

Anonymous Referee #1 Received and published: 8 February 2020

The manuscript entitled “Marine organic matter in the remote environment of the Cape Verde Islands – An introduction and overview to the MarParCloud campaign” by van Pinxteren et al. describes the conditions and early results for a campaign designed to study the chemical interactions between the ocean and the marine boundary layer, including the formation of boundary layer clouds. It represents an interdisciplinary study of the sort that are increasingly seen in the field as the tight connections between ocean ecology, marine chemistry, atmospheric chemistry, and cloud formation are accepted by the community. The manuscript is generally well-written, but could benefit from more specific language in some places, as described in the comments below. In general, I am excited to see the results that come from this study in greater detail in the future, as some of the results provide new perspectives. The manuscript is recommended for publication in Atmospheric Chemistry and Physics upon consideration of the comments provided.

We thank the Reviewer for the evaluation and the constructive comments. Replies to the specific Referee’s comments are provided below in red and new parts included in the manuscript are marked in *italic*:

Introduction and Motivation: Overall this section could be more specific about the gaps in knowledge that exist, rather than vaguely saying that broad swaths of information are ‘elusive’, for example. We do know quite a lot about ocean surface chemistry as a result of the prior work of many investigators, including many who are a part of this project. Some additional specific comments on this particular subject are listed below

We agree and adopted the suggestions from the reviewer to sharpen the introduction and be more precise as shown in the following.

Lines 96-101 – the word ‘changing’ is used often, but it is not clear what is inducing the change, and from what state a ‘change’ is referenced. Hence the sentence is rather vague. Consider using more active or specific verbs to be more precise about how marine OM will influence each of the important areas listed.

We agree that “changing” was used too often and replaced this word accordingly. In addition, we explained the effects in some more detail. However, we want to underline that these are general important characteristics of the OM in the aerosols but not specifically investigated within this work. Therefore, we did not want to draw too much attention on this by adding detailed studies but rather mention these effects in general and give appropriate citations.

It now reads: “In particular, the role of marine organic matter (OM) with its sources and contribution to marine aerosol particles, is still *elusive*. For example, where this particle fraction might lead to a variety of effects such as *impacting health through the generation of reactive oxygen species, OM composition increasing or decreasing the absorption of solar radiation and therefore radiative properties, and impacting marine ecosystems via atmospheric deposition* (e.g. Abbatt, et al. 2019; Brooks and Thornton 2018; Burrows, et al. 2013; Gantt and Meskhidze 2013; Pagnone, et al. 2019; Patel and Rastogi, 2020).”

Lines 101-103 – the impact of primary aerosol production at the ocean surface has been explored more deeply in recent years (within the last 10 yrs or so) and, while we don’t know everything, I’d say that the ability for particles to act as CCN or INP is not ‘elusive’ –

indicating that we don't know much of anything. I would suggest that we are missing certain important pieces of information about CCN activity and also about what makes marine particles good INP (or not).

We agree and specified this part.

It now reads: "Furthermore, knowledge on the properties of marine organic aerosol particles and their ability to act as cloud condensation nuclei (CCN) or ice nucleating particle (INP) is *not fully understood. The fraction of marine CCN made up of sea spray aerosol is still debated and suggested to comprise about 30% on a global scale (excluding the high southern latitudes) (Quinn, et al. 2017) and important pieces of information about marine CCN are still missing (e.g. Bertram, et al. 2018). Ocean-derived INPs were suggested to play a dominating role in determining INP concentrations in near-surface-air over the remote areas such as the Southern Ocean, however their source strength in other oceanic regions as well as knowledge about which physicochemical properties determine the INP efficiency are still largely unknown (Burrows, et al. 2013; McCluskey, et al. 2018a; McCluskey, et al. 2018b).*"

Line 122-123 – "or through a more direct transfer of OM from ocean compartments to the marine particles". This is vague – other than bubble bursting aerosol generation, what mechanisms are being discussed here?

We agree that this expression was not straightforward and changed it to:

"The SML is involved in the generation of sea-spray (or primary) particles including their organic fraction by transfer of OM to rising bubbles before they burst out *to jet droplets and film droplets (de Leeuw, et al. 2011).*"

Line 133 – "occurs as particulate and chromophoric dissolved organic matter" Imposing such a view limits one's conception of a vast array of chemicals existing in the SML ,as is the case. There are fractions that are non-chromophoric and also not defined as particulate.

We agree that the phrasing was not comprehensive and rephrased it to:

Within the SML, OM is a mixture of different compounds *including polysaccharides, amino acids, proteins, lipids, and chromophoric dissolved organic matter (CDOM) that are either dissolved or particulate.*

It is great to see the bullet list of questions in this section. I have a few small comments/questions about them, hopefully in the search for greater clarity.

Line 174 – Perhaps this is vague on purpose, but "To what extent" by which measure? By absolute mass? By absolute number of particles containing organic matter? What about the particle mixing state? As a fraction of total ambient aerosol mass? The way this question is asked has a profound effect on the environmental effects that it will speak to.

We thank for these suggestions and addressing also the suggestions of referee #2, we included the specific metrics that we investigated here, and it now reads:

- *To what extent is seawater a source of OM to aerosol particles (regarding number, mass, chemical composition, CCN and INP concentration) and in cloud water?*

Line 176 – What are “OM groups”? Can a more specific wording be used here? Are you referring particular chemical functionality (fatty acids, carbohydrates, etc), operationally defined classes of material (DOM, POM, etc), or some other definition?

In agreement with the suggestions of referee #2 we changed the question to:

- *What are the important chemically-defined OM groups (proteins, lipids, carbohydrates - as sum parameters and on molecular level) in oceanic surface films, aerosol particles and cloud water and how are they linked?*

Line 189 – Are the authors asking whether the presence of marine OM in the surface ocean drives the concentration of CCN in the MBL? As written, the question does not presume the ‘direction’ of the relationship...presumably the implied direction is (in general terms): ‘Does the ocean influence the atmosphere?’ Being specific about this directionality allows this question to commute better with the final question about emission parameterizations.

We made the question more specific and took the reviewers’ suggestion and re-phrased this it to

- *Does the presence of marine OM in the surface ocean drive the concentration of CCN in the MBL?*

Experimental Line 304 – Were cloud droplets actively removed from aerosol particle measurements? If so, which measurements? The reader may be able to deduce this from the size cuts (e.g., PM_{2.5}, lower stages of cascade impactors) but it’s less clear for some of the more indiscriminate samplers.

For the aerosol samplers with defined size cut, the size of sampled particles/droplet is defined via the size cut. The size-resolved aerosol particles, sampled with the Berner impactor were conditioned via a 3 m heated tube. The PM₁₀ sampler without defined size cut it is possible that during cloud events, cloud droplets were sampled to some extent. We included this information in the SI part “Aerosol particle sampling and chemical analysis of inorganic ions, OC/EC and WSOC” and it reads now:

“To avoid condensation of atmospheric water on the surface of the aluminium foils, a conditioning unit was mounted between the impactor inlet and the sampling unit consisting of a 3 m tube. By heating the sampled air, high relative humidity of the ambient air was reduced to 75-80% before the collection of the aerosol particles. The temperature difference between the ambient air at the impactor inlet and the sampled air after the conditioning unit was below 9 K.”

In addition, in the experimental part we added “It needs to be pointed out that the aerosol particle samplers run continuously and aerosol particles were also sampled during cloud events. *The cloud droplets were efficiently removed due to the pre-conditioning of the aerosol particles sampled with the Berner impactor (more information in the SI) and due to the size cut the PM_i sampler. However, for aerosol particles sampled with the PM₁₀ sampler, small cloud droplets can be collected as well. In addition, the particles sampled with the low volume TSP sampler can be influenced by cloud droplets to some extent.*”

Conditions Section 4.2: In addition to primary producers, the state and dynamics of other portions of the microbial ecosystem have been shown to be key aspects that control how marine OM is incorporated into aerosol. Were any other biological metrics (heterotrophic bacteria, zooplankton, etc) assessed? If not, for clarity, please make a statement so that

other readers and interested parties will understand the extent of data availability. [***Note: the reviewer later saw the section on marine bacteria in the 'Measurements' section. Perhaps this means that section 4.2 should be presented as 'Measurements' as well. The comment above is clearly addressed by the authors in the manuscript, but I'll leave it here as a signal that a reader may be similarly confused about the order of presentation.]

We thank the referee for pointing this out. We understood that the order of presentation may lead to some confusion and have re-structured this part (following also the suggestions of reviewer #2). In the revised version, we mention the chl-a concentrations in section 4.2. and shifted the discussion of the pigment results to section 5.4.1. To underline, that pigments as well as bacteria were analysed we:

i) renamed section 4.2.1 to "Pigment and bacteria concentration in seawater"

ii) included this information in section 4.2.1 and it now reads "*Chl-a concentrations varied between $0.11 \mu\text{g L}^{-1}$ and $0.6 \mu\text{g L}^{-1}$, and are more thoroughly discussed together with the pigment composition in section 5.4.1. Moreover, as other but phytoplankton organisms can contribute to the OM pool, bacterial abundance was analysed in the SML and bulk water samples and these data are reported in section 5.7.3.*"

iii) concluded section 5.4.1. with: "First analyses show that the DOC concentrations were not directly linked to the increasing chl-a concentrations, however their relation to single pigments, to the microbial abundance, to the background dust concentrations and finally to wind speed and solar radiation will be further resolved to elucidate potential biological and meteorological controls on the concentration and enrichment of DOC."

Due to the inclusion of the pigment discussion in chapter 5.4.1. (that therefore became very long) we have added another subsection for the comparison of DOC data from the two sampling techniques: 5.4.2 DOC concentrations: manual glass plate vs. MarParCat sampling

Measurements and Selected Results Section 5.1.1: Does the small fraction of sea spray aerosol determined by size distribution measurements comport with the chemical measurements in Section 5.1.2? While this may be the subject of a future paper, a evidence that different aerosol measurements agree in a general sense is an important point to make in a paper of this type.

Thank you for this advice. We included more information on CCN in general in Chapter 5.1.1., and to address the comparison between physical and chemical aerosol measurements, we added information concerning the particle hygroscopicity in the following text:

"The hygroscopicity parameter kappa (κ) averaged 0.28, suggesting the presence of OM in the particles (see Gong et al., 2020a). Particle sizes for which κ was determined (i.e., the critical diameters determined during CCN analysis) were roughly 50 to 130 nm. The low value determined for κ is in line with the fact that sodium chloride from sea salt was below detection limit in the size segregated chemical analysis for particles in this size range (Figure 10), while insoluble EC and WSOM made up 30% of the main constituents at CVAO on average. A thorough statistical analysis of N_{CCN} and particle hygroscopicity concerning different aerosol types is reported in Gong, et al. (2020a)."

In chapter 5.1.2. we respectively added the following:

"...the chemical composition aligned well with the κ value from the hygroscopicity measurements (Gong, et al. 2020a)."

As well as:

“From the chemical composition no indications for anthropogenic influences was found as concentrations of elemental carbon and submicron potassium were low (see Tab. S5). However, according to the dust concentrations (Table 2) and the air mass origins (Fig. S1), as well as the PNSD (Gong et al. 2020a), the air masses during this period experienced low dust influences, that was however not visible from the main chemical constituents studied here and warrants more detailed chemical investigations (like size-resolved dust measurements), a distinction between mass-based and number-based analysis as well as detailed source investigations that are currently ongoing.”

We added in the conclusion:

“These findings underline that further in depth studies differentiating between submicron and supermicron particles as well as between aerosol number and aerosol mass are strongly required.”

Section 5.1.2: It is stated, somewhat simply, that the mass fraction of sodium and chloride in cloud water illustrates that supermicron particles were a dominant factor in cloud formation. However, mass-based chemical analysis, especially when not size resolved, is very easy to misinterpret. The key metric in cloud formation is the number concentration of droplets. The mass of supermicron particles increases as roughly the cube of the diameter, so particles that are 1 micron vs 100 nm contribute 1000x more mass to the cloud water! At the same time, particles larger than $d = 200$ nm activate at just about any relevant supersaturation relevant to this environment. The ‘control’ on the cloud drop number concentration, therefore, comes from the size range under 200 nm (down to, say 50 nm or so). Mass measurements will, therefore not tell us much about which particles actually control differences in cloud optical thickness, CDNC or droplet size – the climate relevant microphysical properties. Perhaps a clearer message concerning what we would like to learn from these measurements would help the description of the results, otherwise the results may be misinterpreted by the less well-initiated reader.

We thank the reviewer for these comments and fully agree that the mass vs. number discussion was not clearly addressed. We accordingly included the suggestions in Chapter 5.1.2 and it now reads:

“These compounds were also observed in the coarse fraction of the aerosol particles, suggesting that the coarse mode particles served as efficient CCN and were efficiently transferred to the cloud water. To emphasize, these chemical analyses are based on mass, but the control of the cloud droplet number concentration comes from CCN number concentrations, including all particles with sizes of roughly above 100 nm. As larger particles contribute more to the total mass, chemical bulk measurements give no information about a direct influence of sea spray particles on cloud droplet concentrations, but it can show that the chemical composition is consistent with an (expected) oceanic influence on cloud water.”

And at the end of the paragraph:

“In summary, cloud water chemical composition seemed to be dominated by coarse mode aerosol particle composition, and the presence of inorganic marine tracers (sodium, methane sulfonic acid) shows that material from the ocean is transported to the atmosphere where it can become immersed in cloud droplets. More detailed investigations on the chemical composition, including comparison of constituents from submicron aerosol particles and the SML with the cloud water composition are planned.”

Another aspect that suggests an influence of marine-derived particles on cloud processes is the finding of TEP (particles that are clearly of marine origin), in submicron aerosol particles. While these data are preliminary, the occurrence of these ocean-derived compounds in very small particles might be related to cloud processes that will be investigated in future studies.

We have mentioned this in chapter 5.7.2 and underlined it more clearly:

“Interestingly, a major part of TEP seems to be located in the sub-micron aerosol particles (Fig. 19). Sub-micron aerosol particles represent the longest living aerosol particle fraction and have a high probability to reach cloud level and *to contribute to cloud formation* and the occurrence of TEP in cloud water, which strongly underlines a possible vertical transport of these ocean-derived compounds.”

Finally, we included the particle mass/number issue in the conclusion as follows:

We clearly see a link between the ocean and the atmosphere as (i) the particles measured at the surface are well mixed within the marine boundary layer up to cloud level and (ii) ocean-derived compounds can be found in the (*submicron*) aerosol particles at mountain height and in the cloud water. The organic measurements will be implemented in a new source function for the oceanic emission of OM. From a perspective of particle number concentrations, the marine contributions to both CCN and INP are, however, rather limited. *These findings underline that further in depth studies differentiating between submicron and supermicron particles as well as between aerosol number and aerosol mass are strongly required.*

Line 618-619: The dominance of C16:0 and C18:0 fatty acids aligns well with the findings of Cochran et al. (Environ Sci Technol, 2016) from sea spray tank studies. Making this type of connection for the reader may help their interpretation of the rather quick overview of this topic in this paper.

Thank you for this recommendation. We have included this reference, and it now reads: “This result aligns well with the findings of Cochran, et al. (2016) from sea spray tank studies that connected the transfer of lipid-like compounds to their physicochemical properties such as solubility and surface activity.”

Figure 20: There is an error in the axis label for panel (a). The exponent is missing.

This is actually not an error. We explain in the figure caption that “*In panel a, please note the different power values between SML/ ULW (10^6 cells mL^{-1}) and cloud water samples (10^4 cells mL^{-1})*”.

Section 5.7.3: Based on using just a few measurements of total bacterial abundance without process-level context, it is challenging to see that the question about the involvement of bacteria in this ocean surface/marine boundary layer system will be adequately addressed. While general reporting of the numbers is provided and is another data point to compare with across the globe, the identity of the bacteria involved is going to be of utmost importance. Some bacteria that are in high abundance are not very productive (reduced carbon utilization), so bulk number concentrations may mask the active processes that control the overall behavior driven by bacteria as a whole.

Thank you for this comment. We absolutely agree about the limitations of bacterial abundance data to describe the direct influence of bacteria on air-sea interaction processes. During our campaign, we performed several incubation experiments with aerosol samples to determine the oxygen turnover of aerolised bacterial communities. Although we used samples with varying biomass collected (i.e. aerosol sampling times) and performed different incubation times (up to > 1 day) during these experiments, most rates obtained were close to/at the detection limit, hinting for a low (due to low abundance and/or high stress?), but yet to be determined activity pattern of aerosol communities. We do not present these data, as we want to avoid mis- or overinterpretation of these activity measurements. In line with the reviewers' suggestion, however, we are currently analysing the bacterial community structure by 16S rDNA amplicon sequencing from a subsequent study. These results will be used to study the selective transport of bacteria from the ocean, through the SML into the aerosol fraction. We envision similar approaches with our water and aerosol samples taken at the Cape Verde. This approach will certainly allow a better understanding of bacterial involvement in air-interaction processes, e.g. OM turnover. In order to actually assess the role of microorganism in air-sea interaction processes, a direct link between activity and identity would be needed in future studies, such as applying stable isotope probing in combination with molecular biology techniques (e.g. RNA-SIP). We address this point by including the following sentence in the revised manuscript in chapter 5.7.3 and added: "*Further ongoing investigations aim to determine the bacterial community composition by 16S sequencing approaches. The resulting comparison of water and aerosol particle samples will help to better understand the specificity of the respective communities and to gain insights into the metabolic potential of abundant bacterial taxa in aerosol particles.*"

Additional information: Data availability: We uploaded our data on World Data Centre PANGAEA (<https://www.pangaea.de/>) and included the respective DOIs in the revised manuscript.