Referee 2:

Comment on “High number concentrations of transparent exopolymer particles (TEP) in ambient aerosol particles and cloud water – A case study at the tropical Atlantic Ocean” by Manuela van Pinxteren et al.

1. The manuscripts deals with an interesting and quite new topic and presents some potentially important hypothesis and scientific questions (Are “secondary” TEPs more important than “primary” ones in the marine atmosphere? Is the marine aerosol TEP population connected in any way to the INP population?). The paper is well written and sufficiently clear. I recommend publications once the following (minor) issues are clarified.

   We thank the Reviewer for the evaluation and the constructive comments. We like the term “secondary” formation in relation to TEP that was introduced by the reviewer and included it in the manuscript (abstract and conclusion).

   Replies to the specific Referee’s comments are provided below in red and new parts included in the manuscript are marked in **green**. Line numbers refer to the revised (clean) version.

2. L40. The TEP concentrations reported do not represent supermicron aerosols. They correspond to particles larger than 4.5 microns (as correctly stated above), which represents a subset of the supermicron TEP population. Please modify for major accuracy.

   We agree with the reviewer that not the entire population of supermicron particles was covered in the analysis and corrected it accordingly. In the abstract, we included this aspect:

   Line 37-40:“Here, we report number concentrations of TEP with a diameter> 4.5 µm, **hence covering a part of the supermicron particle range**, in ambient aerosol and cloud water samples from the tropical Atlantic Ocean as well as in generated aerosol particles using a plunging waterfall tank that was filled with the ambient seawater.”

3. L42-43. I would suggest to add that the conversion was based on the observed cloud LWC.

   This was included and now reads:

Line 42-45: “Cloud water TEP concentrations were between $4x10^6$ and $9x10^6$ #TEP L^{-1} and, according to the measured cloud liquid water content, corresponding to equivalent air concentrations of 2 – $4x10^3$ #TEP m^{-3}.”

4. L43-46. The TEP concentration in the tank headspace has no atmospheric relevance. It results from the experimental parameters chosen to operate the tank and can be modified just by varying them (e.g. headspace flush flow, intensity of the plunging jets, and so on…). The only general and valuable information that can be extracted from sea-spray tanks regards the (size-dependent) relative chemical composition of the produced sea-spray particles. I am not against presenting the obtained TEP concentration in the tank, but it should not be reported in the abstract. More comments on this issue follow below.

   We agree and deleted the tank concentration from the abstract and only included the enrichment factors. In addition, we included more information on the tank aerosol as reported in detail below. Please see our responses to comments No. 6 and 10.

5. L81. Instead of “contain” maybe “have” would be more correct?

   We agree and changed the term accordingly.

6. L303-321. Please clarify where the seawater TEP concentration used to derive the EFs comes from. Reading further on, one understands that it derives from Engel et al. (2020). For major clarity, this information should be added here.

   We agree that the reference of the origin of the seawater TEP concentration is an important point. The seawater TEP data were achieved from Engel et al. (2020), which was stated in Table 1. We added the following text (that was originally put in the supporting information):

   Line 420-423: “However, the TEP number concentrations in the ocean surface water were obtained from an additional measurement campaign, taking place in the biologically productive Mauritanian Upwelling region in the year 2012, hence at another time and season (Tab. 1).”

7. L330-333. Please, provide a more quantitative comparison between the TEP concentration in aerosol and cloud water. If the authors think that this is not possible, they should re-consider the following sentence: “suggesting that the majority of the TEP particles are activated to cloud droplets when a cloud forms”. Judging by the plot in Figure 2 and comparing the cloud cases with the corresponding aerosol samples (which is

a very raw approach), I would say that less than 30% of TEPs are activated into a cloud. This is in contrast with the above statement. If the authors have data to support their statement, I would invite them to discuss them quantitatively. By the way, the highlighted statement seems to be contradicted by the authors themselves in Lines 543-545.#

We thank the reviewer for this comment. This was clearly a mistake and the term "the majority of the TEP are activated to cloud droplets" was not correct. Unfortunately, the cloud water sampling cases for TEP measurements were limited. However, as the reviewer suggested, we compared the #TEP concentrations in cloud water to the #TEP concentrations in the ambient aerosol particles when sampling times coincided, i.e. on 20.09., 28.09., and 04.10. 2017. For these dates, the cloud water #TEP concentrations made up between 10 and 34% (average: 20%) of the #TEP ambient aerosol concentrations. In addition, we related the average cloud water #TEP concentrations to the average #TEP concentrations in the ambient aerosol, which showed that the cloud water #TEP concentrations made up 24% of the #TEP ambient aerosol concentrations. Regarding these numbers, we conclude that the #TEP concentrations in cloud water were **about 20%** of the #TEP concentrations in the ambient aerosol (with a good agreement regarding the matching dates and the average values). This finding is now in line with the statement that the reviewer referred to in Line 543-545 "*the lower concentrations in cloud water (2 – 4x10^3 #TEP m^{-3}) compared to ambient aerosol particles (7x10^2 – 3x10^4 #TEP m^{-3}).*"

We revised the manuscript as follows:

Line 336-338: "Comparing the #TEP concentrations in cloud water to the ones in the ambient aerosol particles suggested that about 20% of the ambient TEP particles are activated to cloud droplets when a cloud forms."

8. L336-341. The concentration of TEP in the sea-spray aerosol generated by the tank is not an atmospheric relevant information; it depends only on the chamber design and settings. Therefore, there is no reason to compare the tank TEP concentration with that of atmospheric samples, either by performing a statistical test or not. The fact that the chamber produced lower concentrations of TEP with respect to what observed in ambient samples is irrelevant; the only informative data available from the tank are the EF data (because they are based on the relative chemical composition i.e., TEP/Na+), which the authors use correctly to infer about TEP sources later on in the text.

   We agree that tank studies cannot represent the ambient environment and on the caveats regarding the chamber design etc. However, tank studies are helpful for regarding the ocean-atmosphere transfer via (only) bubble bursting by eliminating aerosol processing and additional aerosol sources. As the reviewer suggested, we rather focus on the comparison of the enrichment factors of the tank experiments with the ambient studies. In addition, we added the information on the tank data; please see our detailed answers to comment No. 10.

9. L347. "besides for the…". Please double check English.

We rephrased this sentence to "In addition to…"

10. L429-433. [Par. 3.2]. Which seawater TEP concentration was used to calculate the EF for the sea-spray tank samples? Where TEP directly measured in the same seawater used for the bubbling experiments? Or did the authors use the average ETNA values from Engel et al. (2020)? Please provide this information here and in the Experimental Section. This may be quite a critical point. Considering how variable biochemical parameters may be in seawater, assuming that the average TEP concentration measured by Engel et al. (2020) is representative of the water samples used for the bubbling experiments is quite risky. The comparison of TEP EFs between atmospheric and tank samples is the only solid base that supports the (very interesting) hypothesis of important "secondary" TEP formation processes in the atmosphere. If the EF calculated for the tank samples are biased by assuming a seawater TEP concentration that does not truly represent the real situation in the tank, this base appears much less solid. In this case, I must invite the authors to add some caveat in the text, making it clear to the readers that the hypothesis, although very interesting, needs to be further demonstrated as doubts still persist at this stage given the uncertainties inherent to the EF calculations for tank samples.

The reviewer raised an important point here. As stated above, the seawater TEP data were obtained from Engel et al. 2020. We added an error discussion with regards to the oceanic TEP measurements and pointed out that the here reported EF_{atm} represent a lower limit. We want to underline that even though absolute numbers can vary (due to the potential biases resulting from the seawater data), the strong differences between the $EF_{aer.\ ambient}$ and $EF_{aer.\ tank}$ (Tab. S3) are evident, as they result from the same type of seawater.
In addition, in the revised version, we compared the total TEP number concentrations used in this study to previous measurements performed at the Cape Verde islands (south of São Vicente at 16°44.4'N, 25°09.4'W) and found a difference of a factor of 2. However, from the study of Engel et al. (2015) solely the total number concentrations are available. In the present work we exclusively used the number concentrations in the size range between 4 and 10 µm (to cover the same range as used for the atmospheric TEP size ranges) and therefore, we cannot use the values from Engel et al. 2015 for calculating the enrichment factor and kept the original values from the ETNA (Engel et al. 2020). We included this comparison in the revised version as shown below.

The following information was originally placed in the Supporting information, but as the reviewer rightly stated, they are important for classifying the results and were consequently added to the revised manuscript as follows:

Line 423-434: "Compared to other oceanic regions, the TEP values from the Mauritanian Upwelling region were at the higher end (Engel et al., 2020). The region around the CVAO is rather oligotrophic and Chlorophyll-a values during the MarParCloud campaign were relatively low with 0.1 up to 0.6 µg L^{-1} (van Pinxteren et al., 2020). As TEP production is often connected to phytoplankton activity, the TEP concentration at the CVAO might be lower compared to more productive regions (Robinson et al., 2019a). A previous study showed the total TEP number concentrations (covering TEP sizes between 1 and 200 µm) at the Cape Verde islands (south of São Vicente at 16°44.4'N, 25°09.4'W)

were by a factor of 2 lower that the data reported here, in detail $0.9x10^7$ L^{-1} (Engel et al., 2015) vs. $2x10^7$ L^{-1} (Tab. S5). Lower TEP concentrations would result in higher $EF_{atm.}$ (Equation 1) regarding the ambient as well as the tank measurements as the same type of seawater was used for the calculations. Hence, the here reported $EF_{atm.}$ represent lower limits."

In addition, we like to point out that the "sea spray generation" in the tank was successful, as the sodium concentrations in the tank aerosol particles were even higher than the ambient sodium concentrations, but TEP concentrations were comparably low in the tank aerosol. This is an important information that we did not make clear in the original manuscript. We added the following text:

Line 450-455: "It should be noted that the lower enrichment in the tank resulted from the lower TEP number concentrations in the generated aerosol particles, as the particulate sodium concentrations in the tank aerosol were even higher than in the ambient particles (Tab. S3). This suggests that, although an artificial tank study cannot represent the ambient environment, the generation of sea spray aerosol was in progress; however, TEP transfer seemed to be not pronounced."

Furthermore, we like to underline that the higher $EF_{aer.\ ambient}$ compared to EF tank is not the only solid base that supports the hypothesis of the "secondary" TEP formation processes. The finding that the $EF_{aer.\ ambient}$ are really high for particles with a diameter> 4.5 µm points to additional processes (besides bubble bursting), as such high enrichment for this aerosol particles size is uncommon and larger than previously reported in the literature, indicating additional (secondary) processes. This is summarized in the discussion Lines 458-471.

We think that with the applied changes we have addressed this issue more clearly and showed the limitations of the study. In the conclusion, we underlined the strong need for additional studies regarding this topic.

11. L479-484. "the high abundance and enrichment of #TEP in the ambient aerosol particles compared to literature data (Kuznetsova et al., 2005) and compared to the concentration and enrichment of the #TEP from the plunging waterfall tank performed here, suggests that additional TEP sources in the ambient atmosphere exist from which TEPs are added to their primary transfer by bubble bursting from the oceans". I stress again that the difference in concentration of TEP between atmospheric and tank samples is not supporting the existence of secondary TEP formation processes in the atmosphere. It is only the result of the tank properties. Only the difference in the TEP enrichment with respect to Na between tank and atmosphere supports this. Please, remove the references to "abundance" and "concentration" in the above sentence.

We thank the reviewer for this comment. To account for this, in the revised version we have prioritized our focus on the enrichment factors rather than on the (tank) concentrations (see our detailed answers to question No. 10). The major reasons are the

high enrichment of ambient TEP compared to tank TEP (while there was strong evidence that sea spray generation was in progress) as well as the generally high TEP ambient enrichment compared to literature studies. We underlined that additional studies are strongly needed.

As suggested by the reviewer we deleted the reference from this sentence.

12. Par3.3.2. This paper focuses on atmospheric particles larger than 4.5 µm, which are characterized by fairly short atmospheric residence times. It may be worth discussing if the atmospheric lifetime of these particles is consistent with the timescale of TEP (biotic and abiotic) formation reactions. Data should be available at least for the seawater compartment if not for the atmosphere.

We picked up this interesting thought and in the revised version, we included references that investigated abiotic and biotic transformation of TEP and similar substances (EPS). We compared them with the lifetime of supermicron aerosol particles (where the here investigated TEP are part of). We found that the transformation rates are within the lifetime of aerosol particles and therefore concluded that these processes might be relevant for TEP formation in the atmosphere, although care must be taken when transferring ocean processes to atmospheric processes and further studies are required on this topic.

We included the following parts for the abiotic and biotic processing:

Line 535-551: “In the ocean, the dissolved polysaccharides are known TEP precursors (Passow, 2002) and Wurl et al. (2011) determined abiotic TEP formation rates from dissolved polysaccharide concentration in various oceans. The rates were on average 7.9 ± 5.0 µmol C L^{-1} d^{-1} and therefore significant, considering that the average TEP concentration was 18.1 ± 15.9 µmol C L^{-1} and the average dissolved polysaccharide concentration was 12.2 ± 3.8 µmol C L^{-1} in the surface seawater (Wurl et al., 2011). Robinson et al. (2019b) showed that rising bubbles can lead to an enhanced TEP formation already after some minutes. The lifetime of supermicron aerosol particles, to which the TEP particles studied here belong, are between hours and days, for example, Madry et al. (2011) calculated an average lifetime of supermicron sea salt particles of 50 hours. Hence, abiotic TEP formation processes lie within the lifetime of supermicron aerosol particles and we suggest that spontaneous TEP formation from the (high) abundant dissolved polysaccharides likely contributed to the high TEP concentrations observed in the ambient atmosphere in the present study. However, it needs to be considered that the abiotic TEP formation processes as described by Wurl et al. (2011) and Robinson et al. (2019b) were relevant for the oceanic environment and might not directly translated to atmospheric processes. Further studies are required on this topic.”

and

Line 615-619: “Regarding time scales of biotic processing, Matulova et al. (2014) showed that the Bacillus sp. 3B6, isolated from cloud water, was able to bio-transform saccharides that are present in the atmosphere. The saccharides formed exopolymer substances (EPS), of which TEP are a subgroup. The formation of EPS was revealed after 48 h of incubation and therefore within the lifetime of supermicron aerosol particles (Madry et al., 2011).”

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