

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

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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.

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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.

However, several major improvements on representing and discussing this dataset can be made. 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. 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 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 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 (K_{ow}) 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 K_{ow} . 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.

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

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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.

Specific comments

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?

Page3 Line 3 Consider quoting Becker et al. 2018 on TG's as storage compounds in phytoplankton.

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.

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 acids' i.e. if TG is present in SSA, it is not necessarily an indicator of freshly emittance. Also relevant on page 13, line 8.

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.

Page 4 Line 19 A map illustrating seawater sampling stations and CVAO location in-

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cluding distances and height of tower (!) would be helpful. Also, wind directions over the sampling period seem crucial to your study.

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?

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?

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 ($>0.7\mu\text{m}$). 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)?

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

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?

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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.

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.

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... .

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 $0.7\mu\text{m}$ (i.e. dissolved) contributed to submicron aerosols (PM1).

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)

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

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the reader under the impression that Wilson et al. 2015 have assessed lipids and concluded they contribute to the biogenic INP pool.

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.

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.

Technical comments

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.

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.

Line 24 Include \sum *to align style to the rest of the text.*

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 'aerosols'.

Line 32 Separate 'physico-chemical' to align style to the rest of the text.

Page 2 Keywords: consider to replace rather generic words such as 'seawater', 'concerted measurements', 'transfer' by e.g. 'sea surface microlayer', 'sea spray aerosols'

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to characterize the work.

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.

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)?

Page 7 Line 14 Exclude, since this is a repetition of line 12: ' . . .but considered a 'trend' to be valid. . . '.

Page 8 Line 8 Maybe introduce the PE/PG ratio along with LI and EF's in the experimental section.

Line 10 Replace 'afterwards' with 'towards the end'.

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 phytoplankton-dominated contributions to the lipid pool.'

Page 9 Line 18 Include the articles ' . . .release in the SML compared to the ULW. . . '.

Page 10 Line 32 Exclude 'the': ' . . .it is most likely that the bacteria have influenced. . . ' Check for consequential mistakes.

Page 11 Line 23 ' . . .OM compound groups. . . ' I think, this is redundant, use groups or compounds instead.

Line 28 Instead of 'regarded' use 'considered'.

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.

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Line 8 ‘...in the particulate fraction. In the particulate fraction...’ Try to rephrase due to repetition.

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.

Line 13 Use ‘physicochemical descriptors’ instead of ‘physical processes’.

Line 28 Caption of Fig. S11 states ‘dissolved’ lipids in aerosols particles, which is probably a mistake.

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.

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

Line 10 Replace ‘maritime samples’ by ‘of marine origin’.

Page 15 Line 9 This is misleading, better state ‘aerosol particles’ instead of ‘particle phase’.

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.’

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

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outside. Otherwise, the caption should state 'during the process of a bubble rising through the water column'...

Line 12 Rephrase 'contain... abilities'.

Page 18 Line 11-12 Replace 'by...' with 'of sea spray aerosols'.

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).

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.

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

Page 25 Line 1 Adjust the predicate 'Van' to the same format i.e. 'van'.

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

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

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