fatty acids in a crystalline phase was relevant for freezing ~~by~~of sea spray aerosols. ~~Burrows et al. (2013)~~Burrows et al. (2013) suggested that marine biogenic INP most probably played a dominant role in the INP concentrations studied in near-surface-air over the Southern Ocean. Wilson et al. (2015) proposed that there are ice active macromolecules in the OM of SML. Moreover, they pointed out that global model simulations of marine organic aerosol in connection with their measurements indicated that marine OM might be an important source of INP in remote marine environments, e.g. the Southern Ocean, North Pacific Ocean and North Atlantic Ocean (Wilson et al. (2015), and references therein). The relationships presented here between the lipids in general and in particular the lipid classes with assigned biological context (PE, FFA) and INP activity at higher temperatures (-10 °C, -15 °C) in the ambient SML ~~samples are consistent with the results of Wilson et al. (2015)~~ indicating that lipids in the tropical North Atlantic Ocean have the potential to contribute to (biogenic) INP activity when transferred to the atmosphere. However, it remains unclear to what extent INPs transferred from the ocean into the atmosphere contribute to the INP pool in the atmosphere, since further studies have identified other sources of INPs besides sea spray aerosol (~~Gong et al. (2020)~~Gong et al. (2020), and references therein).

4. Conclusion

~~At the CVAO, concerted~~Concerted measurements of lipids ~~as representatives of their respective classes~~ were performed ~~during the MarParCloud campaign~~in proximity to ~~determine their concentrations in seawater and SML (as dissolved and particulate lipids) and on~~the Cape Verde Islands to compare the concentration of specific lipid classes in submicron aerosol particles~~. In seawater,~~ and in the ~~detailed~~dissolved and particulate fraction of seawater (ULW and SML). The analysis of ~~the~~ lipid classes in seawater showed that, although ~~the~~ concentrations ~~of PL~~in the particulate and ~~DL~~dissolved fraction are generally very ~~similiar~~similar, the ~~composition~~contribution of ~~the lipids to the PL and DL groups exhibits several differences~~lipids within fractions differed. This suggests that different production and degradation mechanisms for DL and PL contribute to the respective lipid composition. On the aerosol particles, the lipid composition resembles the lipid composition of the dissolved fraction in seawater. Although the lipids are reported as fast reactive compounds, our results suggest that ~~they are more stable in the DL and PL in ULW and more degraded in the PL in SML.~~the DL are somewhat more resistant to degradation. The phytoplankton groups chlorophytes, cyanobacteria and diatoms probably influence the lipid abundance as shown by pigment measurements. ~~However, the concentration of chl *a*, as often used proxy for biological production via phytoplankton, is not sufficient to describe the lipid concentration.~~ Our results indicate that, besides phytoplankton, bacteria also play an important role in lipid abundance in the oligotrophic North Atlantic, as shown by the PE/PG ratio and the abundance (and slight SML enrichment) of TCN. The concentration and enrichment of lipids in the ambient SML is not related to their physico-chemical properties describing the surface activity, at least not in the short term, probably due to parallel in-situ formation and degradation processes. This is underlined by the fact that lipids in the top 100 µm of the SML are not as highly enriched as other (less surface active) compound, such as amino acids.

For aerosol, however, the high enrichment of total lipids corresponds well with the consideration of their high surface activity. The EF_{aer} agrees with the considerations from modelling and laboratory studies that, among the marine OM groups, lipids are the most highly enriched compounds and indicates that the transfer of lipids from the SML to the aerosol phase in the complex marine field is consistent with processes described in laboratory studies. In addition, the EF_{aer} of lipids was one to two orders of magnitude higher than the EF_{aer} of the less surface-active amino acids previously reported. In terms of the individual lipid groups on the aerosol particles, a mild relation between EF_{aer} and lipophilicity (expressed by the K_{OW} value) was observed, which was missing in SML. In general, however, the parameters representing the surface activity of the lipid classes (density, K_{OW} value and TPSA) were not sufficient to describe their transfer to the aerosol particles. The fact that bacteria are strongly involved in lipid abundance underlines that models using chl-*a* are not enough to describe OM in general ~~and lipids in particular.~~. In addition, physico-chemical OM properties such as surface activity, are not sufficient to describe lipid abundance in the complex marine environment. Further processes such as biotic formation and degradation, as shown by the investigation of the individual lipid classes, contribute to lipid abundance in seawater, SML and on aerosol particles in the marine environment and must be included in the consideration of lipid transfer and finally in OM transfer models. Beyond that, our data suggest that the enrichment of the lipid classes on aerosol particles may be related to the distribution of the lipid on their respective adsorption coefficients in water (K_{aq}) and in air (K_a). Compounds which are preferably arranged within the bubble

interface (K_{aq}~K_a), namely TG and ALC, are transferred to the aerosol particles to the highest extend. Finally, our results showed that lipids had the potential to contribute to (biogenic) INP activity when transferred to the atmosphere.

Altogether, we showed that the diverse group of lipids represent an important and complex OM group in seawater and on marine aerosol particles. To the best of the author's knowledge, the present study is the first to analyze several lipid classes simultaneously in seawater including ULW and SML and on submicron aerosol particles (PM_1) in such detail to obtain indications on their sources and sea-air linkage in the marine environment.

Data availability. The data are ~~currently uploaded to~~available through the ~~AWI~~ World Data Centre PANGAEA ~~(~~under the following link: https~~:\\ww~~://doi.pangaea.de~~/).~~/10.1594/PANGAEA.921832.

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

References

Arts, M. T., Ackman, R. G., and Holub, B. J.: "Essential fatty acids" in aquatic ecosystems: a crucial link between diet and human health and evolution, Canadian Journal of Fisheries and Aquatic Sciences, 58, 122-137, 10.1139/f00-224, 2001.

Barati, F., Yao, Q., and Asa-Awuku, A. A.: Insight into the Role of Water-Soluble Organic Solvents for the Cloud Condensation Nuclei Activation of Cholesterol, ACS Earth and Space Chemistry, 3, 1697-1705, 10.1021/acsearthspacechem.9b00161, 2019.

Becker, K. W., Collins, J. R., Durham, B. P., Groussman, R. D., White, A. E., Fredricks, H. F., Ossolinski, J. E., Repeta, D. J., Carini, P., Armbrust, E. V., and Van Mooy, B. A. S.: Daily changes in phytoplankton lipidomes reveal mechanisms of energy storage in the open ocean, Nature Communications, 9, 5179, 10.1038/s41467-018-07346-z, 2018.

Bhattacharya, B., and Habtzghi, D.: Median of the p Value under the Alternative Hypothesis, The American Statistician, 56, 202-206, 2002.

Bikkina, P., Kawamura, K., Bikkina, S., Kunwar, B., Tanaka, K., and Suzuki, K.: Hydroxy Fatty Acids in Remote Marine Aerosols over the Pacific Ocean: Impact of Biological Activity and Wind Speed, ACS Earth and Space Chemistry, 3, 366-379, 10.1021/acsearthspacechem.8b00161, 2019.

Bligh, E. G., and Dyer, W. J.: A rapid method of total lipid extraction and purification, Canadian Journal of Biochemistry and Physiology, 37, 911-917, 1959.

Burrows, S. M., Hoose, C., Pöschl, U., and Lawrence, M. G.: Ice nuclei in marine air: biogenic particles or dust?, Atmos. Chem. Phys., 13, 245-267, 10.5194/acp-13-245-2013, 2013.

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

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

Christodoulou, S., Marty, J.-C., Miquel, J.-C., Volkman, J. K., and Rontani, J.-F.: Use of lipids and their degradation products as biomarkers for carbon cycling in the northwestern Mediterranean Sea, Mar. Chem., 113, 25-40, 10.1016/j.marchem.2008.11.003, 2009.

Cochran, R. E., Jayarathne, T., Stone, E. A., and Grassian, V. H.: Selectivity Across the Interface: A Test of Surface Activity in the Composition of Organic-Enriched Aerosols from Bubble Bursting, J. Phys. Chem. Lett., 7, 1692-1696, 10.1021/acs.jpclett.6b00489, 2016a.

Cochran, R. E., Laskina, O., Jayarathne, T., Laskin, A., Laskin, J., Lin, P., Sultana, C., Lee, C., Moore, K. A., Cappa, C. D., Bertram, T. H., Prather, K. A., Grassian, V. H., and Stone, E. A.: Analysis of Organic Anionic Surfactants in Fine and Coarse Fractions of Freshly Emitted Sea Spray Aerosol, Environ. Sci. Technol., 50, 2477-2486, 10.1021/acs.est.5b04053, 2016b.

Cunliffe, M., Upstill-Goddard, R. C., and Murrell, J. C.: Microbiology of aquatic surface microlayers, FEMS microbiology reviews, 35, 233-246, 10.1111/j.1574-6976.2010.00246.x, 2011.

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

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

~~Dai, Z., Dukhin, S., Fornasiero, D., and Ralston, J.: The Inertial Hydrodynamic Interaction of Particles and Rising Bubbles with Mobile Surfaces, J Colloid Interface Sci, 197, 275-292, 10.1006/jcis.1997.5280, 1998.~~

DeMott, P. J., Mason, R. H., McCluskey, C. S., Hill, T. C. J., Perkins, R. J., Desyaterik, Y., Bertram, A. K., Trueblood, Jonathan V., Grassian, V. H., Qiu, Y., Molinero, V., Tobo, Y., Sultana, C. M., Lee, C., and Prather, K. A.: Ice nucleation by particles containing long-chain fatty acids of relevance to freezing by sea spray aerosols, Environmental Science: Processes & Impacts, 20, 1559-1569, 10.1039/C8EM00386F, 2018.

Derieux, S., Fillaux, J., and Saliot, A.: Lipid class and fatty acid distributions in particulate and dissolved fractions in the north Adriatic sea, Organic Geochemistry, 29, 1609-1621, 10.1016/S0146-6380(98)00089-8, 1998.

Descy, J.-P., Sarmento, H., and Higgins, H. W.: Variability of phytoplankton pigment ratios across aquatic environments, European Journal of Phycology, 44, 319-330, 10.1080/09670260802618942, 2009.

Duhamel, S., Kim, E., Sprung, B., and Anderson, O. R.: Small pigmented eukaryotes play a major role in carbon cycling in the P-depleted western subtropical North Atlantic, which may be supported by mixotrophy, Limnol. Oceanogr., 64, 2424-2440, 10.1002/lno.11193, 2019.

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.

Facchini, M. C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E. D., de Leeuw, G., Martino, M., Woeltjen, J., and O'Dowd, C. D.: Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates, Geophys. Res. Lett., 35, doi:10.1029/2008GL034210, 2008.

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.

Frka, S., Gašparović, B., Marić, D., Godrijan, J., Djakovac, T., Vojvodić, V., Dautović, J., and Kozarac, Z.: Phytoplankton driven distribution of dissolved and particulate lipids in a semi-enclosed temperate sea (Mediterranean): Spring to summer situation, Estuar. Coast. Shelf Sci., 93, 290-304, 10.1016/j.ecss.2011.04.017, 2011.

Frka, S., Pogorzelski, S., Kozarac, Z., and Ćosović, B.: Physicochemical Signatures of Natural Sea Films from Middle Adriatic Stations, The Journal of Physical Chemistry A, 116, 6552-6559, 10.1021/jp212430a, 2012.

Gagosian, R. B., Zafiriou, O. C., Peltzer, E. T., and Alford, J. B.: Lipids in aerosols from the tropical North Pacific: Temporal variability, Journal of Geophysical Research: Oceans, 87, 11133-11144, 10.1029/JC087iC13p11133, 1982.

Galasso, C., Corinaldesi, C., and Sansone, C.: Carotenoids from Marine Organisms: Biological Functions and Industrial Applications, Antioxidants (Basel), 6, 96, 10.3390/antiox6040096, 2017.

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.

Gašparović, B., ~~Kozarac, Z., Saliot, A., Ćosović, B., and Möbius, D.: Physicochemical Characterization of Natural and ex-Situ Reconstructed Sea-Surface Microlayers, J Colloid Interface Sci, 208, 191-202, 10.1006/jcis.1998.5792, 1998.~~

~~Gašparović, B.,~~ Godrijan, J., Frka, S., Tomažić, I., Penezić, A., Marić, D., Djakovac, T., Ivančić, I., Paliaga, P., Lyons, D., Precali, R., and Tepić, N.: Adaptation of marine plankton to environmental stress by glycolipid accumulation, Marine environmental research, 92, 120-132, 10.1016/j.marenvres.2013.09.009, 2013.

Gašparović, B., Frka, S., Koch, B. P., Zhu, Z. Y., Bracher, A., Lechtenfeld, O. J., Neogi, S. B., Lara, R. J., and Kattner, G.: Factors influencing particulate lipid production in the East Atlantic Ocean, Deep Sea Research Part I: Oceanographic Research Papers, 89, 56-67, 10.1016/j.dsr.2014.04.005, 2014.

Gašparović, B., Kazazić, S. P., Cvitešić, A., Penezić, A., and Frka, S.: Improved separation and analysis of glycolipids by Iatroscan thin-layer chromatography-flame ionization detection, J. Chromatogr. A, 1409, 259-267, 10.1016/j.chroma.2015.07.047, 2015.

Gašparović, B., Kazazić, S. P., Cvitešić, A., Penezić, A., and Frka, S.: Corrigendum to “Improved separation and analysis of glycolipids by Iatroscan thin-layer chromatography–flame ionization detection” [J. Chromatogr. A 1409 (2015) 259–267], J. Chromatogr. A, 1521, 168-169, 10.1016/j.chroma.2017.09.038, 2017.

Gašparović, B., Penezić, A., Lampitt, R. S., Sudasinghe, N., and Schaub, T.: Phospholipids as a component of the oceanic phosphorus cycle, Mar. Chem., 205, 70-80, 10.1016/j.marchem.2018.08.002, 2018.

Gong, X., Wex, H., van Pinxteren, M., Triesch, N., Fomba, K. W., Lubitz, J., Stolle, C., Robinson, T. B., Müller, T., Herrmann, H., and Stratmann, F.: Characterization of aerosol particles at Cape Verde close to sea and cloud level heights – Part 2: ice nucleating particles in air, cloud and seawater, Atmos. Chem. Phys., 20, 1451–1468, 10.5194/acp-20-1451-2020, 2020.

Goutx, M., Acquaviva, M., and Gérin, C.: Iatroscan-measured phospholipids from marine microalgae, bacteria and suspended particles. Inform-International news on fats, oils and related materials, American Oil Chemists Society Publishers, 4, 516-517, 1993.

Goutx, M., Guigue, C., and Striby, L.: Triacylglycerol biodegradation experiment in marine environmental conditions: definition of a new lipolysis index, Organic Geochemistry, 34, 1465-1473, 10.1016/S0146-6380(03)00119-0, 2003.

Goutx, M., Guigue, C., D, D. A., Ghiglione, J. F., Pujo-Pay, M., Raybaud, V., Duflos, M., and Prieur, L.: Short term summer to autumn variability of dissolved lipid classes in the Ligurian sea (NW Mediterranean), Biogeosciences, 6, 1229-1246, 10.5194/bg-6-1229-2009, 2009.

Govindarajan, A. G., and Lindow, S. E.: Phospholipid requirement for expression of ice nuclei in Pseudomonas syringae and in vitro, The Journal of biological chemistry, 263, 9333-9338, 1988.

Grant, C. S., and Louda, J. W.: Microalgal pigment ratios in relation to light intensity: Implications for chemotaxonomy, Aquatic Biology, 11, 10.3354/ab00298, 2010.

Grasshoff, K., Kremling, K., and Ehrhardt, M.: Methods of Seawater Analysis - 3rd edition, edited by: Grasshoff, K., Kremling, Klaus, Ehrhardt, Manfred, Wiley-VCH Weinheim , Germany, 1999.

Guschina, I. A., and Harwood, J. L.: Algal lipids and effect of the environment on their biochemistry, in: Lipids in Aquatic Ecosystems, edited by: Kainz, M., Brett, M. T., and Arts, M. T., Springer New York, New York, NY, 1-24, 2009.

Hoffman, E. J., and Duce, R. A.: Factors influencing the organic carbon content of marine aerosols: A laboratory study, Journal of Geophysical Research (1896-1977), 81, 3667-3670, 10.1029/JC081i021p03667, 1976.

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.

Kattner, G.: Lipid composition of Calanus finmarchicus from the north sea and the arctic. A comparative study, Comparative Biochemistry and Physiology Part B: Comparative Biochemistry, 94, 185-188, 10.1016/0305-0491(89)90031-X, 1989.

Kawamura, K., Ishimura, Y., and Yamazaki, K.: Four years' observations of terrestrial lipid class compounds in marine aerosols from the western North Pacific, Global Biogeochemical Cycles, 17, 1003, 10.1029/2001GB001810, 2003.

Kelly, C. P., Cramer, C. J., and Truhlar, D. G.: Predicting Adsorption Coefficients at Air−Water Interfaces Using Universal Solvation and Surface Area Models, The Journal of Physical Chemistry B, 108, 12882-12897, 10.1021/jp037210t, 2004.

Khozin-Goldberg, I.: Lipid Metabolism in Microalgae, in: The Physiology of Microalgae, edited by: Borowitzka, M. A., Beardall, J., and Raven, J. A., 6, Springer International Publishing, 413-484, 2016.

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

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.

Marić, D., Frka, S., Godrijan, J., Tomažić, I., Penezić, A., Djakovac, T., Vojvodić, V., Precali, R., and Gašparović, B.: Organic matter production during late summer–winter period in a temperate sea, Continental Shelf Research, 55, 52-65, 10.1016/j.csr.2013.01.008, 2013.

Marie, D., Shi, X. L., Rigaut-Jalabert, F., and Vaulot, D.: Use of flow cytometric sorting to better assess the diversity of small photosynthetic eukaryotes in the English Channel, FEMS Microbiology Ecology, 72, 165-178, 10.1111/j.1574-6941.2010.00842.x, 2010.

Marty, J. C., Saliot, A., Buat-Ménard, P., Chesselet, R., and Hunter, K. A.: Relationship between the lipid compositions of marine aerosols, the sea surface microlayer, and subsurface water, Journal of Geophysical Research: Oceans, 84, 5707-5716, 10.1029/JC084iC09p05707, 1979.

~~Marty, J. C., Žutić, V., Precali, R., Saliot, A., Ćosović, B., Smodlaka, N., and Cauwet, G.: Organic matter characterization in the Northern adriatic sea with special reference to the sea surface microlayer, Mar. Chem., 25, 243-263, 10.1016/0304-4203(88)90053-9, 1988.~~

Michaud, J. M., Thompson, L. R., Kaul, D., Espinoza, J. L., Richter, R. A., Xu, Z. Z., Lee, C., Pham, K. M., Beall, C. M., Malfatti, F., Azam, F., Knight, R., Burkart, M. D., Dupont, C. L., and Prather, K. A.: Taxon-specific aerosolization of bacteria and viruses in an experimental ocean-atmosphere mesocosm, Nature Communications, 9, 2017, 10.1038/s41467-018-04409-z, 2018.

Mochida, M., Kitamori, Y., Kawamura, K., Nojiri, Y., and Suzuki, K.: Fatty acids in the marine atmosphere: Factors governing their concentrations and evaluation of organic films on sea-salt particles, Journal of Geophysical Research: Atmospheres, 107, AAC 1-1-AAC 1-10, doi:10.1029/2001JD001278, 2002.

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, 2010.

Nguyen, Q. T., Kjær, K. H., Kling, K. I., Boesen, T., and Bilde, M.: Impact of fatty acid coating on the CCN activity of sea salt particles, Tellus B: Chemical and Physical Meteorology, 69, 1304064, 10.1080/16000889.2017.1304064, 2017.

~~Novak, T., Godrijan, J., Pfannkuchen, D. M., Djakovac, T., Mlakar, M., Baricevic, A., Tanković, M. S., and Gašparović, B.: Enhanced dissolved lipid production as a response to the sea surface warming, Journal of Marine Systems, 180, 289-298, 10.1016/j.jmarsys.2018.01.006, 2018.~~

Palaiomylitou, M. A., Kalimanis, A., Koukkou, A. I., Drainas, C., Anastassopoulos, E., Panopoulos, N. J., Ekateriniadou, L. V., and Kyriakidis, D. A.: Phospholipid Analysis and Fractional Reconstitution of the Ice Nucleation Protein Activity Purified fromEscherichia coli Overexpressing the in a Z Gene of Pseudomonas syringae, Cryobiology, 37, 67-76, 10.1006/cryo.1998.2102, 1998.

Parrish, C. C., Wangersky, P. J., Delmas, R. P., and Ackman, R. G.: Iatroscan-measured profiles of dissolved and particulate marine lipid classes over the Scotian Slope and in Bedford Basin, Mar. Chem., 23, 1-15, 10.1016/0304-4203(88)90019-9, 1988.

Parrish, C. C.: Lipids in Marine Ecosystems, ISRN Oceanography, 2013, 16, 10.5402/2013/604045, 2013.

Peña-Izquierdo, J., Pelegrí, J. L., Pastor, M. V., Castellanos, P., Emelianov, M., Gasser, M., Salvador, J., and Vázquez-Domínguez, E.: The continental slope current system between Cape Verde and the Canary Islands, 2012, 76, 14, 10.3989/scimar.03607.18C, 2012.

Perezgonzalez, J. D.: Fisher, Neyman-Pearson or NHST? A tutorial for teaching data testing

Front Psychol, 6, 223-223, 10.3389/fpsyg.2015.00223, 2015.

~~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~~

~~2014.~~

Quinn, P. K., 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, 2015.

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

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

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

Robinson, T.-B., Wurl, O., Bahlmann, E., Jürgens, K., and Stolle, C.: Rising bubbles enhance the gelatinous nature of the air–sea interface, Limnol. Oceanogr., 0, 10.1002/lno.11188, 2019.

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.

Šantl-Temkiv, T., Lange, R., Beddows, D., Rauter, U., Pilgaard, S., Dall'Osto, M., Gunde-Cimerman, N., Massling, A., and Wex, H.: Biogenic Sources of Ice Nucleating Particles at the High Arctic Site Villum Research Station, Environ. Sci. Technol., 53, 10580-10590, 10.1021/acs.est.9b00991, 2019.

Schiffer, J. M., Luo, M., Dommer, A. C., Thoron, G., Pendergraft, M., Santander, M. V., Lucero, D., Pecora de Barros, E., Prather, K. A., Grassian, V. H., and Amaro, R. E.: Impacts of Lipase Enzyme on the Surface Properties of Marine Aerosols, The Journal of Physical Chemistry Letters, 9, 3839-3849, 10.1021/acs.jpclett.8b01363, 2018.

Schmitt-Kopplin, P., Liger-Belair, G., Koch, B. P., Flerus, R., Kattner, G., Harir, M., Kanawati, B., Lucio, M., Tziotis, D., Hertkorn, N., and Gebefügi, I.: Dissolved organic matter in sea spray: a transfer study from marine surface water to aerosols, Biogeosciences, 9, 1571-1582, 10.5194/bg-9-1571-2012, 2012.

Scholz-Böttcher, B., Ahlf, S., Vázquez-Gutiérrez, F., and Rullkötter, J.: Natural vs. anthropogenic sources of hydrocarbons as revealed through biomarker analysis: A case study in the southern Gulf of Mexico, Boletin de la Sociedad Geologica Mexicana, 61, 10.18268/BSGM2009v61n1a5, 2009.

Simoneit, B. R. T., and Mazurek, M. A.: Organic matter of the troposphere—II.**For Part I, see Simoneit et al. (1977). Natural background of biogenic lipid matter in aerosols over the rural western united states, Atmospheric Environment (1967), 16, 2139-2159, 10.1016/0004-6981(82)90284-0, 1982.

Stillwell, W.: Chapter 5 - Membrane Polar Lipids, in: An Introduction to Biological Membranes (Second Edition), edited by: Stillwell, W., Elsevier, 63-87, 2016.

Stolle, C., Ribas-Ribas, M., Badewien, T. H., Barnes, J., Carpenter, L. J., Chance, R., Damgaard, L. R., Quesada, A. M. D., Engel, A., Frka, S., Galgani, L., Gašparović, B., Gerriets, M., Mustaffa, N. I. H., Herrmann, H., Kallajoki, L., Pereira, R., Radach, F., Revsbech, N. P., Rickard, P., Saint, A., Salter, M., Striebel, M., Triesch, N., Uher, G., Upstill-Goddard, R. C., Pinxteren, M. v., Zäncker, B., Zieger, P., and Wurl, O.: The MILAN campaign: Studying diel light effects on the air-sea interface, Bull. Amer. Meteorol. Soc., null, 10.1175/bams-d-17-0329.1, 2019.

Sutherland, K. L.: Physical Chemistry of Flotation. XI. Kinetics of the Flotation Process, The Journal of Physical and Colloid Chemistry, 52, 394-425, 10.1021/j150458a013, 1948.

Tervahattu, H., Juhanoja, J., and Kupiainen, K.: Identification of an organic coating on marine aerosol particles by TOF-SIMS, J. Geophys. Res.-Atmos., 107, 7, 10.1029/2001jd001403, 2002.

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. Discuss., 2020, 1-24, 10.5194/acp-2019-976, 2020.

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

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.

van Pinxteren, M., Fomba, K. W., Triesch, N., Stolle, C., Wurl, O., Bahlmann, E., Gong, X., Voigtländer, J., Wex, H., Robinson, T. B., Barthel, S., Zeppenfeld, S., Hoffmann, E. H., Roveretto, M., Li, C., Grosselin, B., Daële, V., Senf, F., van Pinxteren, D., Manzi, M., Zabalegui, N., Frka, S., Gašparović, B., Pereira, R., Li, T., Wen, L., Li, J., Zhu, C., Chen, H., Chen, J., Fiedler, B., von Tümpling, W., Read, K. A., Punjabi, S., C. Lewis, A. C., Hopkins, J. R., Carpenter, L. J., Peeken, I., Rixen, T., Schulz-Bull, D., Monge, M. E., Mellouki, A., George, C., Stratmann, F., and Herrmann, H.: Marine organic matter in the remote environment of the Cape Verde Islands – 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., vanvan 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.

Van Wambeke, F., Goutx, M., Striby, L., Sempéré, R., and Vidussi, F.: Bacterial dynamics during the transition from spring bloom to oligotrophy in the northwestern Mediterranean Sea: Relationships with particulate detritus and dissolved organic matter, Marine Ecology-progress Series - MAR ECOL-PROGR SER, 212, 89-105, 10.3354/meps212089, 2001.

Wakeham, S. G., Hedges, J. I., Lee, C., Peterson, M. L., and Hernes, P. J.: Compositions and transport of lipid biomarkers through the water column and surficial sediments of the equatorial Pacific Ocean, Deep Sea Research Part II: Topical Studies in Oceanography, 44, 2131-2162, 10.1016/S0967-0645(97)00035-0, 1997.

Weber, M. E., Blanchard, D. C., and Syzdek, L. D.: The mechanism of scavenging of waterborne bacteria by a rising bubble, Limnol. Oceanogr., 28, 101-105, 10.4319/lo.1983.28.1.0101, 1983.

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

Wurl, O., and Holmes, M.: The gelatinous nature of the sea-surface microlayer, Mar. Chem., 110, 89-97, 10.1016/j.marchem.2008.02.009, 2008.

Wurl, O., Wurl, E., Miller, L., Johnson, K., and Vagle, S.: Formation and global distribution of sea-surface microlayers, Biogeosciences, 8, 121-135, 10.5194/bg-8-121-2011, 2011.

Yoshimura, K., Ogawa, T., and Hama, T.: Degradation and dissolution properties of photosynthetically-produced phytoplankton lipid materials in early diagenesis, Mar. Chem., 114, 11-18, 10.1016/j.marchem.2009.03.002, 2009.