Comment to Reviewer 1

Thank you for your comments, as a native english speaker I tried to pay particular attention to my linguistic choices, however using the specific points you have given I will attempt to re-word certain sections and sentences which may be unclear for an international audience. Regarding the materials and methods sections, we are uncertain as to which aspects were unclear for you, we have described the study areas, the sampling techniques, all analyses and statistical procedures. Additionally, the second reviewer found it precise and fluent. I would like to also point out that we did find consistent features of TEP in the SML. Firstly, for all regions there was a general enrichment of TEP in the SML which is in line with earlier studies. Secondly, within and between regions, TEP was found to be enriched in the oligotrophic waters of Cape Verde even when abundance was low and TEP enrichment features in the Baltic Sea were linked to biological activity. All of these features are described in section 3.2 in the manuscript.

1. Reviewer Comment: L9: In my opinion and the authors described, TEP is not a single substance, it is a generic name; so anyone cannot say they were major or not. We cannot measure carbon of TEP or weight of TEP exactly, in particular in the field experiments.
   Author Response: L9- It's unclear what is meant by "TEP is a generic name and thus can't be described as a major source for OM and carbon transport." TEP is a generic name for a substance which can and has been measured, as well the carbon content of TEP has been measured. The following review article may help (Mari et al. 2017).

2. Reviewer Comment: L13 "study of TEP enrichments". Before here, the authors did not describe "enrichment", and thus very confusing. Please describe what the authors did before describing the results.
   Author Response: L13- We were not talking about Enrichment Factors which would indeed need to first be explained. We are simply stating enrichment, which is a common word so does not need the definition explained.

3. Reviewer Comment: L17: I cannot understand the sentence.
   Author Response: L17- Since comments from other reviewers found the language to be clear, without further explanation of why the sentence is unclear, it is difficult to re-write it in a more comprehensible way.

4. Reviewer Comment: L18: I cannot understand what the authors want to describe. A homogenous and heterogeneous profile of TEP concentration was observed in the same profile?
   Author Response: L17-The sentence has been changed to "For two regions with a total of 20 depth profiles, a maximum variance of TEP concentration of 1.39×10^6 µg XG eq2 L-2 between depths and a minimum variance of 6×10^2 µg XG eq2 L-2 was found. Showing that the vertical distribution of TEP was both heterogeneous and homogeneous at times."

   L18– The following was added to line 17 to show total number of depth profiles taken and show that heterogenous and homogenous profiles were seen throughout these 20 total profiles. "For two regions with a total of 20 depth profiles."

5. Reviewer Comment: L20: Results. . .has?
   Author Response: L20- Changed to "have"

6. Reviewer Comment: L21-Why the authors can conclude the message.

Author Response: L21- Due to the relationship of phytoplankton as the main source for TEP production and enrichment, when phytoplankton biomass (chl a used as the common proxy) is low, it means that the enrichment of TEP in the SML must come from another source, while bacteria are also known to produce TEP within the SML and could potentially be a source, bacterial cell counts were not enriched in the SML compared to the ULW during this campaign and so with neither phytoplankton or bacteria as a source, enrichment of TEP in the SML most likely comes from abiotic sources, as there are many abiotic factors which are also known to increase upward transport of TEP and self aggregation within the SML. Please refer to lines 303-317 in the manuscript.

7. Reviewer Comment: L30: EPS was used only at once in the text.
   Author Response: L30- EPS has been changed to be fully spelled out.

8. Reviewer Comment: L51: Is the investigation the purpose of this study? The investigation is the way to accomplish a purpose.

   Author Response: L51- The following paragraph has been changed to clear up any confusion

"The purpose of this study was to understand if there are single drivers of TEP verticle distrubition in the upper 2 meters and if these drivers are consistant between regions. To accomplish this, we investigated the abundance and enrichment of TEP between the SML and ULW, in various regions of the ocean and its relation to biochemical factors. A further aim was to determine if 1 meter depth is a good reference for TEP and other parameters, and how important depth is in sampling within the top 2 meters. We present data from three field campaigns which show the accumulation of TEP in the upper 2 meters and how it relates to water column stratification, primary production and sea surface conditions"

9. Reviewer Comment: 2.1. Please show maps for better understanding of the observations.

   Author Response: 2.1- A map of the study areas has been added.

10. Reviewer Comment: 2.2 I cannot understand how many days and how many stations did the authors were observed. What "total" indicate? The sampling days or stations numbers whose location was different?

    Author Response: 2.2- There are 19 days between September 18th and October 6th. Of those 19 days, samples were collected on 12 days, on 7 days samples were not collected due to bad weather as noted in the sentence "weather permitting".

11. Reviewer Comment: L80- The citation style was wrong. I think the authors use the reference manager such as Endnote, but please review before submission. Same mistakes were observed in several parts (L108, L127, L129, L277, L292).

    Author Response: L80, L108, L127, L277, L292- citation format fixed.

12. Reviewer Comment: L84- To collect 20L of SML water, 2*10ˆ3 m-2 are necessary when assumed the SML is 100 μm deep. Is it possible and during the sampling, how long did the sampling do? Does it mean that the waters keep their characters during the samplings?

    Author Response: L84- Because the Catamaran has 6 glass discs all simultaneoulsy collecting the SML and a rotation speed of 7rpm, it has a collection rate of approximately 20L h^{-1}. (Ribas-Ribas et al. 2017; Shinki et al. 2012). The catamaran will easily cover an area of 20m x 100m within the one hour of collection. Furthermore, since these are an average of what was collected over an

hour, it boasts a better representation than for example what would be collected over only 10 minutes.

13. Reviewer Comment: L87- When the authors measured the temperature profiles in this scale, why they didn't discuss the stratification of physical difference between SML and ULW.

    Author Response: L87- Please note, tempurature was only measured for the SML and ULW at 1 m depth. Thus stratification could not be discussed for the 0-2m depths. Additionally, no relation was found between TEP concentration or EF and tempurature differences between SML and ULW at 1m.

14. Reviewer Comment: L95- Why the authors judge as near "enough"?

    Author Response: L95- if a different body of water was sampled then ULW at 1m depth would consitantly show different results from the other ULW depths, since it was taken from the catamaran with the SML. This was the purpose of collecting 1 m depth ULW from the catamaran instead of taking it from the vertical sampler.

15. Reviewer Comment: L99- Before measuring the POC, did the authors do the acid treatment? The authors described they use acid-washed GF/F but not mentioned after samplings.

    Author Response: L99- We did not treat POC samples with acid, as PIC was assumed to be negligable as in no indication of diatom booms.

16. Reviewer Comment: L104- Here, the authors described they measured nitrate and phosphate as nutrients, but silicate concentration was reported in the manuscript. If they used GF/F-filtered seawater for the silicate analysis, how did they avoid the contamination of silicate during the filtering processes?
    Author Response: L104- Since we don't discuss silicate data, we have removed it from the manuscript.

17. Reviewer Comment: L106- Chlorophyll is not a proper noun.

    Author Response: L106- capitalization removed.

18. Reviewer Comment: L120- How many replicates did the authors were collected? In other words, how did they calculate the error bars of TEP concentrations?

    Author Response: L120- TEP samples are taken in triplicates. Sentence changed to "TEP was measured by filtering seawater, in triplicates, onto 0.2 µm...."

19. Reviewer Comment: L139- "Anova was significant"? Rewrite such as "the difference was significant in ANOVA"

    Author Response: L139- sentence changed to "when the difference was significant in ANOVA"

20. Reviewer Comment: L141- What is "subsurface bulk water"? This is very important because the authors discussed on enrichment factors.

    Author Response: L141- sentence changed to "corresponding ULW taken at 1 m depth."

21. Reviewer Comment: L144- ug may be µg

    Author Response: L144- u changed to µ throughout document.

22. Reviewer Comment: L147- Table 1 and 2 should be supplemental materials. Please show them the contour figure and bar plot, respectively.

    Author Response: L147- sentence changed to "General characteristics of parameters and enrichment for all three campaigns is shown in Fig 2 and Fig 3."

23. Reviewer Comment: Table 1- At L90, the parameters were averaged for 2 hours, but in Table 1, PAR was averaged for 24 hours? Which is correct?

    Author Response: Table 1- Averages for 2 hours and 24 hours are given in table 1

24. Reviewer Comment: L155- Please show the location of the fjord.

    Author Response: L155- It will be shown in the map suggested in previous comment.

25. Reviewer Comment: L162- Strictly, the authors defined TEP as transparent exopolymer particle"s", and so they cannot use them as the adverb.

    Author Response: L162- TEP is not used as an adverb, it is not used modify or qualify anything.

26. Reviewer Comment: L162- As same as Chlorophyll (L106), phosphate and silicate are not proper nouns.

    Author Response: L162- Capitalizations removed.

27. Reviewer Comment: L166- I cannot find the aim of this sentence. Was The Baltic sea observation the time-series observations? If so, please describe as the date.

    Author Response: L166- sentence has been re-written as " TEP enrichment factors were ≥1 for the first half of the cruise (St. 3-5) and <1 for the second half of the cruise (St. 8-12)."

28. Reviewer Comment: L176- "Highest" should be "higher"

    Author Response: L176- "Higher" is used to compare two things, for describing 3 or more "highest" should be used.

29. Reviewer Comment: L188- Enrichment"s"?

    Author Response: L188- In this case "enrichment" not "enrichments" because the words "and" and "both" were used, thus it distinguishes TEP and Chl a as two separate things.

    Reviewer Comment: L192- In section 2, the observations Cape Verde is described at the top, but here, at the bottom.

    Author Response: L192- Section 2.2 "Sampling: Cape Verde" was moved to after section 2.3, for the sake of fluidity.

30. Reviewer Comment: L199- "the" samples?

    Author Response: L199- "the samples" or "samples" are both technically correct, this is more a matter of style.

31. Reviewer Comment: L199- "the lowest concentration" is the area mean value or a value from a sample?

    Author Response: L199- It is a regional area mean value

32. Reviewer Comment: L200- Phosphate level should be phosphate concentration

    Author Response: L200- sentence change to "phosphate concentrations"

33. Reviewer Comment: L210- The authors should refer to Fig. 1

    Author Response: L210- Sentence changed to "Figure 2 shows that…"

34. Reviewer Comment: L221- Vertical distributions should be shown as figures.

    Author Response: L221- Sample figures (see figures 3 and 4) are shown to reduce unnecessary clutter of images, while the table is used to present all data.

35. Reviewer Comment: L224- In my opinion, the homogeneity and heterogeneity should be shown with CV. I cannot understand why the authors select variance.

    Author Response: L224- You are correct CV would be more appropriate for the mathematical comparison of homogeneity, however we found that the resulting units it produced for TEP might be confusing to read and since we are only using CV or Variance to show comparable homogeneity we chose to stay with variance.

    Reviewer Comment L230- Please divide the results and discussion. These sentences are the discussion.

    Author Response: L230- Paragraph was moved to the discussion.

"This is possibly due to the short depth scale or the region, Yamada et al. 2017 found a positive correlation in the Arctic Ocean but this was on a much larger depth scale (0-4000 meteres) and no correlation was found in the Pacific Ocean. Additionally, any *in situ* production of TEP or consumption by prokaryotes was likely masked by the large increase in phytoplankton abundance during the second half of the cruise."

    Reviewer Comment: L240- When the authors want to use the TKE, please briefly describe in the Materials and Methods section.

    Author Response: L240- Sentence changed to "Additionally no correlation was found between TEP and turbulent kinectec energy (TKE), measured with an acoustic Doppler velocimeter (data not shown)."

36. Reviewer Comment: L241- I cannot understand the logic after "Thus".

    Author Response: L241- Sentence changed to "TEP profiles shown in Figure 4 were chosen based on min, median and max variance and presented as such, since no correlation could be found to any other parameter." Unlike for the Baltic Sea which had a clear trend of phytoplankton biomass increase between the first and second half of that cruise.

37. Reviewer Comment: L250- Cite the references.

    Author Response: L250- Mari et al. 2017 reference added.

38. Reviewer Comment: L252- "The" previous?

    Author Response: L252- In this case "Previous" not "The previous"

39. Reviewer Comment: L253- has -> have

Author Response: L253- have is correct and already used

40. Reviewer Comment: L262- Did the authors show biochemical processes? What processes did the authors show?

    Author Response: L262- the biochemcial processes are the reasons for the results shown, not the results themselves.

41. Reviewer Comment: L260- Which paper assumes the homogenous environments including the SML? I know some paper assumes that chemical character is homogenous in the mixed layer, but they usually did not consider the SML.

    Author Response: L260- The papers mentioned in line 253 which this sentence refers to do not measure the SML separately, they measure from 3-5 meter and below, and disregard the near surface as a homogenously mixed area of bulk water, hence our argument that not only does the SML need to be included but profiles to establish the homogeneity of the ULW are needed.

42. Reviewer Comment: L264- relation is not wrong, but it is usually focused on the person to person. I think the relationship is better than relation.

    Author Response: L264- relation is also used for things (ex: where is the store in relation to our office?) and relation tends to imply not only that two things are connected but that the effect one thing has on the other while relationship implies more the status of wether two things are connected or not.

43. Reviewer Comment: L265- I cannot understand this sentence.

    Author Response: L265- It means that the SD was higher within each region than between regions.

44. Reviewer Comment: L271- Same with L265.

    Author Response: L271- Beginning of sentence changedto "This suggests…."

45. Reviewer Comment: L274- Why EF was related to the concentration? I cannot see the logic.

    Author Response: L274- Similar reason as comment #7

46. Reviewer Comment: L287- Sun et al 2017 should put the end of the sentence.

    Author Response: L287- Reference moved to the end of the sentence.

47. Reviewer Comment: L291- Same with L274

    Author Response: L291- Similar reason as comment #7

48. Reviewer Comment: L291-302- What is the theme of discussion here?

    Author Response: L291-302- The theme is to discuss how Chl a and TEP concentrations are related between the regions, since many studies find TEP concentration and enrichment to be higher in areas with high phytoplankton biomass (Chl a) and productivity (primary production).

49. Reviewer Comment: L303- Again, I cannot find any logics between concentration and EF

    Author Response: L303- Please see comment #7 and further details can be found in Wurl et al. 2011b as reffered to in our manuscript.

50. Reviewer Comment: L334- "changed daily" The observations were time-series observations? The authors did repeated observation? If not so, why thay can discuss the daily variation?

    Author Response: L334- Sentence changed to "changed from station to station."

51. Reviewer Comment: L347-351- I cannot understand the English here. This sentence was too long.

    Author Response: L347-351- comma changed to period ". Suggesting that…"

52. Reviewer Comment: L352- What indicate they? Biological sources or chemical characteristics?

    Author Response: L352- It refers to biological sources and is grammatically correct.

53. Reviewer Comment: 4.4 The authors did not investigate the flux. I think that the authors cannot judge that TEP in the SML is produced at the SML, or transported from the ULW.

    Author Response: 4.4- That is correct that we did not measure fluxes, but this discussion is based on the vertical distribution of TEP, here we want to highlight that TEP can have an upward flux as a particle due to it's boyancy. That is helpful in order to understand the observed vertical distributions of TEP in the upper meters of the oceans.

54. Reviewer Comment: L367- These are not a new idea of the authors in the present study

    Author Response: L367- We do not claim any new ideas in line 367 and properly cited references to highlight phytoplankton as a main source of TEP.

55. Reviewer Comment: L372- Again, the authors cannot estimate the flux.

    Author Response: L372- replaced "conclude" with "suggest"

56. Reviewer Comment: Table4- Is this correct? For example, in the column of Baltic vs Norweigan, TEP man diffs were only -0.04 and SE was 0.31; however, their difference was significant. While the Chl a concentration was different -0.3, and its SE value was limited to 0.15, however, its difference was "not" significant. Please re-check.

    Author Response: Table 4- Thank you for catching this, indeed the wrong numbers were given, all data was checked again and fixed.

Citations Mentioned

57. Mari, X., U. Passow, C. Migon, A. B. Burd, and L. Legendre. 2017. Transparent exopolymer particles: Effects on carbon cycling in the ocean. Progress in Oceanography **151:** 13-37.

58. Ribas-Ribas, M., N. I. Hamizah Mustaffa, J. Rahlff, C. Stolle, and O. Wurl. 2017. Sea Surface Scanner (S3): A Catamaran for High-Resolution Measurements of Biogeochemical Properties of the Sea Surface Microlayer. Journal of Atmospheric and Oceanic Technology **34:** 1433-1448.

59. Shinki, M., M. Wendeberg, S. Vagle, J. T. Cullen, and D. K. Hore. 2012. Characterization of adsorbed microlayer thickness on an oceanic glass plate sampler. Limnology and Oceanography: Methods **10:** 728-735.

60. Yamada, Y. and others 2017. Transparent exopolymer particles (TEP) in the deep ocean: full-depth distribution patterns and contribution to the organic carbon pool. Marine Ecology Progress Series **583:** 81-93.

Comment to Reviewer 2

Thank you for your comments, we found all your suggestions to be helpful in improving the manuscript.

1. Reviewer Comment: L16- 'a novel small-scale vertical sampler' : In my opinion it would be a valuable addon to provide a photograph or sketch of the HSV (e.g. in the supplementary material).
   Author Response: L16- Image of HSV has been added to supplementary figures (S3)

2. Reviewer Comment: -L231-232- 'total cell numbers (TCN) and small autotroph profiles': Please provide some more information on the flow cytometry part in the material and methods section. How do you define small autotrophs?
   Author Response: L231-232- The following details have been added:

   "**The total cell numbers (TCN) of prokaryotic and small autotrophic cells were determined by flow cytometry following a modified protocol from Marie et al. (2000).** For determination of cell numbers, water samples were fixed with glutaraldehyde (1% final concentration), incubated at room temperature for 1 h, and stored at $-18°C$ until further analysis. Prokaryotic cells were stained with SYBR Green I (2.5 mM final concentration, Molecular Probes, Schwerte, Germany) for 30min in the dark. Samples were measured on a flow cytometer (C6 FlowCytometer, BD Bioscience, fluorescence accuracy of FITC <75; PE <50), and cells were counted according to side-scattered light and emitted green fluorescence. We used 1.0 µm beads (Fluoresbrite Multifluorescent, Polysciences) as internal reference to monitor the performance of the device. **Their cell counts include heterotrophic and photoautotrophic prokaryotes. Pico and nano-autotrophic cells were counted after addition of red fluorescent latex beads (Polysciences, Eppelheim, Germany) and were detected by their signature in a plot of red (FL3) vs. orange (FL2) fluorescence, and red fluorescence vs. side scatter (SSC). We did not further differentiate between different groups of prokaryotic and eukaryotic autotrophs.**"

3. Reviewer Comment: -L253- typo/grammar –> replace 'has been found'
   Author Response: L253: sentence has been changed to "…TEP has been found…"

4. Reviewer Comment: -L259-261: 'this study is the first to. . .' : No it is not. Consider e.g. Zäncker, Cunliff & Engel 2018 Front.Microbiol. Please change this part and consider to incorporate according reference.
   Author Response: L259-261: We refer here not to the enrichment in comparison to a single reference depth but to the vertical distribution in the upper 2 meters, i.e. TEP concentrations at 7 depths. Zancker et al. 2018 measured TEP in the SML relative to 20cm depth, thus reporting typical enrichment similar to earlier studies and not vertical gradients. To our best knowledge, our manuscript reports for the first time vertical gradients of TEP near the ocean's surface.

5. Reviewer Comment: -L275: Do you have any additional data to support that the high enrichment factors in the Cape Verde region are not an artifact due to a different sampling strategy in comparison to the other locations? Did you take for instance any technical replicates using the glass plate technique of Cunliffe and Wurl 2014/Harvey and Burzell 1982 and/or syringe samples on the Norwegian and Baltic Sea cruises?

<u>Author Response:</u> L275: In this study, we did not further compare sampler with rotating glass disks and the glass plate. However, in the study by Shinki et al. (2012) such comparison were made using a similar catamaran with rotating glass disks, and the collected thickness between catamaran and plate samples were comparable. We added the following text to line 277:

"While manual sampling techniques were employed in Cape Verde in comparison to rotating glass disc samples in the other campaigns, earlier comparative studies by Shinki et al. (2012) found both methods to collect similar SML thickness and associated biochemical parameters. Since our catamaran was modelled after Shinki et al. (2012) we are therefore able to compare the results from both versions of the glass plate method."

Shinki, M., Wendeberg, M., Vagle, S., Cullen, J. T., & Hore, D. K. (2012). Characterization of adsorbed microlayer thickness on an oceanic glass plate sampler. Limnology and Oceanography: Methods, 10(10), 728-735.

6. <u>Reviewer Comment:</u> L306- Please provide some more information on the tank experiment. For instance, you could give a short outline in the supplementary material.
<u>Author Response:</u> L306- The following has been added

"The tank was made of 10-mm polyvinyl chloride (PVC) plates in a size of 120 cm length × 110 cm width × 100 cm height. The tank had a volume of 1400 L with a 500 L aerosol chamber on top. Materials in contact with seawater were made from Teflon, including liners for the wall using Teflon bags."

7. <u>Reviewer Comment:</u> Figures- The numbering of the figures is not corresponding to the order in which they occur in the text. For example Fig.1 is appearing very late in the text. Please adjust the order of all figures.
<u>Author Response:</u> Figures- Figure order has been adjusted and now includes the new map as figure 1.

Depth is Relative: The Importance of Depth on TEP in the Near Surface Environment

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Abstract. Transparent exopolymer particles (TEP) are a major source for both organic matter (OM) and carbon transfer in the ocean and into the atmosphere. Consequently, understanding the vertical distribution of TEP and the processes which impact its movement are important in understanding the OM and carbon pools on a larger scale. Additionally, most studies looking at the vertical profile of TEP have focused on large depth scales from 5 to 1000s meters and have omitted the near surface environment. Results from a study of TEP enrichment in the sea surface microlayer (SML) in different regions (tropical, temperate) has shown that while there is a correlation between ~~TEP abundance~~TEP concentration and primary production (PP) on larger or seasonal scales, such relationships break down on shorter time and spatial scales. Using a novel small-scale vertical sampler, the vertical distribution of TEP within the uppermost 2 meters was investigated. For two regions with a total of 20 depth profiles, ~~With~~ a maximum variance of TEP concentration~~abundance~~ of ~~between depths (~~1.39×10^6 µg XG eq^2 L^{-2} between depths~~)~~ and a minimum variance of ~~(~~6×10^2 µg XG eq^2 L^{-2} was found. Showing that~~)~~ the vertical distribution of TEP was ~~found to be~~ both heterogeneous and homogeneous at times. Results from the enrichment of TEP and Chl *a* between different regions ha~~ve~~s shown TEP enrichment to be greater in oligotrophic waters, when both Chl *a* and ~~TEP abundance~~TEP concentration was low, suggesting the importance of abiotic sources for the enrichment of TEP in the SML. However, considering multiple additional parameters that were sampled, it is clear that no single parameter could be used as a proxy for TEP heterogeneity, other probable biochemical drivers of TEP transport are discussed.

1 Introduction

The sea surface microlayer (SML), a thin layer 10µm-1mm thick, lays at the top of the ocean. It has distinct chemical, biological and physical properties (Cunliffe et al., 2013; Sieburth, 1983; Wurl et al., 2016) setting it apart from underlaying water (ULW). As the boundary layer between the ocean and atmosphere, it significantly controls the flux of such important parameters as CO_2 and organic matter (OM)(Engel et al., 2017; Wurl et al., 2016).

The SML is further characterized by its gelatinous nature (Sieburth 1983), being thoroughly permeated with extracellular polymeric substances ~~(EPS)~~, the largest faction of which is transparent exopolymer particles (TEP)(Cunliffe and Murrell, 2009; Wurl and Holmes, 2008). These gel particles can form in two ways; abiotically via the collision of colloidal material by physical forces, or biotically via the breakdown and secretion of precursor material from organisms, with phytoplankton being the largest source (Passow, 2002a). These gels are "sticky" by nature and thus can aggregate to themselves but also to other solid particles, making them a large source for the transport of OM in the ocean (Passow, 2002b). Unattached, TEP have a low density and are positively buoyant (Azetsu-Scott and Passow, 2004), so that unless enough highly dense matter (e.g. mineral, phytoplankton cells, fecal pellets) is attached or a dense enough aggregate is formed to cause sinking, these aggregates will rise to the surface and help to form the SML (Wurl and Holmes, 2008). Meanwhile, when these OM rich aggregates sink, they help to feed both the chemical and biological pumps (Engel, 2004; Mari et al., 2017). Due to the role of TEP in OM and carbon fluxes both within the ocean and into the atmosphere, it is important to understand what parameters can enhance TEP distribution and enrichment in the ocean. Additionally, because TEP are a part of a complex biochemical process, cross regional examination of TEP can help to understand underlying characteristics of TEP.

There have been multiple studies which have looked at the vertical distribution of TEP in the ocean to understand the rising and sinking of these aggregates and their relation to other parameters (Busch et al., 2017; Cisternas-Novoa

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et al., 2015; Kodama et al., 2014; Ortega-Retuerta et al., 2017; Wurl et al., 2011a; Yamada et al., 2017). However, until recently, most studies have focused on large scale vertical distributions between 5-1000's meters and always considered the top 5-10 meters of the ocean as homogenous. As the importance of the SML in air-sea exchanges has grown, more studies have begun to investigate the relationship and enrichment of the SML in comparison with
50   under laying water (ULW). To date, there is no consistent measuring depth for what is termed (ULW), it is dependent solely on the individual setup of the researchers but is often operationally defined at 1 meter.

The purpose of this study was to understand if there are single drivers of TEP vertical distribution in the upper 2 meters and if these drivers are consistent between regions. To accomplish this, we investigated the abundance and enrichment of TEP between the SML and ULW, in various regions of the ocean and its relation to biochemical
55   factors. A further aim was to determine if 1 meter depth is a good reference for TEP and other parameters, and how important depth is in sampling within the top 2 meters. We present data from three field campaigns which show the accumulation of TEP in the upper 2 meters and how it relates to water column stratification, primary production and sea surface conditions~~The purpose of this study was to investigate the abundance and enrichment of TEP between the SML and ULW, in various regions of the ocean and its relation to biochemical factors. A further aim was to~~
60   ~~determine if 1 meter depth is a good reference for TEP and other parameters, and how important depth is in sampling within the top 2 meters. We present data from three field campaigns which show the accumulation of TEP in the upper 2 meters and how it relates to water column stratification, primary production and sea surface conditions.~~

65   **2 Methods**

2.1 Study areas:

Water samples were collected as part of the MarParCloud project Cape Verde campaign in the nearshore water in Cao Vicente, on the research cruise HE491 in the North/Norwegian Sea and fjords and from the research cruise EMB184 in the Baltic sea (Fig. 1). The sampling areas represent uniquely different regions; Cao Vicente is
70   oligotrophic tropical water with large influences from Saharan dust deposition, the Norwegian fjords and Baltic Sea are both temperate climates, but the inner and outer Norwegian fjord systems have large interaction from North Atlantic water while the Baltic Sea is semi-enclosed with larger anthropological interaction and little interaction with North Atlantic water.

~~**2.2 Sampling: Cape Verde**~~

75   ~~Samples were taken once a day, weather permitting, between September 18th and October 6th, 2016 within the same nearshore water (~1km) with a total of 12 stations sampled. SML and ULW samples were collected from fisher boats in the nearshore waters. SML samples were collected using the glass plate technique (Cunliffe and Wurl, 2014; Harvey and Burzell, 1972) and ULW was collected from 1 meter depth using a large syringe. Wind speed was recorded using an anemometer placed at the nearby Cape Verde Atmospheric Observatory (CVOA) station. A~~
80   ~~handheld Global Position System (Garmin etrex) was used to track fisher boat movement during sampling and for coordinates of each sampling station.~~

2.2~~3~~ Sampling: Norwegian (HE498) and Baltic Sea (EMB184) r~~R~~esearch cruises

North/Norwegian Sea and fjord samples were collected between July 8 to 25th, 2017 aboard the R/V Heinke. Samples were collected once per day, weather permitting, from each station with a total of 13 stations spanning
85   inner fjord, outer fjord and open ocean areas. Samples were collected from both the North Sea and the Norwegian Sea, but for the purpose of clarity will from here on be called the Norwegian Sea. Baltic Sea samples were collected between May 30th and June 10th, 2018 aboard the R/V Elisabeth Mann Borgese with a total of 8 stations used. SML and ULW samples were collected using the radio-controlled Sea Surface Scanner S^3 as described in Ribas-Ribas et al. (2017), ~~(Ribas-Ribas et al., 2017),~~ which has six rotating glass discs partially immersed in the water to sample
90   the SML by its surface tension. ULW (1 meter depth) and SML water were pumped through two separate flow through systems with onboard sensors at a rate of 1.2L min^{-1} using peristaltic pumps. SML and ULW water are

collected in 1L bottles by the pilot's command and in addition collected into large volume carboys. Large sample volumes (~20L) were collected for multiple analyses by all groups involved in the campaigns. The S^3 also collects multiple meteorological parameters; PAR, solar radiation, wind speed, and humidity. Salinity was measured on SML and ULW using a multi-parameter meter (MU 6100 H, VWR) before the collection of the sample into a container, high precision in situ temperature was constantly measured for the SML and ULW using a reference thermometer (P795, Dostmann Electronics GmbH). Specifications for instrument precision and accuracy can be found in Ribas-Ribas et al. 2017. All in situ data was averaged for the 2 hours surrounding the sampling of discrete water samples. A new device termed the "High-volume Sampler for the Vertical (HSV)" was deployed to collect water from five depths between the SML and 2 meters. The HSV is made of a vertical polypropylene pipe with five polypropylene tubes set at five distinct depths in the pipe and a float attached to the top which has been ballasted to ensure accuracy in depth. Peristaltic pumps, similar to that on the S^3, pump water into collection containers. The HSV was deployed during the collection time of discrete SML and ULW samples by the S^3 and near enough to the S^3 so that it would sample the same body of water but wouldn't interfere with the glass plate sampling.

2.32 Sampling: Cape Verde

Samples were taken once a day, weather permitting, between September 18th and October 6th, 2016 within the same nearshore water (~1km) with a total of 12 stations sampled. SML and ULW samples were collected from fisher boats in the nearshore waters. SML samples were collected using the glass plate technique (Cunliffe and Wurl, 2014; Harvey and Burzell, 1972) and ULW was collected from 1 meter depth using a large syringe. Wind speed was recorded using an anemometer placed at the nearby Cape Verde Atmospheric Observatory (CVOA) station. A handheld Global Position System (Garmin etrex) was used to track fisher boat movement during sampling and for coordinates of each sampling station.

2.4 POC, PON, POP and Nutrients

Samples for particulate organic carbon (POC), nitrogen (PON) and phosphorous (POP) were filtered onto acid-washed and pre-combusted glass-fiber filters (Whatman GF/C). Filters for POC and PON were dried at 60°C for three days (Norwegian cruise) or 130°C for two hours (Baltic cruise and Cape Verde), put in tin capsules and measured using an elemental analyser (Thermo, Flash EA 1112 and Elementar Analysensysteme, precision of 0.01 ±0.2 ‰). POP was measured by molybdate reaction after digestion with potassium peroxydisulfate ($K_2S_2O_8$) solution (Wetzel and Likens, 2000). The filtered water was collected and analysed for dissolved nutrients (PO_4, NO_3) by a continuous-flow analyser according to (Grasshoff et al., 1999).

2.5 Chlorophyll a

During the Cape Verde and Baltic (EMB184) campaign, cChlorophyll a (Chl *a*) was measured by filtering 500-1000ml of seawater onto pre-combusted (4h, 450°C) GF/F filters (Whatman). The filters were stored frozen (-18°C) until processed. Chl *a* was then analysed according to the method described by Wasmund et al. (2006) (Wasmund et al., 2006) using a fluorometer (Jenway 6285, precision of 0.01 ± <1ng/ml). During the Norwegian cruise (HE491), in vivo Chl *a* was measured with a hand fluorometer (TURNER DESIGNS, AquaFluorTM, precision of 0.001 absorption) and related to μug of Chl *a* using calibration factor between filtered Chl *a* (Chl *a* Standard in EtOH as reference) and in vivo absorbance.

2.6 Bacterial cell numbers (only for Baltic cruise)

The total cell numbers (TCN) of prokaryotic and small autotrophic cells were determined by flow cytometry following a modified protocol from Marie et al. (2000). For determination of bacterial cell numbers, water samples were fixed with glutaraldehyde (1% final concentration), incubated at room temperature for 1 h, and stored at –18°C until further analysis. Prokaryotic cells were stained with SYBR Green I (2.5 mM final concentration, Molecular Probes, Schwerte, Germany) for 30min in the dark. Samples were measured on a flow cytometer (C6 FlowCytometer, BD Bioscience, fluorescence accuracy of FITC <75; PE <50), and cells were counted according to side-scattered light and emitted green fluorescence. We used 1.0 μm beads (Fluoresbrite Multifluorescent, Polysciences) as internal reference to monitor the performance of the device. Their cell counts include heterotrophic

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and photoautotrophic prokaryotes. Pico and nano-autotrophic cells were counted after addition of red fluorescent latex beads (Polysciences, Eppelheim, Germany) and were detected by their signature in a plot of red (FL3) vs. orange (FL2) fluorescence, and red fluorescence vs. side scatter (SSC). We did not further differentiate between different groups of prokaryotic and eukaryotic autotrophs.

2.7 Transparent Exopolymer Particles (TEP)

TEP was measured by filtering seawater, in triplicates, onto 0.2um polycarbonate filters under low vacuum (<100mm Hg) and staining with alcian blue solution (0.02 g alcian blue in 100 mL of acetic acid solution of pH 2.5) for 5 sec. 0.2µm filters collect both large TEP aggregates and smaller colloidal TEP material. Filters were stored at -18°C until processed. Alcian blue stain was extracted for 2 hours in 80% Sulfuric Acid, with gentle agitation applied to reduce bubble formation, and analysed using a spectrophotometer (VWR UV-1600PC, precision of 1 ± 0.2% T) and the spectrophotometric method (Passow and Alldredge, 1995). The stock solution of alcian blue was calibrated using xanthan gum (Carl Roth) standard according to Passow and Alldredge (1995). (Passow and Alldredge, 1995). TEP concentrations are shown in relation to xanthan gum equivalence. Recent calibration issues with xanthan gum were not observed in our studies and thus the new method by (Bittar et al., 2018) was not required.

2.8 Primary production

To estimate local primary production, we used an adjusted version of the *Vertically Generalized Production Model* (VGPM) (Behrenfeld and Falkowski, 1997) as described by (Wurl et al., 2011b). Estimation is based on concentration of Chl a, depth of euphotic zone estimated from the Secchi depth, photoperiod and photosynthetic active radiation (PAR)

2.9 Data analysis

Statistical analyses of the data set were performed using Graphpad PRISM Version 8. Differences, null hypothesis testing, and correlation were considered significant when $p < 0.05$. The data were log transformed, if required, for parametric and analysis of variance (ANOVA) tests, further post hoc tukey analysis was run for comparison of means when the difference was significant in ANOVA was significant. Unless otherwise indicated, results are presented as means ±standard deviations. Enrichment factors (EF) were calculated as the ratio of concentrations in the SML sample to that of corresponding ULW taken at 1-meter depth. the corresponding subsurface bulk water sample. For vertical sample profiles, the variance of each depth measurement from the average was used to determine homogeneity. Variance is the squared deviation from the mean of all depths and is thus given in units squared (e.g. μug ^{2} L^{-2}).

3 Results

3.1 General Conditions

General characteristic of parameters for all three campaigns is shown in Fig. 2 and Fig. 3 Table 1 and enrichment in Table 2. We observed low (<2 m s^{-1}), moderate (2-5 m s^{-1}) and high (>5 m s^{-1}) wind regimes (Wurl et al., 2011b). Average wind speed was 3.8 ± 0.3, 4.2 ± 2, 5.6 ± 1.8 m s^{-1} for the Baltic Sea, Norwegian Sea, and Cape Verde respectively. PAR averages were 1172 ± 145 and 739 ± 251 µmol m^{-2}s^{-1} for the Baltic sea and Norwegian sea respectively and sea surface temperature (SST), measured from the SML, was 14.8 ± 1.9 and 14.9 ± 1.4°C. Stations for the Baltic cruise were sampled within the same area (~1km) and thus had similar salinity measurements (8.92 ± 0.2 psu) relative to the Norwegian cruise. Meanwhile, the stations for the Norwegian cruise covered inner and outer fjord and open ocean areas and thus had larger differences of salinity. SML salinity was (32.4 ± 2 psu; 23.5 ± 0.4 psu; 6.7 ± 3.5 psu) for outer fjord/open ocean, Trondheim fjord and Sognefjord, respectively. ULW salinity was (32.7 ± 2 psu; 23.9 ± 0.2 psu; 6.6 ± 3.5 psu) for outer fjord/open ocean, Trondheim fjord and Sognefjord, respectively. PAR, SST and salinity data were not collected for the Cape Verde campaign due to logistical constraints. Primary Production (PP) ranged from 426-734 mg m^{-2} d^{-1} during the Baltic cruise but had a higher range

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during the Norwegian cruise with 318-1194 mg m^{-2} d^{-1}, again this is likely due to the differing water masses sampled during the Norwegian cruise.

3.2 TEP distribution in the SML across different regions:

185 **Baltic Sea**

TEP concentrations ranged from 123-1340 µg XG eq L^{-1} in the Baltic Sea. Nitrate and ~~p~~Phosphate were at the lower limit of detection (nitrate: <0.1 µmol L^{-1}; phosphate: <0.2 µmol L^{-1})~~., however Silicate was relatively high with an average of 14.23±0.9 µmol L^{-1}~~. The Baltic sea was also marked with the highest levels of POC in the SML with a range of 27.4- 274 µmol L^{-1}. POC enrichment in the SML matched TEP and PON enrichment trends which showed

190 enrichment factors (EF)>1 for St. 4, 5 and EF<1 for St. 9,10. TEP enrichment factors were ≥1 for the first half of the cruise (St. 3-5) and <1 for the second half of the cruise (St. 8-12). ~~TEP enrichment was ≥1 factor for the beginning of the cruise (St.3-5) and <1 factor for the second half of the cruise (St.8-12).~~ However, total TEP concentration in the SML and ULW increased substantially in the second half of the cruise (St. 9-12), with TEP in the SML averaging 341 ± 150 and in the ULW 269 ± 104 µg XG eq L^{-1} at the beginning and in the SML 946 ± 386 and in

195 the ULW 1916 ± 671 µg XG eq L^{-1} for the second half. Chl a wasn't enriched in the SML at any station while Chl a concentrations ranged between 0.68- 1.56 µg L^{-1} with the highest concentrations at St. 9 and 10. PP matched trends of TEP except at St. 11, which showed relatively low levels of Chl a (0.80 µg L^{-1}) and a resulting decrease in PP (from 734 down to 553 mg^{-2} d^{-1}) but relatively high levels of TEP (2313 µg XG eq L^{-1}) (Fig. 3~~2~~b).

Norwegian sea

200 TEP concentrations during the Norwegian cruise ranged from 50-424 µg XG eq L^{-1} and had sporadic enrichment with 50% of observations showing EF≥1 and 50% showing EF<1. The highest enrichments were observed at St. 3 (EF=1.6) which was the furthest open ocean station and St. 13 and 14 (EF=1.5; 1.4) which were in the Trondheim fjord. Nitrate and Phosphate were both homogenously low for all stations (0.04±0.04; 0.07±0.03 µmol L^{-1}) ~~while silicate had a larger range of 0.26- 7.98 µmol L^{-1} with all outer fjord stations and open ocean stations showing low~~

205 ~~(<1 µmol L^{-1}) concentrations and both inner fjords showing higher (>1 µmol L^{-1}) concentrations. The Sognefjord had markedly higher silicate concentrations than the Trondheim fjord with an average of 7.62±0.6 µmol L^{-1} versus 1.25 and 2.12 µmol L^{-1}.~~ PON concentrations in the SML ranged 0.6-2 µmol L^{-1} and were never enriched, mainly due to low over all concentrations in the water. However, PON in the ULW was higher (>1 µmol L^{-1}) in both inner fjords compared to the outer fjord and open ocean (<1 µmol L^{-1}). POC in the ULW was also higher in both inner

210 fjords (20.5±6.1 µmol L^{-1}) compared to the outer fjord and open ocean stations (10.7±1.1 µmol L^{-1}). ~~S~~similar to PON, POC in the SML showed no general enrichment and had EF<1 for most stations except St. 3, 8, 11. Chl a concentrations in the SML ranged from 0.29- 1.64 µg L^{-1} with lowest concentrations in the outer fjords and open ocean stations and highest concentrations in the Trondheim fjord. Enrichment of TEP and Chl a were both sporadic and did not have matching trends, with Chl a sometimes enriched when TEP wasn't (St. 5, 12) and TEP enriched

215 when Chl a wasn't (St.14,15). However, this appears to be influenced by the fjord systems, when only the open ocean and nearshore stations were considered, TEP and Chl a enrichment trends did match.

Cape Verde

The nearshore water in Cao Vicente, Cape Verde is oligotrophic, which was supported by low Chl a concentrations during our campaign (SML: 0.28 ± 0.2 µg L^{-1}; ULW: 0.29 ± 0.1 µg L^{-1}). Enrichment of Chl a in the SML was

220 sporadic, with 4 out of the 12 stations showing EF>1 and 5 out of the 12 stations showing EF<1. TEP concentrations in the SML ranged from (94- 187 µg XG eq L^{-1}) and were enriched (EF>1) for all days except day 4 and 12. Enrichment of TEP began high at the start of the campaign with (EF=2.6) and was relatively high for the first five days and then decreased to just above unity for the last half of the campaign, excluding the two days of depletion previously mentioned. Of the three regions, samples from Cape Verde showed the lowest TEP concentrations,

225 however not to the same order of magnitude that Chl a showed. Phosphate concentrations~~levels~~ were similar to the other regions with (0.09 ± 0.1 µmol L^{-1}) but nitrate levels were higher (0.37 ± 1.3 µmol L^{-1}). ~~Silicate concentrations in the SML were lower than in the other regions with an average of 0.95±0.4 µmol L^{-1}. Silicate SML concentration and EF had the same trend as TEP EF with higher enrichment at the beginning of the campaign, which then begin to~~

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~~drop in the second half.~~ POC and PON data ranged from 37 ± 32.1 and 2 ± 0.2 µmol L^{-1} with higher values at the first half and lower values in the second half of the campaign. Unfortunately, POC and PON data are only available for half of the stations but are temporally spaced well to assist in showing trends.

3.3 TEP, Chl *a* and POC in different regions

A Tukey's one way analysis of variance was used to compare the concentration and enrichment of the main three parameters between each region: TEP, Chl *a* and POC. Figure~~Table~~ 2 shows that TEP concentrations were significantly higher in the Baltic Sea and significantly lower in Cape Verde (SML: $p<0.0005$, n=11; ULW: $p<0.0009$, n=11) while TEP enrichment was significantly higher in Cape Verde and significantly lower in the Baltic Sea ($p<0.0418$, n=8). Samples from the Norwegian cruise fell between the other two cruises in significance for all parameters. Chl *a* concentrations matched TEP with significantly higher concentrations in the Baltic Sea and lower in Cape Verde (SML and ULW: $p<0.0001$, n=8). However, Chl *a* enrichment had no significant difference found between the regions, likely due to overall low enrichment values. POC enrichment was significantly lower in the Norwegian Sea than in Cape Verde ($p<0.0062$, n=5) but not compared to the Baltic Sea. Statistical analysis for POC could not be run using data from the Baltic Sea due to low n value (n=4). However, both SML and ULW POC concentrations were not significantly different between the Norwegian Sea and Cape Verde but POC enrichment was ($p<0.01$, n=6).

3.4 Vertical Distribution of TEP

The vertical distribution of TEP is shown in Table 3. Variance between concentrations is used to express the relative homogeneity of the parameter within the upper 2 meters and results are given in units squared. During the Baltic cruise there was a distinct change in TEP distribution between the first and second half of the cruise (Fig. 4). TEP concentrations were lower and homogenous (average variance = 8.63x10^3 µg XG eq^2 L^{-2}) for stations 3-8 but rose in concentration and became heterogeneous (average variance = 6.47x10^5 µg XG eq^2 L^{-2}) during stations 9-12. Variances of Chl *a* were highest at stations 9,10 and 12 and lowest at stations 3-5, showing a positive linear correlation between average vertical concentration and homogeneity ($R^2=0.95$, $p<0.0001$, n=8): no such correlation was observed for TEP ($R^2=0.29$, $p=0.16$, n=8). The vertical profiles for microbial counts were also taken in the Baltic Sea to investigate if there was any correlation to TEP depth profiles due to the importance of the microbial loop in TEP production and consumption(Busch et al., 2017; Yamada et al., 2013). However, no correlation or direct connection could be found between TEP profiles and microbial profiles, given as total cell numbers (TCN) and small autotroph profiles (supplementary material: Figure S1). ~~This is possibly due to the short depth scale or the region, Yamada et al. 2017 found a positive correlation in the Arctic Ocean but this was on a much larger depth scale (0-4000 meteres) and no correlation was found in the Pacific Ocean. Additionally, any *in situ* production of TEP or consumption by prokaryotes was likely masked by the large increase in phytoplankton abundance during the second half of the cruise.~~

During the Norwegian cruise, the vertical distribution of TEP varied greatly between stations with the highest variance at station 3 (open ocean station) and the lowest variance at stations 5,7 and 11 (fjord/nearshore). There was no relation between TEP variance and geographical location, e.g. near shore vs. fjord systems, vs. open ocean. Additionally, no correlation was found between TEP and turbulent kinetic energy (TKE), measured with an acoustic Doppler velocimeter (data not shown). TKE data during the Norwegian cruise are presented in Banko-Kubis et. al. 2018. T~~h~~EP profiles shown in Fig. 5 were chosen based on min, median and max variance and presented as such, since no correlation could be found to any other parameter~~us, TEP vertical distribution is shown based solely on its variance (Fig 4) to show how much it can change within the Norwegian sea~~. It is important to note that station 3 had a variance nearly 24 magnitude times larger than the second highest variance (S~~s~~t. 9). Chl *a* and POC showed a moderate correlation between concentration and variance (Chl *a*: $R^2=0.67$, $p<0.0006$, n=13; POC: $R^2=0.63$, $p<0.0013$, n=13). However, TEP showed no similar correlation when the putative outlier variance from St. 3 was excluded ($R^2=0.02$, $p=0.66$, n=12). During both cruises, TEP was found to be enriched even when POC wasn't, but POC was never enriched without TEP also being enriched.

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4 Discussion

TEP is one of the main drivers for the transformation of DOM to POM and its uptake into the biological pump(Mari et al., 2017). Thus, it is important to understand the vertical distribution of TEP and what parameters drive its distribution. Previous studies focusing on vertical TEP distributions have considered depth on large scales of 5-1000 meters (Cisternas-Novoa et al., 2015; Kodama et al., 2014; Ortega-Retuerta et al., 2017) and TEP has been found to vary greatly depending on depth. Due to operational interference from research vessels and the use of large rosette water samples, most studies sample at 3-5 meters for the shallowest depth and assume this surface water to be homogenous towards the surface, and therefore equally representative. However, the importance and influence of the SML has been thoroughly supported (Cunliffe et al., 2013; Engel et al., 2017; Hardy, 1982; Liss and Duce, 1997; Wurl et al., 2011b) and thus there is a need to better understand the biogeochemical cycling occurring in the near surface water and how they relate to organic matter transfer to deeper water masses. This study is the first to take a higher resolution look at the vertical distribution of TEP and other related parameters in the upper 2 meters of the ocean. Our results show that the variability of multiple parameters can be high within the near surface water, due to a complex biochemical system, and can occur on much smaller depth scales than previously assumed.

4.1 Relation between Chl *a* and TEP enrichment

Comparing the enrichment of the SML between each region showed a higher variability of enrichment within each region than between the regions (Table 2), supporting that SML enrichments is a global phenomenon (Wurl et al., 2011b). Interestingly, while there was a significant but weak correlation between Chl *a* and ~~TEP abundance~~TEP concentration in both the ULW and SML (ULW: R^2=0.32, p<0.0007, n=30; SML: R^2=0.36, p<0.0005, n=30), there was no significant correlation between the enrichment of TEP and enrichment of Chl *a* (R^2=0.045, p=0.27, n=30). This suggests~~Further supporting~~ that while phytoplankton are the main source for TEP production, the transport mechanisms for TEP and phytoplankton differ. In large part due to the motility of phytoplankton species, which are known to have vertical migration patterns (Bollens et al., 2010; Schuech and Menden-Deuer, 2014) and can have motility responses to physical changes like turbulence (Sengupta et al., 2017).

While the highest abundances of TEP were found in the Baltic sea, and the lowest abundances in Cape Verde (Fig. 2~~1~~d), the highest enrichment factors were found in Cape Verde (Fig. 2~~1~~c). As the near shore Cape Verde waters are oligotrophic, this compliments with previous studies by Wurl et al. (2011a); Wurl et al. (2011b). ~~(Wurl et al., 2011b)~~ which found the highest enrichment of surfactants to be in oligotrophic waters compared to mesotrophic and eutrophic. While manual sampling techniques were employed in Cape Verde in comparison to rotating glass disc samples in the other campaigns, earlier comparative studies by Shinki et al. (2012) found both methods to collect similar SML thickness and associated biochemical parameters. Since our catamaran was modelled after Shinki et al. (2012) we are therefore able to compare the results from both versions of the glass plate method.

4.2 Effect of wind Speed on TEP Enrichment

We observed enrichment of all parameters irrespective of either instantaneous wind speeds (2 hour average) or wind speed history (24 hour average), including higher wind speeds > 7 m s^{-1}. This supports previous studies which found enrichment of material even at wind speeds >8 m s^{-1} (Kuznetsova et al., 2004; Reinthaler et al., 2008), including the enrichment of TEP in the SML at moderate wind speeds (Wurl et al., 2009). Breaking waves from moderate wind regimes can create bubble plumes in the near surface water (Blanchard and Woodcock, 1957; Deane and Stokes, 2002), and this bubbling has proven to be an effective transport mechanism for TEP and DOM (Robinson et al., 2019; Zhou et al., 1998) to the SML. Thus, bubbling and turbulence at moderate wind speeds can induce more complex enrichment processes and subdue any direct correlation with wind speed. We never observed wind speeds greater than 8 m s^{-1}, which has been found to be the threshold speed for the breakup of TEP ~~(Sun et al., 2017)~~ during experiments in a wind-wave tunnel (Sun et al., 2017). Thus, the moderate wind speeds we observed likely had an indirect positive effect on enrichment.

4.3 Effect of PP on TEP Enrichment

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While TEP concentrations mimic Chl *a* or PP due to the large contribution phytoplankton play in TEP creation (Ortega-Retuerta et al., 2017; Passow, 2002a), the enrichment of TEP is driven by many other processes. Wurl et al. (2011a) found TEP enrichment to be irrespective of PP or negatively related with highest enrichment in oligotrophic waters with the lowest PP. Considering the relationship of PP and TEP enrichment within each region, we found this to be true for the Baltic Sea but not for the Norwegian Sea. In the Baltic Sea, as PP increased enrichment of TEP decreased, due to a larger increase of TEP concentration in the ULW caused from a post bloom state (Fig. 32). However, in the Norwegian sea, TEP enrichment matched PP, most likely due to the changing water bodies in that study, whereas the same body of water was sampled over time for the Baltic Sea and offshore Cape Verde. While we do not have PP data for Cape Verde, considering the positive relationship between PP and Chl *a* concentration in the SML for the Baltic and Norway data, Chl *a* concentration in the SML can be used here as proxy for PP in Cape Verde. Under this premise, Chl *a* in Cape Verde SML was similar to the Baltic in that while, Chl *a* and TEP SML concentrations were correlated ($R^2=0.68$, $p<0.012$, $n=8$), enrichment wasn't ($R^2=0.19$, $p=0.24$, $n=8$).

The oligotrophic waters of Cape Verde present an interesting scenario for TEP production. We found the highest enrichment of TEP in the SML here, while simultaneously observing the lowest concentrations of both Chl *a* and TEP. We suggest that this is due to the abundance of precursor material as well as the increased formation of TEP via the abiotic pathway. A tank experiment with the same setup as used by (Robinson et al., 2019), with different techniques to bubble the water, was also employed in Cape Verde, using water from the same near shore area as field samples. The tank was made of 10-mm polyvinyl chloride (PVC) plates in a size of 120 cm length × 110 cm width × 100 cm height. The tank had a volume of 1400 L with a 500 L aerosol chamber on top. Materials in contact with seawater were made from Teflon, including liners for the wall using Teflon bags. The unfiltered seawater was bubbled using the waterfall technique (Cipriano and Blanchard, 1981; Haines and Johnson, 1995) and via bubbling, large abundances of TEP were created (supplementary Figure S2). This suggests that while TEP abundanceTEP concentration in the near shore water was low, the colloidal and precursor material for TEP was present and only required sufficient formation mechanisms to form aggregates in the size range to be identified as TEP. Such precursor material may have been deposited from the atmosphere, Cape Verde is known for its Saharan dust deposition events and indeed dust events were observed during our campaign (supporting data will be shown in this special issue). This dust deposition has been shown to increase the abiotic formation of TEP (Louis et al., 2017) and is potentially a large contributing factor to higher enrichment of TEP in Cape Verde. If true, this presents interesting implications for the residence time of dust which ends up floating in the SML with sufficient time for photochemical processing.

In contrast, in mesotrophic and eutrophic water, there is more biological activity present in the ULW which can increase the complexity of the system by which TEP and its precursor material is recycled or altered before it can reach the SML. Such increase in biologically derived complexity can be seen in the depth profile data from the Baltic Sea, which showed increased heterogeneous mixing of TEP in the water when PP was higher during the second half. Indeed, the HSV data for all parameters shows that the vertical flux processes are not straightforward to interpret.

4.4 Down and upward flux of TEP

Previous studies have found chemical characteristics to be heterogeneous in the upper 1-2 meters (Goering and Wallen, 1967; Manzi et al., 1977; Momzikoff et al., 2004) substantiating the notion that vertical flux processes are too complex and strong to assume homogenous mixing. Additionally, phytoplankton communities and abundance have also been found to be heterogeneous in the water column (Cheriton et al., 2009; Deksheniecks et al., 2001; Mitchell et al., 2008). Considering the importance of ULW concentrations in estimating enrichment, the presumption of ULW as homogenous becomes problematic. When considering a parameter like TEP which bridges the boundary of biological and chemical parameters and is so fundamentally affected by both, these studies become even more crucial indicators for the likelihood of TEP distributions to be heterogeneous, at least in surface water.

Vertical profiles were sampled for the Baltic and Norwegian seas and in both regions, the vertical distribution of TEP, Chl *a*, POC, PON were found to change from station to stationdaily. In the Baltic Sea, the vertical variance of TEP appears to be linked to PP and the creation of TEP from the biotic pathway. Higher deviation was seen in the second half when TEP and Chl *a* abundance increased. One possible biological cause for this heterogeneous mixing

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could come from its link to phytoplankton. For example, (Bjørnsen and Nielsen, 1991; Carpenter et al., 1995; Nielsen et al., 1990) found vertical phytoplankton patches within the water column in open North Sea and Baltic Sea. Additionally, (Cheriton et al., 2009) found that vertical oscillations cause stratification of phytoplankton into thin vertical patches. Thus, if these same processes were to occur in the near surface, stratification of plankton could result in TEP precursor material being released in patches, and with rapid aggregation, create heterogeneous distribution of TEP. Especially with the majority of TEP produced by diatoms, which are non-mobile phytoplankton who would be more susceptible to grouping and patchiness by physical forcing. This is hinted at by the heterogeneous mixing of Chl a observed during both cruises (Fig. 4~~3~~ and 5~~4~~), which always showed heterogeneous mixing. However, this cannot be the only mechanism as the peak ~~TEP abundance~~TEP concentration was not always seen at the same depth as Chl a. Further studies on vertical phytoplankton distribution in the near surface (>2 meter) environment are needed in order to substantiate the role their patching might have on DOM and TEP. Furthermore, there was a significant correlation between high variance of Chl a and high variance of TEP in the Baltic Sea (R^2=0.65, p<0.028, n=7, S~~s~~t. 4 excluded) but no correlation in the Norwegian Sea (R^2=0.00, p=0.92, n=13)~~.~~. S~~s~~uggesting that with sufficient phytoplankton abundances, and reduced influence from the open ocean, the biological influences on TEP heterogeneity can dominate.

While biological sources are likely to determine the chemical characteristic of TEP, they aren't the only influence. TEP are operationally defined polymers of acidic polysaccharides, and naturally positively buoyant with highly surface active properties (Zhou et al., 1998). When unballasted by detritus or other organic matter, TEP have a positive buoyance and can rise to the surface at rates of 0.1-1 m d^{-1} (Azetsu-Scott and Passow, 2004). However, TEP is never unattached from some type of OM and it is this OM which helps to determine the sinking velocity of TEP (Passow, 2002a). Additionally, the density of TEP is dependent on the formation of its precursor material e.g. the resulting density and therefore sinking or rising velocity of TEP produced from diatoms vs. bacteria will differ as well as TEP produced from nutrients depletion vs. temperature stress (Mari et al., 2017). In near surface water where the ambient density of water is stratified, this could result in the immobilization of TEP particles into layers of water with equal density. Thus, heterogeneous mixing of TEP may be caused by a sort of vertical filtering via TEP density and surrounding water density.

5 Conclusion

The vertical profiles for TEP, Chl a and POC during the Norwegian cruise showed no correlation with any of the sea state parameters. The same was true during the Baltic cruise, which had matching increases in TEP and Chl a concentrations but differing depth profiles (Fig. 4~~3~~). On seasonal scales, TEP has been shown to match Chl a and POC trends (Mari et al., 2017; Ortega-Retuerta et al., 2017; Wurl et al., 2011a; Zamanillo et al., 2019) supporting the notion of phytoplankton blooms as a main source for TEP production in the ocean and subsequently TEP as a main source of POC uptake. This is corroborated in our data. However, when considering the vertical transport of these parameters, this relationship is broken or interrupted by the influence of additional mechanisms. Due to the lack of direct correlation between any one parameter and ~~TEP abundance~~TEP concentration or enrichment, we suggest~~conclude~~ that the vertical flux mechanisms of TEP in the near surface environment are complex. Any positive effects on enrichment, such as wind speed and bubble formation, are only partially responsible. However, with the consistent changing of vertical profiles of TEP, it is clear that these complex fluxes can often result in heterogeneous layering of TEP within the upper 2 meters of the ocean. Indeed within a few cm, ~~TEP abundance~~TEP concentration can change by up to 291%, with no parameter acting as a proxy to suggest homogeneity or heterogeneity. Therefore, it is important for future studies to accommodate this uncertainty of ULW values and for a standardised depth for all ULW to be incorporated.

Data availability

Data have been submitted to PANGAEA database~~-~~: https://doi.pangaea.de/10.1594/PANGAEA.903834~~and a doi will be supplied once it is received.~~

Author Contribution

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All authors have substantially contributed to this manuscript by their involvement in the research cruises, the collection of data, analysis of the data, or contributing to the writing and discussion of the manuscript.

420 **Competing interests**

The authors declare that they have no conflict of interest.

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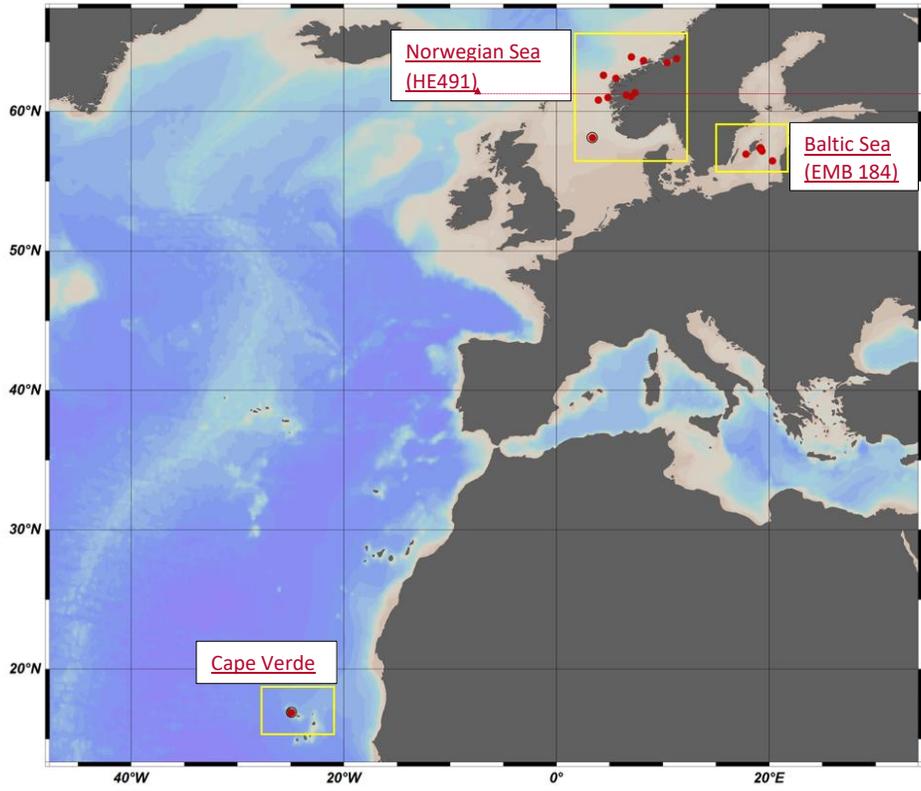
Figure 1: Map showing field campaign areas and stations.

Norwegian Sea (HE491)

Baltic Sea (EMB 184)

Cape Verde

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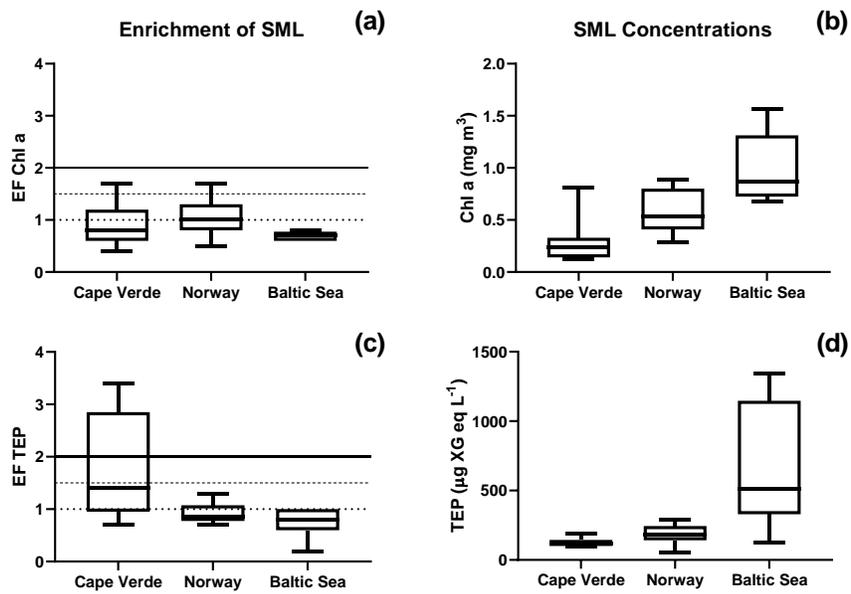
575   **Figure 2~~1~~:** Regional comparison of enrichment and SML concentrations for Chl *a* (**a,b**) and TEP (**c,d**).

(a)   **(b)**
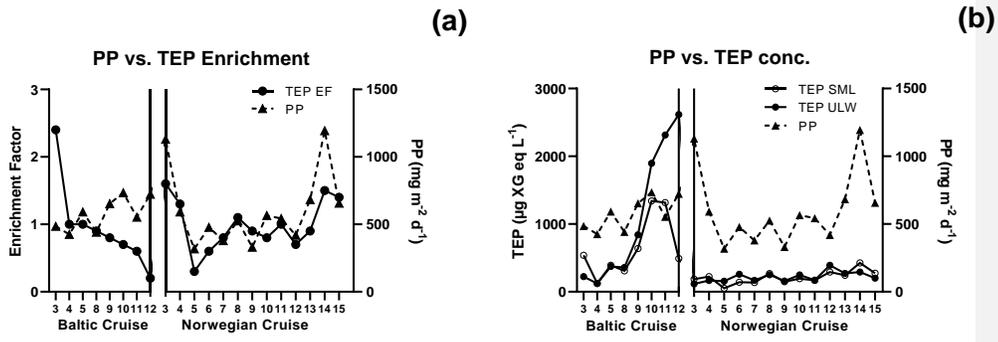
Figure 32: Comparison of **(a)** TEP enrichment and **(b)** concentration with primary production (PP) along the cruise
580   tracks for the Baltic and Norwegian cruises.

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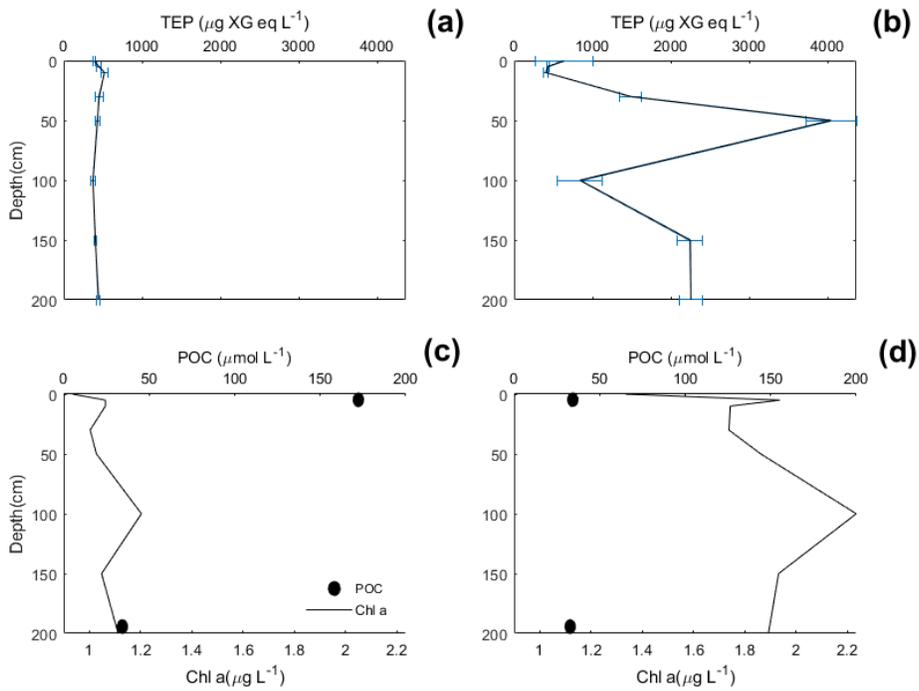
Figure 4̶3: Vertical profiles from stations 5 and 9 during the Baltic cruise, showing the vertical distribution of TEP (**a,b**) and Chl *a*/POC (**c,d**). Stations were chosen to represent the general vertical TEP trends seen in the first and second half of the cruise.

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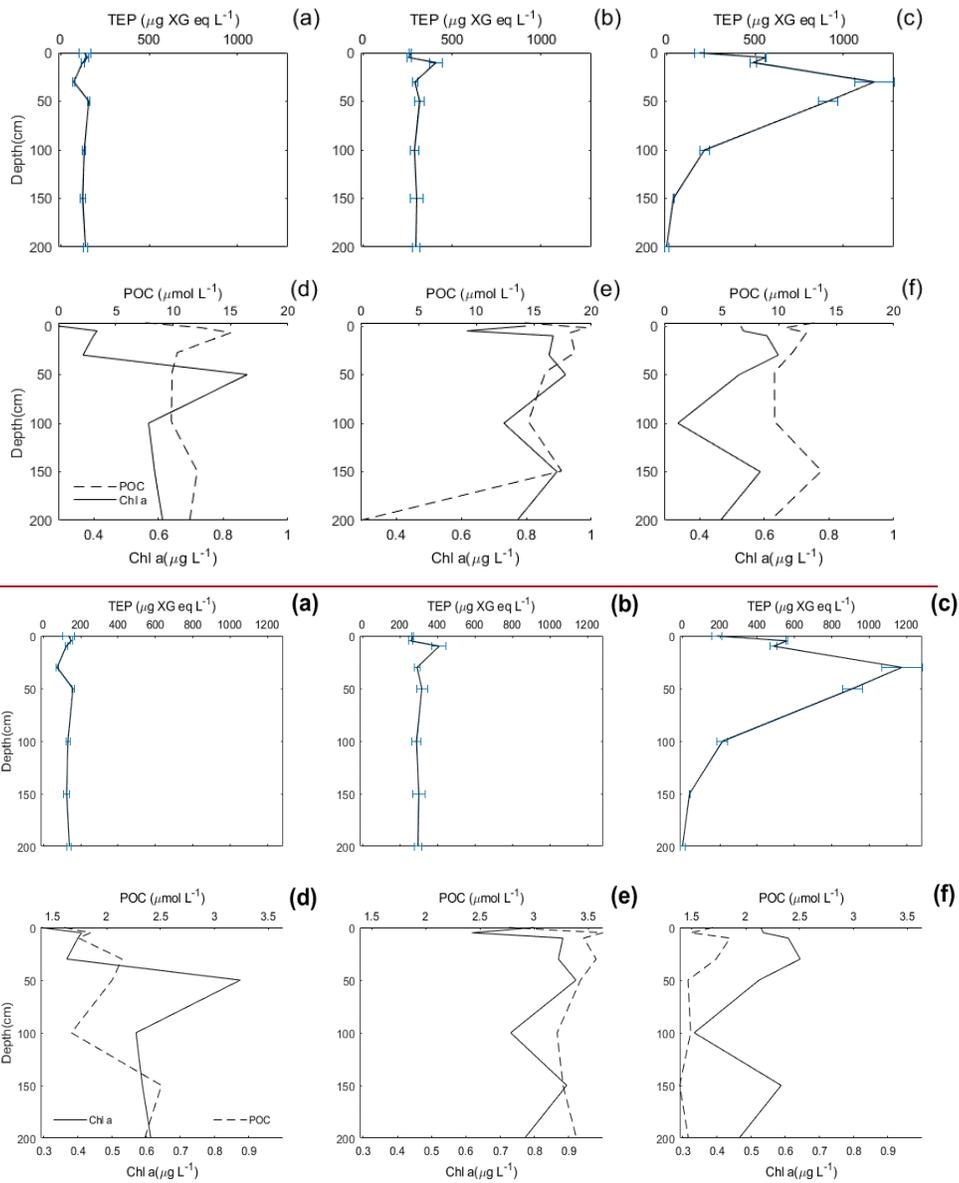
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Figure 54: Vertical profiles from stations 3, 7, 12 during the Norwegian cruise, showing the vertical distribution of TEP (**a,b,c**) and Chl *a*/POC (**d,e,f**). Stations were chosen based on the minimum, median, and maximum vertical variance of TEP.

Table 1: S^3 data with averages ± SD from 2 hours surrounding discreet sampling and 24hr average for PAR and SI data. HE491 St. 7 was sampled in morning compared to the rest which were sampled in afternoon.

									S^3 sensor 24 hour average	
Campaign	Date	Station	Salinity ULW psu	Salinity SML psu	SST °C	PAR µmol m^{-2}s^{-1}	Solar irradiance Wm^{2-}	Wind Speed ms^{-1}	PAR µmol m^{-2}s^{-1}	Solar irradiance Wm^{2-}
	01.06.18	3	n/a	n/a	14 ± 0.18	1644 ± 32	637 ± 34	3.9	1235 ± 378	637 ± 56
	02.06.18	4	n/a	n/a	16 ± 0.15	1555 ± 162	620 ± 51	3.3	1287 ± 331	638 ± 121
	03.06.18	5	n/a	n/a	16.88 ± 0.5	1497 ± 97	675 ± 189	3.6	10868 ± 438	496 ± 196
Baltic Sea	06.06.18	8	8.97 ± 0.04	9.06 ± 0.04	14.22 ± 0.16	1444 ± 361	580 ± 226	3.6	1088 ± 568	499 ± 252
(EMB184)	07.06.18	9	9.05 ± 0.01	9.16 ± 0.02	14.03 ± 0.06	1477 ± 103	452 ± 33	4.4	1176 ± 230	601 ± 79
	08.06.18	10	8.8 ± 0.03	8.84 ± 0.03	10.84 ± 0.06	1470 ± 107	438 ± 35	4.2	892 ± 663	670 ± 81
	09.06.18	11	8.97 ± 0.04	8.97 ± 0.04	16.54 ± 0.11	1310 ± 150	695 ± 135	3.8	1197 ± 267	526 ± 130
	10.06.18	12	8.61 ± 0.04	8.57 ± 0.04	16.11 ± 0.03	1583 ± 73	652 ± 55	3.8	1411 ± 239	652 ± 102
	10.07.17	3	34.83 ± 0.09	34.28 ± 0.09	13.79 ± 0.09	918 ± 97	369 ± 83	4.2	715 ± 313	331 ± 114
	11.07.17	4	32.18 ± 0.09	31.88 ± 0.07	14.24 ± 0.08	903 ± 46	442 ± 154	6.5	870 ± 299	498 ± 152
	12.07.17	5	2.72 ± 0.12	2.75 ± 0.12	15.21 ± 0.15	821 ± 84	303 ± 60	1.8	837 ± 420	437 ± 222
	13.07.17	6	8.72 ± 0.19	8.79 ± 0.20	14.98 ± 0.08	926 ± 143	299 ± 111	4.3	641 ± 414	268 ± 192
	15.07.17	7	28.37 ± 0.15	28.22 ± 0.15	13.53 ± 0.07	256 ± 164	308 ± 167	4.8	683 ± 446	308 ± 168
Norwegian	16.07.17	8	11.22 ± 0.16	11.29 ± 0.17	15.09 ± 0.05	415 ± 21	216 ± 176	6.1	421 ± 340	238 ± 170
Sea	17.07.17	9	3.75 ± 0.08	3.61 ± 0.08	14.31 ± 0.08	553 ± 134	187 ± 50	7.4	377 ± 202	181 ± 72
(HE491)	19.07.17	10	33.95 ± 0.07	34.01 ± 0.05	13.56 ± 0.03	1511 ± 133	711 ± 24	5.8	933 ± 526	534 ± 205
	20.07.17	11	31.33 ± 0.24	30.95 ± 0.26	15.49 ± 0.35	989 ± 88	572 ± 53	1.9	649 ± 521	556 ± 101
	22.07.17	12	34.01 ± 0.13	33.68 ± 0.05	14.21 ± 0.06	949 ± 34	540 ± 45	2.6	849 ± 230	427 ± 161
	23.07.17	13	33.96 ± 0.16	33.56 ± 0.23	13.68 ± 0.13	641 ± 43	245 ± 40	5.7	437 ± 191	184 ± 62
	24.07.17	14	24.10 ± 0.59	23.93 ± 0.67	17.07 ± 0.60	1552 ± 140	661 ± 46	1.2	1362 ± 250	469 ± 260
	25.07.17	15	23.74 ± 0.11	23.06 ± 0.21	18.62 ± 0.33	1039 ± 129	448 ± 222	1.8	828 ± 426	455 ± 191

Table 2: Enrichment factors for each station. EF≥1 shows enrichment in the SML.

Campaign	Date	Station	Enrichment Factor					
			Phosphate	Nitrate	Chl *a*	PON	POC	TEP
Baltic Sea (EMB184)	01.06.18	3	1.0	2.0	0.7	n/a	n/a	2.4
	02.06.18	4	1.0	0.7	0.7	1.4	1.8	1.0
	03.06.18	5	1.0	1.0	0.8	2.0	5.1	1.0
	06.06.18	8	1.0	1.0	0.6	n/a	n/a	0.9
	07.06.18	9	1.0	1.0	0.6	0.8	0.8	0.8
	08.06.18	10	1.0	1.0	0.7	0.7	0.7	0.7
	09.06.18	11	1.0	1.0	0.8	n/a	n/a	0.6
	10.06.18	12	1.0	1.0	0.6	n/a	n/a	0.2
Norwegian Sea (HE491)	10.07.17	3	1.1	n/a	1.3	0.7	1.4	1.6
	11.07.17	4	0.6	0.4	1.1	0.7	0.9	1.3
	12.07.17	5	1.0	n/a	1.6	0.8	0.9	0.3
	13.07.17	6	1.0	6.3	0.6	0.7	0.7	0.6
	15.07.17	7	1.0	2.0	0.5	0.7	0.8	0.8
	16.07.17	8	0.9	20.6	1.1	1.0	1.0	1.1
	17.07.17	9	1.0	1.8	0.7	0.7	0.8	0.9
	19.07.17	10	1.0	n/a	0.8	0.9	0.9	0.8
	20.07.17	11	1.1	0.5	0.9	0.9	1.2	1.0
	22.07.17	12	0.9	n/a	1.7	0.8	0.7	0.7
	23.07.17	13	1.0	0.3	1.0	0.8	0.8	0.9
	24.07.17	14	2.5	0.5	0.7	0.8	0.7	1.5
	25.07.17	15	0.6	1.4	0.9	0.7	0.9	1.4
Cape Verde	20.09.17	1	2.1	1.4	1.7	n/a	n/a	2.6
	22.09.17	2	n/a	n/a	1.0	n/a	n/a	3.1
	25.09.17	3	2.4	2.3	1.0	1.2	2.5	3.4
	26.09.17	4	1.6	0.9	0.6	n/a	n/a	0.7
	27.09.17	5	0.6	1.4	0.6	1.9	3.3	2.1
	28.09.17	6	1.9	1.4	0.4	1.3	4.0	n/a
	02.10.17	7	1.2	0.4	0.8	0.9	1.9	1.1
	03.10.17	8	1.1	1.5	1.4	1.2	1.6	1.4
	04.10.17	9	n/a	n/a	n/a	n/a	n/a	n/a
	05.10.17	10	n/a	n/a	n/a	n/a	n/a	n/a
	06.10.17	11	0.4	1.3	n/a	n/a	n/a	1.1
	07.10.17	12	0.2	1.0	0.6	n/a	n/a	0.8

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Table 3: Vertical distribution of TEP concentrations (µg XG eq L^{-1}), variance between TEP concentration at all depths is shown as an indicator for homogeneity (µg XG eq^2 L^{-2}).

				Baltic Sea (EMB 184)				
Station	3	4	5	8	9	10	11	12
Variance	3x10^4	2x10^0	2x10^3	1x10^3	1x10^6	4x10^5	1x10^5	7x10^5
0	539±339	123±23	392±15	308±14	638±369	1340±781	1317±101	490±91
5	345±218		449±29	380±47	429±16	750±281	2045±135	560±76
10	307±408		520±39	339±12	406±25	2935±423	2254±161	536±46
30	630±288		455±54	376±49	1486±138	2003±575	2274±120	1559±145
50	642±293		431±27	270±3	4046±320	2508±761	2021±164	2587±205
100	224±206	120±16	374±24	358±2	841±283	1896±105	2313±83	2615±159
150	228±113		405±18	316±6	2248±162	2136±137	2506	1454±149
200	658±269		443±21	341±32	2256±150	1591±223	2619	1162±92

						Norwegian Sea (HE491)							
Station	3	4	5	6	7	8	9	10	11	12	13	14	15
Variance	2x10^5	2x10^3	1x10^3	3x10^3	6x10^2	2x10^3	7x10^3	2x10^3	1x10^3	2x10^3	2x10^3	7x10^3	2x10^3
0	185±28	224±12	50±36	142±22	135±33	268±6	148±12	194±7	168±16	291±12	244± 0.1	427±2	273±17
5	558±5	179±3	95±29	235±10	150±8	258±11	374±14	282±17	200±10	270±7	196±8	192±12	211±3
10	489±18	166±13	69±30	245±6	123±8	409±38	211±8	263±8	177±21	254±26	330±10	145±9	204±14
30	1175±109	104±14	78±40	264±1	74±7	291±15	129±14	190±15	107±27	290±20	176±1	205±14	161±28
50	912±55	108±9	103±23	331±32	159±7	317±29	138±22	188±15	97±10		243±2	155±13	261±27
100	214±28	173±6	113±13	309±23	132±10	288±23	129±4	274±27	143±12	391±2	260±20	241±39	208±9
150	39±2		115±15	308±13	124±16	301±35	140±11	196±9		323±7	225±28	180±28	293±0
200	0±14		130±29	284±6	139±11	297±22	114±17	274±12			168±9	202±28	312±9

Table 4: Regional comparison of TEP, Chl a and POC enrichment and concentrations. * p < 0.05 analysed using ANOVA Tukey statistical test (95% confidence interval). POC data from the Baltic Sea was excluded due to low n val~~ue~~ues.

Concentration		Baltic vs. Norwegian			Baltic vs. Cape Verde			Norwegian vs. Cape Verde	
	n	Mean Diff	SE	n	Mean Diff	SE	n	Mean Diff	SE
TEP-SML	8**	457.1	112.8	8***	516.5	118	9	59.38	109.2
TEP-ULW	8**	879	242.4	8***	996.9	242.4	11	117.9	222.5
Chl a-SML	8**	0.4149	0.1156	8***	0.7157	0.1209	9*	0.3008	0.1118
Chl a-ULW	8***	0.8436	0.1654	8***	1.204	0.1625	11	0.3605	0.1486
POC-SML							6	-25.25	26.23
POC-ULW							9	0.498	2.9~
Enrichment									
TEP	8*	-0.1~~738~~0423~~1~~	0.3~~81~~3608	8*	1.068~~0.8611~~	0.3~~475~~361	9*	0.8944~~0.8188~~	0.3634299
Chl a	8	-0.3~~550~~448	0.1~~75~~3272	8	-0.2125	0.16~~34~~16	9	0.14~~09~~2931	0.16~620
POC							6**	-1.76	0.5003

p<0.05*, p<0.01**,
p<0.001***

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