

Report#2

Comments on the revised version of the work by Triesch et al., entitled “Concerted measurements of lipids in seawater and on submicron aerosol particles at the Cape Verde Islands: biogenic sources, selective transfer and high enrichments”

In the amended version of this work, I think that the Authors have done a good job to accomplish the comments/requests raised in the first round of review by two anonymous reviewers.

I have few additional comments that the Authors should consider to improve their work for publication.

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).

1. The text would benefit from a thorough revision by a native English speaker, to correct the syntax and phrasing of some sentences, make some of them more clear and sounding, check verb tenses (past or present? This should be more consistent throughout the text), correct some typos and avoid some improper/odd expressions.

Following this comment, the manuscript and supporting information has been carefully revised by a professional English-speaking person. The main focus was on the comprehensibility of the sentences/paragraphs.

2.a) Some doubts about statistics. I missed what was used as a test to assess significant differences in the comparisons among samples. This should be stated in the “2.2.5 Statistical analysis” section. Moreover, please avoid/correct too general expressions related to the results of the statistical tests performed.

We thank the reviewer for this comment and corrected the general expressions related to the results in the manuscript, please see also comment 2.b). Regarding the statistical analysis and their interpretations, we would like to refer to section 2.2.5. In this section, the terms ‘statistical relevance’ and ‘trend’ were defined. To validate the significance of the correlation, the correlation coefficient (R), the number of samples examined (n) and the p-value were used. 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).

2.b) Here are only some examples from the text, but this aspect should be corrected throughout the text:

We agree with the reviewer and have specified the noted expressions and phrases below.

-“corresponds well”, please be more specific

On page 2, line 1/2, it now read as: “On the aerosol particles, an EF_{aer} (the enrichment factor on the submicron aerosol particles compared to the SML) between $9 \cdot 10^4$ - $7 \cdot 10^5$ is observed.”
On page 16, line 3-7 it read as follows: “In contrast to the SML enrichment, the higher enrichment of the lipids on the aerosol particles observed here corresponds to 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)."

-“becomes lower”, quantitatively? Is it significant? (p value?)

-“increases”, quantitatively? Is it significant? (p value?)

This sentence has been carefully reworded and now reads as follows (page 8, line 22-26): “On sampling days when the PE concentration was high (e.g. 3/10/2017: 41.8 $\mu\text{g L}^{-1}$; 04/10/2017: 41.9 $\mu\text{g L}^{-1}$), the PG concentration, however, was lower (3/10/2017: 8.8 $\mu\text{g L}^{-1}$; 04/10/2017: 12.6 $\mu\text{g L}^{-1}$, see Fig. 1), whereas towards the end of the campaign, the concentration of PE decreased by a factor of 4-5 (e.g. 7/10/2017: 7.6 $\mu\text{g L}^{-1}$; 9/10/2017: 9.8 $\mu\text{g L}^{-1}$), while the concentration of PG (7/10/2017: 14.8 $\mu\text{g L}^{-1}$; 9/10/2017: 14.4 $\mu\text{g L}^{-1}$) increased by a factor up to 2.”

-“showed not only a much lower concentration but also much less pronounced variance”, please be more specific.. Is it significant? What do the Authors mean with “variance”? Did they perform a test based on the confidence intervals of different groups of samples?

The term ‘variance’ was intended to describe the smaller range of concentrations of TG (ULW: 0.9-5.8 $\mu\text{g L}^{-1}$; SML: 2.1-4.5 $\mu\text{g L}^{-1}$) and ST (ULW: 0.3-0.7 $\mu\text{g L}^{-1}$; SML: 0.7-2.4 $\mu\text{g L}^{-1}$) compared to the higher concentrated FFA (ULW: 5.4-14.0 $\mu\text{g L}^{-1}$; SML: 16.1-36.5 $\mu\text{g L}^{-1}$) and PP (ULW: 15.2-54.9 $\mu\text{g L}^{-1}$; SML: 17.6-37.4 $\mu\text{g L}^{-1}$). This sentence has been carefully reworded and now reads as follows (page 8, line 19-21): “Within the PL, the lipid classes FFA (ULW: 5.4-14.0 $\mu\text{g L}^{-1}$; SML: 16.1-36.5 $\mu\text{g L}^{-1}$) and PP (ULW: 15.2-54.9 $\mu\text{g L}^{-1}$; SML: 17.6-37.4 $\mu\text{g L}^{-1}$) had high concentrations in seawater, while other lipid classes such as TG (< 5.8 $\mu\text{g L}^{-1}$) and ST (< 2.4 $\mu\text{g L}^{-1}$) had concentrations lowered by a factor of 4-23.”

-“was always higher [...], with one exception [...]”, this is incorrect phrasing

We agree with this comment and reworded the sentence, which reads now as follows (page 14, line 12/13): “However, although the atmospheric concentration of phospholipids was lower, PE was found to be more concentrated than PG, with only one exception on 27/09/2017 (Fig. 3).”

-“strong” or “strongly” or similar, please check all the times this word is (mis)used, and use a more sounding statistical/scientific wording

We checked the use of “strong” and “strongly” carefully and have changed the respective use as follows:

On page 4, line 1-3, it reads now as: “Cochran et al. (2016b) investigated the fatty acid composition on sub- and supermicron sea spray aerosol particles and reported that about 75 % of the submicron aerosol particles showed clear signals for the presence of long-chain fatty acids.”

On page 8, line 31/32, it reads now as: “These differences between bacterial and phytoplankton sources are not reflected in the total lipid concentrations, because degradation products such as FFA also contribute to total lipids with a high proportion (Fig. 1).”

On page 12, line 34 – page 13, line 3, it reads now as: “A comparison of lipid enrichment with other OM compounds showed that the SML enrichment of lipids seemed to be less pronounced in contrast to other organic species such as amino acids (Reinthal et al.,

2008;Triesch et al., 2021), despite the high surface activity of the lipids (Burrows et al. (2014), and references therein).”

On page 13, line 5-7, it now reads as: “The fact, that other (less surface active) compounds are more 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.”

On page 13, line 9-11, it now reads as: “Regarding the enrichment in the SML within the lipid classes or both fractions (the dissolved and particulate one), clearer differences were found when looking at the individual lipid classes.”

On page 14, line 7/8, it now reads as: “Compared to the seawater lipids, the atmospheric composition showed the same classes of lipids with an increased consistency of the DL composition (high contribution of HC and lower contributions of PP).”

On page 16, line 17-19, it now reads as: “Furthermore, a statistically relevant correlation ($R^2=0.45$, $p=0.028$) was found between the $\log K_{OW}$ and the EF_{aer} of the individual lipid classes (Fig. S11), indicating that the compounds with higher $\log K_{OW}$ and thus a higher lipophilicity are preferably enriched on the aerosol particles.”

On page 20, line 11/12, it now reads as: “The fact that bacteria are clearly involved in lipid abundance underlines that models using chl-*a* are not enough to describe OM in general.”

-“weak relation”, is it significant or not? No sense to distinguish between stronger or weaker significance.

The correlation between $\log K_{OW}$ and EF_{aer} was found to be significant ($R^2=0.45$, $p=0.028$). Therefore, the statement was specified in the abstract as follows (page 2, line 2-4): “Regarding the individual lipid groups on the aerosol particles, a statistically significant correlation ($R^2=0.45$, $p=0.028$) was found between EF_{aer} and lipophilicity (expressed by the K_{OW} value), which was not present for the SML.”

And in the conclusion (page 20, line 7-9): “In terms of the individual lipid groups on the aerosol particles, a statistically significant correlation ($R^2=0.45$, $p=0.028$) between EF_{aer} and lipophilicity (expressed by the K_{OW} value) was observed, which was not present for the SML.”

“somewhat more resistant to degradation” could the Authors be more “quantitative”?

Since the detailed investigation of the biotic and abiotic degradation of the individual lipid classes in both fractions was not part of this field study, only a comparison of the LI between the two lipid fractions is possible. In the future, for example, the degradation of the lipid classes should be investigated in more detail under controlled conditions in order to make a quantitative statement on this. We revised this sentence, which reads now as follows (page 11, line 9-11): “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 more resistant to degradation than the particulate lipids.”

“For aerosol, however, the high enrichment of total lipids corresponds well with the consideration of their high surface activity” this is an example of sentence, which is a bit odd and not clear in terms of statistical sense. Especially in the abstract and conclusions, the Authors should take particular care to use more sounding/scientific expressions.

We agree with the reviewer and rephrased this sentence. In the abstract it now reads as follows (page 2, line 1/2): “On the aerosol particles, an EF_{aer} (the enrichment factor on the submicron aerosol particles compared to the SML) between $9 \cdot 10^4$ - $7 \cdot 10^5$ is observed.”

Additional corrections in the manuscript concerning too general expressions:

The expressions “slightly” higher have been corrected and the sentences now reads as follows (page 9, line 6-9): “Compared to the particulate fraction, higher concentrations of total dissolved lipids were detected by a factor between 1.1 and 1.4 with Σ DL: 39.8-128.5 $\mu\text{g L}^{-1}$ in the ULW and with Σ DL: 55.7-121.5 $\mu\text{g L}^{-1}$ in the SML samples (Fig. 2). The maximum concentrations here were also a factor of 1.3-1.4 higher than the total dissolved lipid concentrations reported by Frka et al. (2011) in the Mediterranean semi-enclosed temperate Adriatic sea (Σ DL: 7.5-92.2 $\mu\text{g L}^{-1}$).”

The expression “significantly lower” has been corrected and the sentence now reads as follows (page 10, line 1/2): “Phospholipids, especially PE and PG, and FFA, which dominated the particulate lipids, showed lower concentrations by a factor of 1.1-2.1 within the total dissolved lipids.”

The expression “slightly increased” has been corrected and the sentence now reads as follows (page 11, line 6/7): “However, on specific days, the LI_{SML} of PL was ≥ 0.5 (Table S5), indicating an increased OM/lipid degradation and metabolite release in the SML compared to the ULW.”

3. Regarding the comment by Rev#1: “R#1-8b) I don’t know if it makes sense, but would it be possible to estimate an EF_{aer} based on ULW properties instead of SML components?”. The Authors’ reply provides interesting information, but the Authors’ conclusion is that this point raised by Rev#1 “does not provide any new insights [...] and therefore we would prefer not to elaborate on this in the manuscript.” Actually, I encourage the Authors to consider this point in the manuscript, as obtaining similar EF_{aer} values if using ULW or SML values is not obvious and discussion about this could be deepened.

We thank the reviewer for his encouragement and have expanded the discussion regarding the EF_{aer} , to include the calculations with ULW as follows.

In section ‘2.2.4 Enrichment factors’, the calculation of EF_{aer} with respect to ULW has been extended as follows (page 7, line 27-33): “To calculate the enrichment factor of the different analytes on aerosol particles (EF_{aer}) relative to seawater (SW), here distinguished between SML and ULW, 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 SW sample using equation (3):

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

In section “3.2.3 Transfer of lipid classes from the ocean to the aerosol particles”, the discussion of EF_{aer} was extended by comparing EF_{aer} based on the ULW and based on the SML as follows (page 15, line 16-18): “The mean $EF_{\text{aer(TL)}}$ calculated based on the ULW concentration is $3.4 \cdot 10^5$, and thus very similar to the mean $EF_{\text{aer(TL)}}$ based on the SML concentrations ($2.6 \cdot 10^5$). This can be attributed to the fact that the lipid concentrations in the ULW and the SML were in the same concentration range, resulting in a comparatively low enrichment in the SML (EF_{SML} : 1.0-1.7, section 3.2.2).”

4. Figures. These could be improved in their graphical outputs (more consistent style - Avoid grey/unuseful lines - Use a heavier stroke to define bar/graph/axes contours – larger color legends – overall higher file resolution). Figure 6 might be a bit “poor” in information. This might be joined/enriched with one of the figures provided in the supplementary file (by transferring that in the main text). Or, just put Figure 6 in the supplementary file as well.

We thank the reviewer for his comment. We have improved the Figures as suggested, e.g. by adding larger color legends. Moreover, we removed the auxiliary line in Figure 4. In Figure 1-3 we would like to not completely omit the auxiliary lines to better understand the displayed concentrations when reading. In our experience, the graphics resolution of the Figures should not be a problem in the final upload of the figures. In addition, we have removed Figure 6 from the manuscript as suggested and now listed it as Figure S18 in the SI.

Additional changes performed by the authors

The previous citation of Triesch et al. (2020) was updated to Triesch et al. (2021) in the revised manuscript and supporting information.

References

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

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.

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.

Triesch, N., van Pinxteren, M., Engel, A., and Herrmann, H.: Concerted measurements of free amino acids at the Cabo Verde islands: high enrichments in submicron sea spray aerosol particles and cloud droplets, *Atmos. Chem. Phys.*, 21, 163-181, 10.5194/acp-21-163-2021, 2021.