Dr. Claire Reeves
Co-Editor, *Atmospheric Chemistry and Physics*
University of East Anglia
Norwich Research Park, Norwich, Norfolk
U.K.

April 2, 2015

Dear Dr. Reeves,

With this letter, I submit a revised version of our manuscript acp-2014-591 entitled “Primary marine aerosol emissions from the Mediterranean Sea during pre-bloom and oligotrophic conditions: correlations to seawater chlorophyll-a from a mesocosm study” for your consideration. We appreciate the opportunity to improve the manuscript based on the reviewer’s and your helpful suggestions and comments.

I have attached to this document our detailed responses to the Reviewer and Short comments (which can also be found in the Interactive Discussion) and a list of broad changes we have made to the manuscript. Also, I have attached a version of the revised manuscript with changes tracked.

We hope that you will find this revised manuscript suitable for publication in Atmospheric Chemistry and Physics.

Best regards,

Allison N Schwier

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***Responses to F. Dulac***

We kindly thank Mr. Dulac for his insightful comments. We address particular concerns below.

*- My most important concern is about particle size distribution fitting and related results discussion. Even if those numbers are stated as approximate by using the sign "~", I cannot find realistic to report with 3 significant digits either mode fractions (e.g. ~0.295, 0.482) or mode diameters (~18.5, 37.5, 91.5 and 260 nm). Table 2 suggests for instance that it would probably be more appropriate to give ranges for every mode. In addition, we miss information on the variability on the geometric standard deviations of the fitted modes when they are needed to fully characterize the size distribution. I believe that we miss in the methodological section 2 a sub-section describing the particle size distribution fitting technique and discussing accuracy of results which are the basis of the paper. This is important that the limits of this fitting have been assessed when discussing differences between experiments. I would also expect to see discussed how robust is the choice of 4 modes for fitting, and how variable are the size distribution results. For instance we miss associated standard deviations in Table 2 and I find that Figure 1 should be completed with another plot that shows the variability (e.g. by plotting all curves obtained on a single plot, or showing envelopes...).*

We thank Mr. Dulac for bringing up these points. We have decreased the number of significant digits and included the standard deviations for the mode diameters. We have added standard deviations for the mode fittings in Table 2 as well as the size distribution spreads in Figure 1.

We have also changed the first paragraph in Section 3.1 to describe the size distributions and mode fitting in more detail. It now reads, "The marine aerosol size distributions remained fairly stable during a given experiment, which lasted around one hour for each water sample. The aerosol size distribution also remained stable throughout the course of each campaign, with a similar distribution shape. Four lognormal modes were fit to the average size distributions of each campaign, with results summarized in Fig. 1 and Table 2. The average size distributions were taken from 214 size distributions for BC and 182 size distributions for BV, and size envelopes are also included within Fig. 1. In order to investigate the size of the aerosol independently of the concentration, the size distributions were normalized using the total aerosol number concentration. We found that the primary marine aerosol size distributions were best described using the three expected modes: nucleation mode (around 20nm), Aitken mode (around 40nm), and accumulation mode (around100nm); and an additional fourth mode around 260nm. Using only three modes for the fitting procedure could not satisfactorily represent the primary marine aerosol size distribution. A mode at around 300nm was also found by Sellegri et al. (2006) during bubbling experiments for which the effect of wind on the surface breaking bubbles was simulated in a similar experiment set-up. The 300nm mode was interpreted by the authors as the result of a thicker bubble film where the bubbles are forced to break by the wind instead of reaching a natural breaking thickness. The four average lognormal modal diameters determined (18.5±0.6, 37.5±1.4, 91.5±2.0, 260±3.2nm) were present in both BC and BV."

*- In section 2.2, I find that we miss information of DMA size channels and measurement integration time for size distributions. How variable is the size distribution measured for a set of given conditions?*

We have added information about the number of channels for the DMA measurements and the size stepping integration time and the stability of the size distribution over the course of an experiment. We have also added information about the dataset size for the average size distribution measurements.

*- I am questioning the negative values of kappa occasionally found. Cannot you tentatively use them to better constrain Kappa-inorg? If you really end up with unrealistic values for Kappa-inorg, is it justified to keep those points in the data set for correlations rather than discarding them (figures 9-10)?*

The Kappa-inorg value is already set to the theoretical kappa value of inorganic sea salt. The variability of the kappa-total measurements around this theoretical value creates unrealistic negative organic fractions. These negative fractions give us the level of uncertainty in the method to determine organic fractions and we believe that they should be kept in the data set.

*- When discussing correlations with biological parameters in section 3.4, I find that you might be more precise by giving significance levels of the correlations (that depend on the number of points used or degree of freedom). Is it really appropriate to state that you "find a correlation" when R is about 0.4 or a bit lower. In the case of the correlation between Synecococcus and DOC, is it really robust or rather driven by the single point with the highest DOC value: what if you fit without this peculiar point? The sigmoid fit used in Fig. 10f seems also more appropriate for most of the correlations (e.g. Fig. 10a, 10c, 10e): is it justified to stick to linear correlations?*

We thank Mr. Dulac for bringing up this point. We have calculated the significance of the correlation coefficient and added p values for all the correlations. We found that all of the correlations were significant ($p<0.05$), even when the $R^2$ values were <0.5. We also believe that the sigmoid fits are more appropriate, especially conceptually because the organic fraction of the PMA cannot be higher than one even after reaching a certain level of chla content. We now mention this in the text, and we have included sigmoid fits for all the correlations, where applicable. However, in order to compare our results with results reported in the literature, we also provide the linear correlation fits.

The following paragraph is now added to Section 3.4: "Sigmoid fits are also shown in Figs. 8 and 9 for all biological parameters where they could be determined. Sigmoid fits might be more appropriate to use in many cases, to conceptually constrain the organic fraction of the primary marine aerosol to one regardless of the chla concentration. We have included both linear and sigmoid fits, with their respective $R^2$ and $\chi^2$ values for completeness."

*Other technical comments:*
*-You should generalize the use of the italic style for all symbols throughout the paper.*
*-Abstract: it would be worth indicating the particle size range of your measurements (10-400 nm) which constrains the size distribution fitting.*
*-Abstract, line 16: specify "kappa (k)".*

We have made these changes.

*- p.26196, line 16: given that the mesocosm diameter is 2.3 m, I rather calculate that 5 L of water corresponds to 1.2 mm in height, not 15 cm.*

We apologize for the confusion. The 15cm indicated the maximum depth to which we collected the surface water. We have clarified this within the text.

*-p.26197, l.11: I think "cm^3" is expected instead of "cm"; I would rather write "of ~10 cm".*
*-p.26202, l.6: specify "the water temperature".*
*-p.26203, l.12: I'd rather use the singular in "no visible changes".*
*-p.26206, l.12: specify that this correlation is "(not shown)".*
*-p.26207, l.25: I'd rather use the singular in "any parameters".*
*-p.26208, l.25-26: the second part of the sentence seems unclear to me as written; I think that the two word groups "Chl a and additional pigments" and "the organic fraction" must be switched in the first part of the sentence.*
*-Acknowledgements: the acronym MISTRALS is missing its terminal S; "MISTRALS/ChArMEx" would be more appropriate.*
*-Fig. 1: Ordinate axis legend should probably state "Normalized number fraction", since the curves appeared normalized by their maximum value.*

These changes have been made.

*-Table 2: It is not clear in the legend that these numbers are averages.*

We thank Mr. Dulac for this point. We have clarified the text to indicate that these are averages.

*-Many figures are difficult to read once printed, with too small characters.*

We have increased the fonts of all figures to make them easier to read.

*-Legend of Table 2, Figures 3 and 6 (and possibly other occurrences): I would specify "CO2-enriched".*

We apologize for the confusion. "Enriched" in all of these contexts indicate that the samples were enriched with the sea surface microlayer. We have tried to clarify this within the text where necessary.

References:

Sellegri, K., O'Dowd, C. D., Yoon, Y. J., Jennings, S. G., and de Leeuw, G.: Surfactants and submicron sea spray generation, *Journal of Geophysical Research*, *111* (D22), D22215, 2006.

***Responses to Reviewer #1***

We thank the reviewer for their helpful comments and discussion. The concerns of this reviewer are addressed below.

*Major comments: - Investigating the impact of ocean acidification on primary marine organic aerosol emissions is one of the major goals of this paper. However, it is not clear for me that simply adding CO2 in marine water during few days can mimic properly the impact of future acidification on marine aerosol emission. I assume that future climate changes may, on a long term run, affect organic content in seawater (phytoplankton species and concentration, virus population . . .) in the Mediterranean. Also, climate change may not only affect pCO2 but also wind speed which is an important parameter in marine aerosol formation (Bopp et al., 2001; 2003). At least few sentences should be added in the manuscript to describe these issues.*

We thank the reviewer for pointing this out. We answer their comment below and in the following comment response. Indeed, our experiment was only focused on the effects of ocean acidification on the composition and function of Mediterranean plankton communities, without taking into consideration the potential effects of climate change related processes such as warming and modifications of wind regimes. These parameters may also change, but were outside the scope of this study. It is important to keep in mind the idea that planktonic organisms have a generation time of a few hours to a few days, and that as such they can react very quickly to an external driver, such as adding $CO_2$ in a mesocosm. Many experiments, with some following the same protocol as in this work (mesocosms deployed for multiple days), have already shown that increased $CO_2$ availability could lead to important modifications of planktonic community compositions and functioning. For more explanation, we invite the reviewer to reference (Gazeau et al., submitted) for more details of these campaigns and the reasoning behind them.

We have modified our introduction to develop these considerations and to better explain why ocean acidification would potentially affect marine aerosol formation, through the modification of plankton community composition and organic matter production. We have added the following paragraph into the introduction to more fully explain this: “The production of organic matter in oceanic surface water is expected to be substantially modified in the coming decades as a consequence of climate change and ocean acidification (Doney et al., 2012). Ocean acidification is defined as the increase in ocean acidity and associated changes in seawater chemistry, due to the absorbance of a very significant amount of anthropogenic $CO_2$ by the oceans (2.5 ± 0.5 Gt C or ~26.3% of anthropogenic emissions, Le Quéré et al., 2014). Since the beginning of the industrial era, the pH in ocean surface waters has already decreased by 0.1 units, on average, equivalent to an increased acidity of 26%. Further acidification is expected by 2100, ranging from 0.06 to 0.32 units, equivalent to an increased acidity of 15 to 110%, depending on the considered $CO_2$ emission scenario (Ciais et al., 2013). Although it is well established that ocean acidification has the potential to significantly impact marine biological processes (see Riebesell and Tortell (2011) and Weinbauer et al. (2011) for a comprehensive review), it is still unclear how these changing biogeochemical water conditions will affect the properties and production of marine aerosols. Furthermore, the effect of such an acidification and consequently the resulting feedback on Mediterranean marine aerosol and the regional climate remains unknown."

We have added the following statement to the conclusions to further expand this point, "It is important to note that there are additional effects, such as wind speed, precipitation levels, and temperatures, that could change with future climate change and that these were not included within this analysis; instead, we focused on ocean acidification effects on Mediterranean Sea plankton communities and subsequent effects on primary marine aerosol. Future studies will need to incorporate additional parameters to determine further effects on primary marine aerosol."

*Why should we investigate ocean acidification specifically in the Mediterranean? This should be better justified (in few sentences). "Mediterranean marine aerosol remains relatively uncharacterized": this may be not enough to justify the need for characterizing them.*

We have modified the introduction to include the following information to describe in more detail the importance of studying acidification experiments of Mediterranean aerosol, "Mesocosms are defined as experimental enclosures from one to several thousands of litres that maintain natural communities under close-to-natural conditions (Riebesell et al., 2013). They have been increasingly used in both aquatic and terrestrial ecology (Stewart et al., 2013), especially on the effects of environmental and/or anthropogenic disturbances on a large variety of chemical and biological processes. In the context of ocean acidification, mesocosms have been used on several occasions for experimental time periods spanning from a few days to a few weeks, and were found to be efficient in studying the effects of this driver over such short time scales (Riebesell et al., 2008, 2013). Archer et al. (2013) recently showed, during a mesocosm experiment in the Arctic, that with seawater acidification and increased $CO_2$ concentrations, average concentrations of DMS decreased by up to 60% at the lowest pH. Inversely, concentrations of DMSP, the precursor to DMS, increased by up to 50%. In the remote ocean, DMS was predicted by modeling studies to be one of the main precursors for CCN in the marine boundary layer, and studies have shown that regional DMS emission changes could affect CCN sensitivity (Cameron-Smith et al., 2011; Woodhouse et al., 2013).

Many past mesocosm experiments which focused on the effects of ocean acidification have been performed in relatively eutrophic conditions or with nutrient addition initially or during the experiment. However, about 60% of the ocean surface is associated with low productivity, termed oligotrophic areas. Decreased nutrient availability and the expansion of low productivity regions are projected with increasing $CO_2$ concentrations, as enhanced thermal stratification is expected to lead to surface layer nutrient depletion (Irwin and Oliver, 2009; Polovina et al., 2008). Nutrient availability also might have strong effects on the community response to ocean acidification (Hare et al., 2007), so there is a clear need to evaluate the sensitivity of oligotrophic marine environments to this anthropogenic effect. The Mediterranean Sea is one of the most nutrient-poor waters in the world with maximum open sea area chlorophyll concentrations of 2-3mg $m^{-3}$. Its' trophic status varies from oligotrophic-mesotrophic in the northwestern basin to extremely oligotrophic in the eastern basin (Moutin and Raimbault, 2002; The Mermex Group, 2011). High biological activity occurs annually in parts of the western Mediterranean, including coastal France in the late winter and early spring (D'Ortenzio and Ribera d'Alcalà, 2009; Siokou-Frangou et al., 2010).

In this work, we collected water from three mesocosms deployed in the Northwestern Mediterranean Sea over two campaigns during different seasons as part of the European Mediterranean Sea Acidification in a changing climate (MedSeA; http://medsea-project.eu) and the Chemistry-AeRosol Mediterranean Experiment (ChArMEx) projects to test the effects of ocean acidification and changes in the biogeochemistry of the seawater on the physical and chemical properties of primary marine aerosol including size distributions and CCN activity."

*The authors did not emphasize enough what is the added value of pelagic seawater/mesocosm when characterizing primary marine organic aerosol emissions.*

Please see the response to the above question.

We have also added the following sentence in Section 2.1 to clarify why these experiments were performed off-shore in the methods section, "For both campaigns, the mesocosms were located off-shore in pelagic waters in order to measure primary marine aerosol properties and biogeochemical parameters of the water while minimizing contamination from anthropogenic sources."

*- A lot of important conclusions (correlations, equations . . .) are drawn based on the use of two datasets (pre-bloom BV and oligotrophic BC) which are very contrasted, showing most of the time two groups of points with respectively high/low values leading obviously to a very good correlation. I am not convinced that it is legitimate to perform such correlation plots unless the authors bring much enough material to demonstrate, for instance, that very similar pre-bloom BV conditions can be observed also at BC and that oligotrophic BC conditions can also observed at BV.*

We thank the reviewer for this point. We refer in the manuscript to (Gazeau et al., submitted) currently under evaluation in the journal Estuarine, Coastal and Shelf Science, which describes in detail both experiments and the two investigated sites. You can see in the figure below (included in Gazeau et al., submitted) that, indeed, these two bays share many similarities with typical bloom conditions in winter-spring and oligotrophic conditions in the summer corresponding to a stratified water column. Pre-bloom conditions are also observed in BC. We have now added the following to point the reader towards this manuscript, “The two bays share many similarities in term of temperature, salinity, phosphate ($PO_4^{3-}$), nitrate+nitrite ($NO_x$) and silicate (Si) seasonal variations, and they both show typical bloom conditions in winter-spring and oligotrophic conditions in the summer, corresponding to a stratified water column. Pre-bloom conditions are also observed at both locations (Gazeau et al., submitted). The presence of pre-bloom and non-bloom conditions was confirmed by the order-of-magnitude difference in the average seawater chla concentrations ($chla_{BC,avg}$ = 0.069±0.009 mg $m^{-3}$, $chla_{BV,avg}$ = 1.005±0.125 mg $m^{-3}$). Detailed site and experimental information for both campaigns that legitimize the comparison to test in these two locations at different seasons can be found in (Gazeau et al., submitted)”.

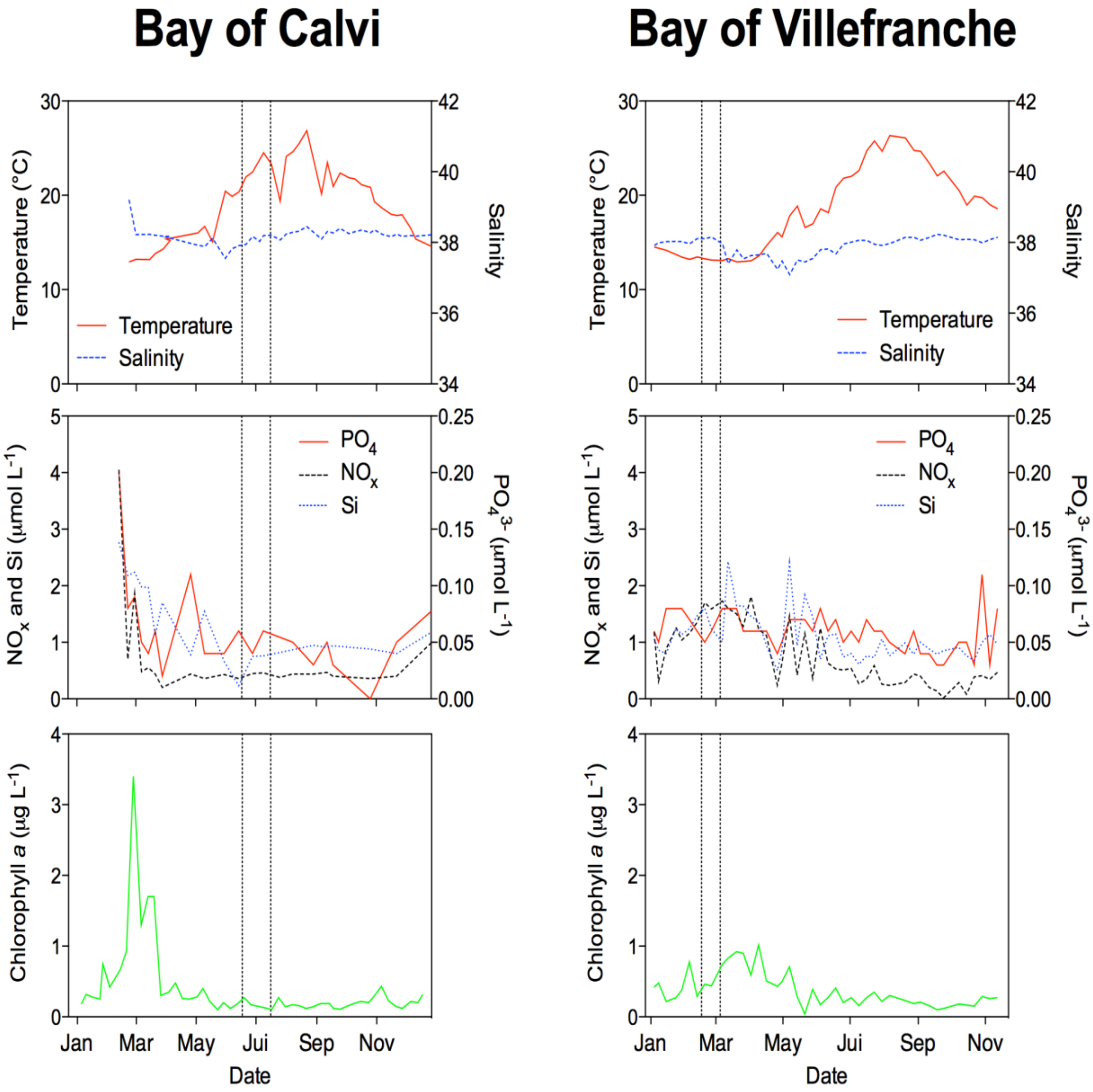

**Figure 1.** Hydrological (temperature and salinity) and biogeochemical (nutrients: nitrate + nitrate, $NO_x$; silicate, Si; and phosphate, $PO_4^{-3}$ and chlorophyll a concentrations) conditions in 2012 in surface waters of the Bay of Calvi (left panel) and in 2013 in surface waters of the Bay of Villefranche (right panel). For all plots, the corresponding experimental periods are identified by vertical dotted lines. [Taken from Gazeau et al., (submitted)].

*Minor comments:*

*Abstract:*

*Line 43: Be more specific regarding marine aerosol. Uncertainties do concern primary (and possibly secondary) organic aerosol emissions*

*Acronyms (Dp; pCO2) to be introduced.*

We have made these changes within the text.

*<u>Introduction:</u>*
*Line 75: ". . .via chemical processing". I would have been more specific (gas-to-particle conversion).*
*Line 77: ". . .and affecting cloud formation". Not only. Also cloud properties (albedo, lifetime). I would have added some references here related to the indirect effect of marine aerosols (there are a lot).*
*Line 82: Should be "primary" marine aerosol. The same in line 103*
*Line 118: What is "SDS"? Not defined in the manuscript. However, essential to understand some statements.*
*Line 146: Should be "chl-a" (and acronym explained once in the text)*
*Line 205: Explain acronyms (MedSeA and ChArMEx)*

These changes have been made.

*Line 173: Can you explain what you mean by "100x". 100 times? Can we write in a paper 100x?*

The reviewer is correct, "100×" means 100 times the typical ocean concentrations. We used the same terminology that was used within the direct source material (Moore et al., 2011) in order to follow the same convention in describing their results.

*Line 174: Are you sure we can investigate in lab experiment cloud formation properties? (not sure).*

In a laboratory setting, it is possible to determine whether the tested organics have impacts on CCN activity, through the formation of organic films or decrease in the aerosol surface tension. This can also provide information on water uptake, which is one aspect of cloud formation. The Moore et al. (2011) publication describes their results in terms of CCN activity and cloud formation properties (focused on surface tension depression from surface-active organics and its effect on CCN activity), and we have followed their convention in describing their results.

*<u>Materials and methods:</u>*
*Lines 217 & 223: Be consistent throughout the paper. Seawater or sea water. Not both*
*Line 226, 246, 259: Explain acronym ETFE, PFA, CTD*

These changes have been made.

*Line 233: How representatives are the concentration of pCO2? Provide a range in ambient (atmospheric) CO2 concentrations.*

In the Bay of Calvi (BC), the six targeted elevated $p\text{CO}_2$ levels were 550, 650, 750, 850, 1000 and 1250µatm. In the Bay of Villefranche (BV), the levels were 450, 550, 750, 850, 1000 and 1250µatm. These $p\text{CO}_2$ levels were chosen in order to cover the range of atmospheric $p\text{CO}_2$ projected for the end of the century following various $\text{CO}_2$ emission scenarios, from the representative concentration pathways (RCP) 2.6 (i.e. radiative forcing of 2.6 W $\text{m}^{-2}$ with a $p\text{CO}_2$ level of 490 ppm) to the pessimistic RCP8.5 (+ 8.5 W $\text{m}^{-2}$, $p\text{CO}_2$ ~ 1370 ppm) as seen in the IPCC report (IPCC, 2013). We have clarified this within the text.

*Line 312: Can you help the reader and state in one sentence how representative are the SS values you have set in your paper?*

We have added the following sentences to clarify this for the reader, "The range of SS values used in this work is typical of those reported in natural clouds. Anttila et al. (2009) found cloud SS values from 0.18 to 0.26% for low-level clouds in Northern Finland, Hegg et al. (2009) obtained a SS range from 0.2 to 0.3% for clouds over the California coast, and Asmi et al. (2012) found SS values from 0.1 to 0.3% at the puy-de-Dôme station in Central France."

*Line 315: Table 1 only concerns BV ? If so, please state it.*

Table 1 includes the activation diameters and supersaturation values used for both campaigns, not only BV. We have clarified this in the text.

*Line 327: ". . . typically less than 10%". Provide a reference.*

The determination to use total organic carbon measurements and refer to them as dissolved organic carbon measurements was specific for our experiments (given the low concentration of particulate organic carbon). There is no reference, as this is not a generalizable trait. We have added the measurements of particulate organic carbon for clarification.

*Line 331: "0.4mm". Do you mean "0.4mm pore size diameter" ?*

We thank the reviewer for this; we have clarified this within the text.

## *Results and Discussion*

*Lines 338-346: You just state here that acidification experiments did not show any difference compared to the control, but you do not say if this is something expected or not. This is an important result having strong implication for the paper but it is not commented at all.*

We thank the review for pointing this out. It is important to note that a goal of the present paper was to characterize the relationship between seawater biochemical composition and primary marine aerosol properties, independent of the level of acidity. We have added the following sentence to the discussion in Section 3, “While several studies have shown the effects of ocean acidification on biogeochemical parameters in eutrophic waters (Galgani et al., 2014; Schulz et al., 2013), observations from the MedSea experiment showed no effect of ocean acidification on most of the biogeochemical parameters in these oligo- to mesotrophic areas. These results are discussed more fully in Gazeau et al., (submitted). As a consequence, we did not expect any impact on the primary marine aerosol physical aerosol properties.” We have also added more discussion about ocean acidification into the introduction.

We have already included discussion of the acidification experiments later in Section 3.4, “The control and acidified mesocosms showed no significant differences in terms of correlations between organic fraction and different biogeochemical parameters. For studies of marine aerosol, this indicates that any acidification effects on these biological parameters impacts the physical and chemical parameters of the aerosol much less than the natural variances caused by organic pre-bloom and bloom periods. It is not yet clear whether this observation can extend beyond the western Mediterranean Sea.”

*Line 352: You give 4 lognormal modes but no information on uncertainties (such as standard deviation). How many data were used / averaged to get these results? These points are clearly missing here.*

We thank the reviewer for bringing up this point. We have added standard deviations and additional relevant information to Section 3.1 on the size distribution and lognormal mode fitting. We have also modified Figure 1 to show the envelope in the size distributions for both campaigns.

*Line 379. “. . .tested synthetic sea salt with a weir”. Can you clarify. What is the weir?*

A weir is another method of forming bubbles to measure the properties of primary marine aerosol. It is fully described in the text of Sellegri et al. (2006).

*Lines 348-389: You compare well your results with the literature but you do not conclude. Where is the reality? It would be helpful for the reader to know what is supposed to be representative of sea salt modes. Wave channel experiment is the closest to reality?*

In Section 3.1, we have added the following, “Differences in the size distribution of laboratory generated primary marine aerosol found in the literature seem to depend on the method used to generate them. Fuentes et al. (2010) observed 4 modes (modal sizes 14, 48, 124, 334nm) generated from plunging-water jet experiments with artificial seawater. Mode 4 was believed to be linked to splashing water from the jet mechanism. Plunging-water jet experiments were found to most closely mimic the size distribution of ambient primary marine aerosol (Fuentes et al., 2010) while generating sufficient aerosol for characterization measurements."

*Line 396-397: Again you compare your results with the literature but you do not conclude. Your temperature increases by 2 to 5 times more than the one reported by Zabori et al. So what?*

We clarified the following paragraph to showcase where our results were different from previous studies and what this could indicate, "This increase is 2-5× times higher than the 1-2°C hr$^{-1}$ temperature increase measured by Zábori et al. (2012). Even with this large temperature range, we did not observe that the increase in the water temperature affected the shape of the size distribution. We were not able to make qualitative statements about the relationship between the number concentration and temperature, with the level of uncertainty in the wind flow stability within these experiments."

Concerning the relationship between temperature and number concentration, we have removed Figure 5 and subsequent discussion from the manuscript. With more analysis, we were not able to make qualitative statements about the relationship between the number concentration and temperature, with the level of uncertainty in the wind flow stability within these experiments.

*Line 413: ". . . the enriched samples showed similar behavior to the non-enriched waters". Hereafter, you compare your results with the literature but again you do not conclude. I would have said that it is somewhat unexpected. No? Please help the reader and provide conclusions.*

An explanation of the addition of the enriched sea surface microlayer was already provided within the text in Section 3.2, "Additionally, the enriched samples showed similar behavior to the non-enriched waters, indicating that the addition of the organic-rich microlayer had little effect on the water uptake for the aerosols. For the experiments incorporating the enriched microlayer, the entire organic-rich volume was added a few minutes before starting the water jet system, rather than being continuously introduced to the tank throughout the entire experiment. This could have led to microlayer depletion over the course of an experiment, explaining why no visible difference was seen between the enriched and un-enriched samples. However, no clear difference was seen between the first (when the microlayer was present) and subsequent size distributions during a given microlayer enriched experiment."

We have added the following statement to the conclusions, "Additionally, experiments including the enriched sea surface microlayer, which increased organic concentrations, showed no marked difference from the un-enriched mesocosm samples, indicating that enrichment did not influence the water uptake of the primary aerosol at the thermodynamic equilibrium reached in the CCN chamber."

*Lines 429-430: How results at SS=0.39% can be more variable with a standard deviation of 2% compared to SS=0.08% (standard deviation of 7%)?*

We thank the reviewer for this comment. We have changed the text to the following, "At BV, the average activation diameter for SS=0.39% over the course of the experiments was $D_{p,50,avg}$= 59.48±1.1nm (Fig. 5), while at SS=0.08% the average activation diameter was $D_{p,50,avg}$= 141.91±10.8nm (Fig. 6).

*Lines 437-442: I am not convinced by the interpretation of Fig. 6. You are dealing here with very different water conditions showing different organics (chla) that is a major factor controlling CCN activity as stated before. The Temperature in Fig. 6 is simply showing the different water conditions (oligotrophic vs pre-bloom). In this Fig 6, we see an anti-correlation at BV (which is more interesting than comparing BC and BV together). However, without a clear view of the temporal variability of other key parameters (Chla, . . .) it remains difficult to conclude here that temperature is a driving factor controlling CCN activity.*

It is important to note that the temperature of the air shown in Figure 6 is not indicative of the different water conditions (oligotrophic vs. pre-bloom). Bloom periods are dependent upon both the season and weather conditions (multiple sunny days in a row) as well as the nutrient levels in the water and water conditions (water temperature and stratification), but air temperature has not been identified to play a strong factor.

We agree with the reviewer that the idea that air temperature in field experiments could be a factor controlling CCN activity is not well defined and certainly not a conclusion of this work. We have used cautious language to mention this relationship, as it is not previously seen in the literature, and no clear conclusions were drawn from this work. However, we believe it is important to highlight this so that future work may see if in fact the air temperature impacts the emission of small particles. It was outside the scope of this work to study the different biogeochemical parameters dependence on air temperature in detail.

*Line 471: Can you confirm that the results from Pringle et al., were also obtained at SS=0.39%? Otherwise, is it legitimate to compare the kappa value at BC with this paper?*

Kappa values from Pringle et al. (2010) were calculated as global annual mean values, and were not calculated specifically at one SS value, but instead for a bulk chemical composition. In Section 3.3, we now write:

"In BC, the average mesocosm kappa value at SS=0.39% was $\kappa_{avg,BC}$=0.95±0.17. In BV, the average mesocosm kappa values for SS=0.39% and 0.08% are $\kappa_{avg,BV}$=0.45±0.13 and 0.78±0.14, respectively. This indicates that the smaller particles (measured at the higher SS) were higher in organic material. The kappa values obtained at SS=0.08% are more representative of the kappa that would be obtained for a bulk chemical composition, as most of the aerosol mass is comprised in the accumulation mode for submicron particles. Our value then falls well into the suggested range of the kappa average of marine aerosol, $\kappa_{marine}$=0.72±0.24 (Pringle et al., 2010)."

*Section 3.4: As mentioned above (major comments), I am not convinced at all that it is legitimate to draw correlations from 2 different datasets (BC and BV). It is like drawing correlation plots with 2 points only. Not statistically relevant.*

We refer the reviewer to the explanation and figure above. As mentioned there, Gazeau et al., (submitted) contains details and a comparison of the two sites to rationalize comparing the two data sets.

*Line 521: "The parameterization derived in this work is a high estimate . . .". Why ? I cannot find the reason. It is a strong statement since hereafter you propose that chla may not be the only driving force controlling the organic fraction. Later, you mention correlation of r2=0.161 with virus-like. Can we state that r2 of 0.161 is good enough to depict a correlation? (not sure).*

In Figure 7, the parameterization from this work gives a higher organic fraction for a given chla content compared to other published chla-organic fraction parameterizations. This could be due to the size dependence of the organic fraction of the aerosol (with higher organic content for smaller particles) as described in the paper. We now include this in the text: "The parameterization derived in this work lays at higher organic content when compared to other parameterizations, even though it does not include secondary organic contributions as do many of the satellite-receptor site studies. This is likely due to the size dependence of the organic fraction that we observed in the BV data. Our parameterization is applicable for Aitken mode type aerosols and would probably shift towards lower organic content for accumulation mode particles."

We have also modified our discussion of other driving forces controlling the organic fraction, a hypothesis that is investigated using other biological populations and tracers. We now include, "It is also possible that organic components in Mediterranean primary marine aerosol are of multiple origins and not solely linked linearly to chla-rich species.

We have included all correlations to showcase the complexity of the relationship between primary marine aerosol organic fraction and different biogeochemical parameters. We have now calculated the significance of the correlation coefficient and added p values for all the correlations. We found that all of the correlations were significant ($p<0.05$), even when the $R^2$ values were <0.5.

*Line 543: Sentence "However, strong anti-correlations were observed between Mode 1 . . .". I cannot find the figure where we can observe this anti-correlation.*

These figures were not included within the paper; we chose only to discuss the correlation between the mode fitting and the different biogeochemical parameters. We have clarified this within the text.

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## ***Responses to Reviewer #3***

We thank the reviewer for their comments and discussion. The concerns of this reviewer are addressed below.

*General comments*

*Since the main objective of the paper is to compare number size distribution for high and low-productivity episodes, more data/discussion need to be provided for the particle size distribution fittings. This is important part of the paper, yet there is only one figure and one table for " an average size distribution." Based on Fig. 2 I gather that the daily-averaged number fraction of DMPS lognormal modes changed considerably as a function of time for different mesocosms. For example, for BC on 06/29 Mode 1 fraction increased by more than 50% (and modes 2, 3, and 4 decreased correspondingly) for P6. For P3 and C3 changes were not so large. Similar picture is observed for BC on 07/02. The differences were also observed for BV (e.g., 02/23 and 03/03). Since the measurements were carried out continuously, I think the authors should show the errorbars for the variability in the number fraction of DMPS lognormal modes. It is important to clearly demonstrate that this variability in smaller than for example, the differences in Mode 2 particle fractions between BV and BC. Please also show the size distribution fittings separately for BC and BV, accompanied by appropriate statistics. This will help the reader to clearly see the influence of biological productivity on the Aitken mode.*

We thank the reviewer for bringing up this point. We have added the size distribution spread for both campaigns in Figure 1, as well as added the mode fitting standard deviation in the text and within Figure 2. We have also adjusted the language at the beginning of Section 3.1 to now read: "The marine aerosol size distributions remained fairly stable during a given experiment, which lasted around one hour for each water sample. The aerosol size distribution also remained stable throughout the course of each campaign, with a similar distribution shape. Four lognormal modes were fit to the average size distributions of each campaign, with results summarized in Fig. 1 and Table 2. The average size distributions were taken from 214 size distributions for BC and 182 size distributions for BV, and size envelopes are also included within Fig. 1. In order to investigate the size of the aerosol independently of the concentration, the size distributions were normalized using the total aerosol number concentration. We found that the primary marine aerosol size distributions were best described using the three expected modes: nucleation mode (around 20nm), Aitken mode (around 40nm), and accumulation mode (around100nm); and an additional fourth mode around 260nm. Using only three modes for the fitting procedure could not satisfactorily represent the primary marine aerosol size distribution. A mode at around 300nm was also found by Sellegri et al. (2006) during bubbling experiments for which the effect of wind on the surface breaking bubbles was simulated in a similar experiment set-up. The 300nm mode was interpreted by the authors as the result of a thicker bubble film where the bubbles are forced to break by the wind instead of reaching a natural breaking thickness. The four average lognormal modal diameters determined (18.5±0.6, 37.5±1.4, 91.5±2.0, 260±3.2nm) were present in both BC and BV."

*The discussion regarding the role of organics for the increase in the Mode 2 particle fraction on page 26200, line 26 should either be removed or re-written. Chapter 3.1 gives no information to conclude that the increase in particle fraction can be attributed to organic material. The fact that other studies may have seen similar changes in lognormal mode distributions and attributed that to organics is not enough justification.*

We agree that the assumption of organics being responsible for the Aitken particle increase was introduced prematurely in the paper. Indeed, it is the increase of the organic content of the Aitken mode particles reported in Section 3.3 that indicates that the increase in the particle fraction of Mode 2 is likely due to the presence of organics. We have changed to text to better explain this. The text of Section 3.1 now reads:

"Throughout the campaign in BC, the fractions of Modes 1-3 were approximately equal in magnitude (0.297), whereas in BV, the magnitude of the Mode 2 (the Aitken mode) fraction relative to the other modes was dominant (0.48). These same trends were observed for all experiments using SS=0.08% and all the enriched mesocosm samples (Figs. 3-4). When augmenting the bacterial abundance in seawater, Collins et al. (2013) observed an increased particle fraction of the smallest lognormal mode diameter with no change to the shape or magnitude of the size distribution; this was attributed to the replacement of internally mixed salt/organic particle types by insoluble organic type particles. Previous studies have also indicated changing size distributions or mode number fractions with increasing organic material (Fuentes et al., 2010; Sellegri et al., 2006). In the present study, we will examine which chemical component is linked to the increase of the Aitken mode particles in Section 3.3. "

Section 3.3 now includes, "The organic fraction of the Aitken mode particles (obtained from measurements performed at SS=0.39%) is significantly increased during the BV experiment compared to the BC experiment. This indicates that the Mode 2 fraction increase observed in the size distribution is due to the presence of organic matter, in agreement with the observations of Collins et al. (2013)."

*I strongly recommend removal of all the discussion regarding ocean acidification. The fact that some CO2 was pumped in seawater tells noting on how the ocean ecosystems, and therefore carbon content/speciation will change in future scenarios of elevated CO2 and changing climate. Such speculations can lead to the erroneous conclusions.*

We thank the reviewer for this point, however we disagree. We have expanded the discussion of ocean acidification within the introduction to make it clearer why this study is important and how it relates to current and past research. It is important to keep in mind the idea that planktonic organisms have a generation time of a few hours to a few days, and that as such they can react very quickly to an external driver. Many experiments, with some following the same protocol as in this work (mesocosms deployed for multiple days), have already shown that increased $CO_2$ availability could lead to important modifications of planktonic community compositions and functioning. Shifts in organic matter production (increased dissolved form concentrations with increasing $CO_2$) will potentially affect marine aerosol production. We agree that our experimental protocol does not fully reflect the environmental conditions of the ocean in 100 years, mostly because we do not consider other climate change related drivers such as temperatures changes, precipitation levels, changing wind speeds, and more. However, we do believe that performing such experimental work as described here has the potential to bring invaluable information that would ultimately need to be incorporated into models in order to refine our predictions for the future decades.

We have added the following statement to the conclusions to further expand this point, "It is important to note that there are additional effects, such as wind speed, precipitation levels, and temperatures, that could change with future climate change and that these were not included within this analysis; instead, we focused on ocean acidification effects on Mediterranean Sea plankton communities and subsequent effects on primary marine aerosol. Future studies will need to incorporate additional parameters to determine further effects on primary marine aerosol."

*I do not believe I understand Figure 5. How were the error bars calculated? If there are no vertical error-bars (like for many P6 measurements) does that mean that within a day Ntot did not change at all?*

We thank the reviewer for bringing this to our attention. We have decided to remove Figure 5 and subsequent discussion from the manuscript. With more analysis, we were not able to make qualitative statements about the relationship between the number concentration and temperature, with the level of uncertainty in the wind flow stability within these experiments.

*According to the methods description, the covers were elevated to ~10 cm above the top of the mesocosms, allowing air to circulate to avoid a confinement effect in the trapped water. I am just curios what was happening during "dangerous wind and wave conditions?" Unless some additional precautions were taken wouldn't seawater spillover into the mesocosms?*

"Dangerous wind and wave conditions" occurred when sampling would have put researchers on rough seas with strong winds. The reviewer is exactly right about spillover, and in fact, sampling was halted for the BV campaign due to seawater spillover into the mesocosms from the high wave conditions. However, for the data shown here for BC and BV, based on the consistency of CTD measurements, there was no observed encroachment of seawater into the mesocosms.

*Specific comments*

*Page 26190, Line 4 (and elsewhere): Please change "sea salt" to sea spray when referring to primary marine aerosol emission.*
*Page 26190, Line 6: Please note that you are referring to particle diameter when using Dp.*
*Page 26190, Line 22: Please use the plural form of "organic".*
*Page 26193, Line 17: Please change "lower diameters" to "smaller diameters".*
*Page 26198, Line 24: Please define the two supersaturations used here and provide the reason behind the selection.*
*Page 26198, Line 24: Please add the temperature scale to "6◦". Same for "3◦" in Line 27.*

These changes have been made.

*Page 26199, Line 17: Please provide the data for particulate organic carbon concentrations to justify the argument that measured TOC is reported as DOC.*

We have added this information to the text. The text now reads, "Total organic carbon (TOC) was measured instead of dissolved organic carbon (DOC) in order to avoid contamination during filtration. However, the TOC measurement is referred to hereafter as DOC, due to the low concentration of particulate organic carbon in both sites (averaged over all mesocosms and all sampling times, BC: 4.32 ± 0.91 μMol, BV: 11.49 ± 5.50 μMol, which was typically less than 10% of TOC)."

References:

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# Broad changes to Manuscript

(exact language is included in the following pages with track changes)

**Abstract:**

Small details added such as definitions of symbols, the range of the size distribution, and deviations for the log-normal modal diameters

**Introduction:**

More information was added describing the importance of ocean acidification on marine aerosol and biogeochemical parameters. A paragraph was added with information about mesocosm experiments, and why these experiments were performed in the Mediterranean Sea.

**Materials and Methods:**

Information was included to relate the two sampling sites together in order to harmonize the two data sets. Information was included for the $CO_2$ concentrations used for these experiments, and why these experiments took place in pelagic waters.
More information was included to discuss ambient supersaturation levels.
Additional information was provided to discuss why TOC measurements were used in place of DOC measurements.

**Results and Discussion:**

Additional information was provided on the size distributions, including standard deviations, and size envelopes. We have expanded the discussion of how the log-normal modal fitting was determined and compared it to previous work. We have also discussed different generation methods of laboratory generated marine aerosol. More information was provided on how the water temperature was important for these experiments.
We provided more background information in order to compare our kappa values to global marine kappa averages. We have also related the increasing organic fraction during the pre-bloom experiment more closely to the Aitken mode.
We have added p values to all of the correlations in order to show their significance. We have also added sigmoid fits to all of the correlations and discussed these parameters within the manuscript.

**Conclusions**

We have added language to showcase the parameters that were not tested within this work that will still be important in future experiments (i.e. wind speed, precipitation levels, and temperatures). We also compare more clearly experiments with and without the sea surface microlayer.

**Tables:**
We have updated the values to decrease the number of significant digits.

**Figures:**
We have increased the size of the figures and added more information, such as size envelopes in Figure 1 and sigmoid fits in Figures 8 and 9.

# Primary marine aerosol emissions from the Mediterranean Sea during pre-bloom and oligotrophic conditions: correlations to seawater chlorophyll-a from a mesocosm study

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## Abstract

The effect of ocean acidification and changing water conditions on primary (and secondary) marine aerosol emissions is not well understood on a regional or a global scale. To investigate this effect as well as the indirect effect on aerosol that changing biogeochemical parameters can have, ~52 $m^3$ pelagic mesocosms were deployed for several weeks in the Mediterranean Sea during both winter pre-bloom and summer oligotrophic conditions and were subjected to various levels of $CO_2$ to simulate the conditions foreseen in this region for the coming decades. After seawater sampling, primary bubble-bursting aerosol experiments were performed using a plunging water jet system to test both chemical and physical aerosol parameters (10-400nm). Comparing results obtained during pre-bloom and oligotrophic conditions, we find the same four log-normal modal diameters (18.5±0.6, 37.5±1.4, 91.5±2.0, 260±3.2nm) describing the aerosol size distribution during both campaigns, yet pre-bloom conditions significantly increased the number fraction of the second (Aitken) mode, with an amplitude correlated to virus-like particles, heterotrophic prokaryotes, TEPs, chlorophyll-a and other pigments. Organic fractions determined from kappa, $\kappa$, closure calculations for the diameter, $D_p$~50nm, were much larger during the pre-bloom period (64%) than during the oligotrophic period (38%), and the organic fraction decreased as the particle size increased. Combining data from both campaigns together, strong positive correlations were found between the organic fraction of the aerosol and chlorophyll-a concentrations, heterotrophic and autotrophic bacteria abundance, and dissolved organic carbon (DOC) concentrations. As a consequence of the changes in the organic fraction and the size distributions between pre-bloom and oligotrophic periods, we find that the ratio of cloud condensation nuclei (CCN) to condensation nuclei (CN) slightly decreased during the pre-bloom period. The enrichment of the seawater samples with microlayer samples did not have any effect on the size distribution, organic content or the CCN activity of the generated primary aerosol. Partial pressure of $CO_2$, $pCO_2$, perturbations had little effect on the physical or chemical parameters of the aerosol emissions, with larger effects observed due to the differences between a pre-bloom and oligotrophic environment.

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## 1. Introduction

With oceans covering 71% of the Earth’s surface, sea spray aerosol comprises a large portion of the natural aerosol emissions, with an estimated contribution between 2,000 and 10,000Tg $yr^{-1}$ for aerosols with diameter $D_p$<20µm (Gantt and Meskhidze, 2013). Marine aerosol can be

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produced from primary processes (e.g. sea spray aerosol from breaking waves) and secondary processes (i.e. formation via chemical processing or gas-to-particle conversion). These aerosols can then have a large impact upon the Earth's radiative budget through both direct effects, such as light scattering, and indirect effects, by becoming cloud condensation nuclei (CCN) and affecting cloud formation and cloud properties (Novakov and Corrigan, 1996; Novakov and Penner, 1993). Due to the large flux of marine aerosol into the atmosphere, it is critical to better understand and determine the physical and chemical properties of marine aerosol as a function of changing marine environment water conditions.

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At wind speeds greater than 4m s$^{-1}$, primary marine aerosol is primarily formed via bubble bursting from breaking waves; three main types of drops, film, spume and jet drops, are produced depending on the mechanism (Lewis and Schwartz, 2004). Based on the size of aerosol formed, the chemical composition ranges from primarily inorganic sea spray particles to particles rich in organic material, yet different studies have shown differing compositions over the same size range. Typically, particles of diameter $D_p>1$µm have been found to be largely sea salt whereas smaller particles $D_p<1$µm contain increasing concentrations of organics with decreasing diameter (Ault et al., 2013; Facchini et al., 2008; Keene et al., 2007; O'Dowd et al., 2004; Prather et al., 2013). For particles in the size range relevant to cloud formation (50-150nm), some have found an absence of hygroscopic salts in particles below 200nm (Bigg and Leck, 2008), while other studies have shown the presence of sea salt and other inorganic elements (Ault et al., 2013; Clarke et al., 2006; Murphy et al., 1998; Quinn and Bates, 2011). Marine organic species remain largely uncharacterized (Benner, 2002) and organic concentrations can vary drastically throughout the water column, both temporally and spatially (Russell et al., 2010). Primary emissions can gain organics either as bubbles traverse through the water column or at the ocean surface from the organic rich microlayer (Barger and Garrett, 1970; Bigg and Leck, 2008; Blanchard, 1964; Blanchard and Woodcock, 1957; Garrett, 1967; Lion and Leckie, 1981; Matrai et al., 2008). The sea surface microlayer has been shown to exhibit physical, chemical and biological differences from oceanic subsurface water (Cunliffe et al., 2013).

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The primary marine aerosol emission flux is characterized by different source functions, the number of aerosols by particle size by area by time (Lewis and Schwartz, 2004). These source functions are dependent on a number of physical parameters, dominated by wind speed and sea surface temperature, but are also affected by the sea state (wave height, shape, etc.) and salinity (Grythe et al., 2014). Aerosol emissions are also dependent on the chemical

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composition of the seawater due to the presence of a rich and varied mixture of organic material. These organics can affect the waters' ability to form whitecaps (Callaghan et al., 2012) and change bubble lifetime (Garrett, 1967). Large-scale marine aerosol source functions used in models have started to include seawater composition (Langmann et al., 2008; Spracklen et al., 2008; Vignati et al., 2010) by focusing on parameterizations of the correlation between surface water chlorophyll-a (chla) concentrations and aerosol organic fractions (O'Dowd et al., 2008; Rinaldi et al., 2013).

Previous studies have indicated changing size distribution with increasing organic material (Fuentes et al., 2010b; King et al., 2012; Sellegri et al., 2006). Sellegri et al. (2006) saw a log-normal mode amplitude shift towards smaller diameters with the addition of sodium dodecyl sulfate (SDS) to artificial seawater; Fuentes et al. (2010b) observed similar behavior in tests with artificial seawater and biogenic exudates, while King et al. (2012) saw an additional lognormal mode at 200nm with the addition of organic material to artificial seawater. Water temperature has also shown an effect on aerosol size distribution and number concentration, though different groups have seen varying trends. Mårtensson et al. (2003) saw increasing number concentrations for particles >350nm and decreasing concentrations for particles <70nm with increasing water temperature in measurements of synthetic seawater. For all diameters in between, there was no clear trend. Sellegri et al. (2006) compared artificial seawater at 4° and 23°C and found that the lognormal modal diameters all decreased with decreasing water temperature. Zábori et al. (2012b) measured the size distribution of NaCl and succinic acid/NaCl aerosol produced from an impinging water jet over a temperature range from 0 - 16°C and found that the temperature did not influence the size distribution, yet it did influence the magnitude of aerosols produced (increasing temperatures led to decreased aerosol production). The dominance of small particles (dry diameter 10-250nm) decreased with increasing water temperature over the range 0-10°C. Above 10°C, total number concentrations were stable regardless of the temperature. Similar results were found testing winter Arctic Ocean water (Zábori et al., 2012a) and Baltic seawater (Hultin et al., 2011), though for the Baltic seawater, the number concentration continued to drop until a water temperature of ~14°C.

Concentrations of marine organic aerosol seem to be highly dependent on the biological productivity at the ocean surface, following a seasonal bloom cycle. Studies performed at Mace Head in the North Atlantic Ocean and Amsterdam Island in the Southern Indian Ocean determined that the organic concentrations as well as the organic:sea salt ratio were highest in

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the spring/summer and the lowest in the winter (Sciare et al., 2000, 2009; Yoon et al., 2007). Phytoplankton blooms lead to increased levels of organic material (OM), both dissolved and particulate (Ducklow et al., 1995), with dissolved organic carbon (DOC) concentrations often greater than 80µM under bloom conditions (Hansell et al., 2009). Different studies have linked the total submicron organic mass fraction of sea spray aerosol to chla levels observed by satellite (Albert et al., 2012; O'Dowd et al., 2008; Rinaldi et al., 2013; Vignati et al., 2010); other studies have shown that the organic mass fraction was correlated with dimethylsulfide (DMS) (Bates et al., 2012) or heterotrophic bacteria abundance (Prather et al., 2013) instead. Hultin et al. (2010) measured seawater at depths of 2m during an ocean cruise west of Ireland and did not observe a correlation between chla and sea spray production, instead finding a relationship with dissolved oxygen. Rinaldi et al. (2013) found that the correlation between chla and OM at Mace Head was higher than the correlation of colored dissolved organic material or seawater particulate organic carbon; however, the optimum correlation between chla and OM was observed with an eight day time lag for chla, indicating a complex, indirect relationship between biological processes and transferable organic matter. Various studies have shown linear correlations between chla concentrations and organic fraction (O'Dowd et al., 2008; Rinaldi et al., 2013); others have observed exponential fitting correlation (Gantt et al., 2011), a power fit correlation (Fuentes et al., 2011), or a Langmuir functional relationship correlation (Long et al., 2011).

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The CCN activity of marine aerosol has been tested in various laboratory experiments. Fuentes et al. (2010a) determined a plunging water jet system to be the bubble generation method most representative of ambient marine aerosol. In a separate study, Fuentes et al. (2010b) collected seawater samples from the West African coast for CCN measurements with phytoplankton exudates and saw a shift towards higher number concentrations and smaller diameters in samples with high biological material. They found a variable relationship between chla concentrations and OM production, stating that organic enrichment might also be dependent on specific conditions of algal blooms. The same dataset showed an increase in critical supersaturation of 5-24% for the samples with high biological material compared to artificial seawater (Fuentes et al., 2011). Moore et al. (2011) performed laboratory experiments with NaCl or artificial seawater in combination with SDS, *Synechococcus*, *Ostreococcus* or oleic acid and found that 100× the normal organic concentration still did not affect the CCN activity or cloud formation properties. King et al. (2012) tested artificial seawater with different organics (palmitic acid, sodium laurate, fructose, mannose, SDS) and

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found that the number concentration decreased with the presence of stronger surfactants, most likely due to surface layer stabilization. The CCN activity was dependent on the contribution of the varying salts in the particle phase rather than the organics. In recent wave channel experiments with natural seawater, Prather et al. (2013) saw the activation diameter augment from 63 to 118nm after a five-fold increase in bacteria abundance; the size distributions remained essentially unchanged (as did phytoplankton, chla and total organic carbon (TOC) abundances and concentrations), leading to the notion that a change in the sea spray chemical composition (the number fraction mode) must have affected the activation diameter. During the same campaign, Collins et al. (2013) observed the hygroscopicity parameter, $\kappa$, reduce by 86±5% over the same time period as the bacterial increase.

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The production of organic matter in oceanic surface water is expected to be substantially modified in the coming decades as a consequence of climate change and ocean acidification (Doney et al., 2012). Ocean acidification is defined as the increase in ocean acidity and associated changes in seawater chemistry, due to the absorbance of a very significant amount of anthropogenic $CO_2$ by the oceans (2.5 ± 0.5 Gt C or ~26.3% of anthropogenic emissions, Le Quéré et al. (2014)). Since the beginning of the industrial era, the pH in ocean surface waters has already decreased by 0.1 units, on average, equivalent to an increased acidity of 26%. Further acidification is expected by 2100, ranging from 0.06 to 0.32 units, equivalent to an increased acidity of 15 to 110%, depending on the considered $CO_2$ emission scenario (Ciais et al., 2013). Although it is well established that ocean acidification has the potential to significantly impact marine biological processes (see Riebesell and Tortell (2011) and Weinbauer et al. (2011) for a comprehensive review), it is still unclear how these changing biogeochemical water conditions will affect the properties and production of marine aerosols. Furthermore, the effect of such an acidification and consequently the resulting feedback on Mediterranean marine aerosol and the regional climate remains unknown.

Mesocosms are defined as experimental enclosures from one to several thousands of litres that maintain natural communities under close-to-natural conditions (Riebesell et al., 2013). They have been increasingly used in both aquatic and terrestrial ecology (Stewart et al., 2013), especially on the effects of environmental and/or anthropogenic disturbances on a large variety of chemical and biological processes. In the context of ocean acidification, mesocosms have been used on several occasions for experimental time periods spanning from a few days to a few weeks, and were found to be efficient in studying the effects of this driver over such short time scales (Riebesell et al., 2008, 2013). Archer et al. (2013) recently showed, during a

**Deleted:** It is still unclear how changing biogeochemical water conditions will affect properties of marine aerosol. Ocean acidification may impact the chemical composition of seawater by affecting marine viruses (Danovaro et al., 2011), pelagic and heterotrophic organisms (Riebesell and Tortell, 2011; Weinbauer et al., 2011), and non-calcifying organisms (Doney et al., 2009).

mesocosm experiment in the Arctic, that with seawater acidification and increased $CO_2$ concentrations, average concentrations of DMS decreased by up to 60% at the lowest pH. Inversely, concentrations of DMSP, the precursor to DMS, increased by up to 50%. In the remote ocean, DMS was predicted by modeling studies to be one of the main precursors for CCN in the marine boundary layer, and studies have shown that regional DMS emission changes could affect CCN sensitivity (Cameron-Smith et al., 2011; Woodhouse et al., 2013).

**Deleted:** Archer et al. (2013) found that in acidification of Arctic seawater, average concentrations of DMS decreased by up to 60% at the lowest pH; inversely, concentrations of DMSP, the precursor to DMS, increased by up to 50%. In particular, the Mediterranean Sea is a rich and complex marine environment, generally classified as an oligotrophic basin (Bosc et al., 2004; Durrieu de Madron et al., 2011) with maximum open sea area chlorophyll concentrations of 2-3mg $m^{-3}$, though high biological activity occurs annually in parts of the western Mediterranean, including coastal France in the late winter and early spring (D'Ortenzio and Ribera d'Alcalà, 2009; Siokou-Frangou et al., 2010). Mediterranean marine aerosol remains relatively uncharacterized, and it is important to quantify the regional effects of ocean acidification.

Many past mesocosm experiments which focused on the effects of ocean acidification have been performed in relatively eutrophic conditions or with nutrient addition initially or during the experiment. However, about 60% of the ocean surface is associated with low productivity, termed oligotrophic areas. Decreased nutrient availability and the expansion of low productivity regions are projected with increasing $CO_2$ concentrations, as enhanced thermal stratification is expected to lead to surface layer nutrient depletion (Irwin and Oliver, 2009; Polovina et al., 2008). Nutrient availability also might have strong effects on the community response to ocean acidification (Hare et al., 2007), so there is a clear need to evaluate the sensitivity of oligotrophic marine environments to this anthropogenic effect. The Mediterranean Sea is one of the most nutrient-poor waters in the world with maximum open sea area chlorophyll concentrations of 2-3mg $m^{-3}$. Its trophic status varies from oligotrophic-mesotrophic in the northwestern basin to extremely oligotrophic in the eastern basin (Moutin and Raimbault, 2002; The Mermex Group, 2011). High biological activity occurs annually in parts of the western Mediterranean, including coastal France in the late winter and early spring (D'Ortenzio and Ribera d'Alcalà, 2009; Siokou-Frangou et al., 2010).

In this work, we collected water from three mesocosms deployed in the Northwestern Mediterranean Sea over two campaigns during different seasons as part of the European Mediterranean Sea Acidification in a changing climate (MedSeA; http://medsea-project.eu) and the Chemistry-AeRosol Mediterranean Experiment (ChArMEx) projects to test the effects of ocean acidification and changes in the biogeochemistry of the seawater on the physical and chemical properties of primary marine aerosol including size distributions and CCN activity.

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## 2. Materials and Methods

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### 2.1 Measurement sites and campaigns

Mesocosm experiments were performed during two intensive campaigns: the first, during summer oligotrophic conditions (hereafter referred to as non-bloom conditions), occurred from 22 June to 10 July 2012 at the Station de Recherches Sous-marines et Océanographiques in the Bay of Calvi (BC), Corsica; the second, performed during winter pre-bloom conditions, took place from 21 February to 5 March 2013 in the Bay of Villefranche (BV), France. The two bays share many similarities in term of temperature, salinity, phosphate ($PO_4^{3-}$), nitrate+nitrite ($NO_x$), and silicate (Si) seasonal variations, and they both show typical bloom conditions in winter-spring and oligotrophic conditions in the summer, corresponding to a stratified water column. Pre-bloom conditions are also observed at both locations (Gazeau et al., submitted). The presence of pre-bloom and non-bloom conditions was confirmed by the order-of-magnitude difference in the average seawater chla concentrations ($\mathrm{chla}_{BC,avg}$ = 0.069±0.009 mg $m^{-3}$, $\mathrm{chla}_{BV,avg}$ = 1.005±0.125 mg $m^{-3}$). Detailed site and experimental information for both campaigns that legitimize the comparison to test in these two locations at different seasons can be found in Gazeau et al. (submitted).

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Briefly, the mesocosms used in this study (volume of ~52$m^3$) were fully described in Guieu et al. (2014). The mesocosms consisted of large bags made of two 500-µm thick films of polyethylene mixed with vinyl acetate (EVA, 19%) with nylon meshing in between to allow maximum resistance and light penetration (HAIKONENE KY, Finland). Natural seawater was filtered through a mesh grid to remove large debris when deploying the mesocosms. In order to avoid actual atmospheric deposition, the mesocosms were covered with UV-transparent ethylene tetrafluroethylene (ETFE) roofs, except during periods of sampling. In this way, transfer of rainwater/deposition was prevented, while preserving the sunlight irradiance of the mesocosms. The covers were elevated to ~10cm above the top of the mesocosms, allowing air to circulate to avoid a confinement effect in the trapped water. Among nine deployed mesocosms, three remained unmodified as controls and six were modified in terms of partial pressure of $CO_2$, $p\mathrm{CO}_2$. The $p\mathrm{CO}_2$ levels used were slightly different between the two campaigns, as a consequence of different ambient $p\mathrm{CO}_2$ levels (i.e. ~450 vs. 350µatm at BC and BV, respectively). In the Bay of Calvi, the six targeted elevated $p\mathrm{CO}_2$ levels were 550, 650, 750, 850, 1000 and 1250µatm. In the Bay of Villefranche, the levels were 450, 550, 750, 850, 1000 and 1250µatm. These elevated $p\mathrm{CO}_2$ levels were reached by adding varying volumes of $CO_2$ saturated seawater to the mesocosms. At both sites, seawater was pumped from near the mesocosms and sieved onto a 5 mm mesh sieve in order to remove large organisms. Pure $CO_2$ was actively bubbled through the water for several minutes in order to achieve saturation; the water was then transferred to 25L plastic containers for addition to the mesocosms. Depending on the targeted $p\mathrm{CO}_2$ level, 50L to more than 500L were added. A diffusing system was used to ensure a perfect mixing of this $CO_2$ saturated seawater inside the mesocosms. In order to minimize the stress induced by the addition of large quantities of acidified water, the acidification of the mesocosms was performed over 4 days, and the experiments started when the targeted $pCO_2$ levels were reached. The $CO_2$ levels were chosen in order to cover the range of atmospheric $CO_2$ concentrations projected for the end of the century following various scenarios (RCP 2.6 to RCP 8.5; (IPCC, 2013)).

For the experiments described here, every morning approximately 5L of surface water (taken within a 15cm depth from the surface) was pumped from each mesocosm using a perfluoroalkoxy alkane (PFA) pump (St-Gobain Performance Plastics) activated by the pressurized air from a diving tank and connected to braided PVC tubing (Holzelock-Tricoflex, I.D. 9.5mm). The water pump was flushed with seawater from the respective mesocosm prior to sampling. Samples were stored in large brown glass bottles outside (avoiding direct sunlight) until the experiments were performed that same day. During the BV campaign, the pump could not be used on 3 March 2013 due to unsafe sea conditions; water was instead manually sampled from the mesocosms with 2.5L glass bottles while wearing long gloves. Additionally, due to dangerous wind and wave conditions, sampling was not performed on 5 March 2013 during the BV campaign. Instrumental failures occurred on 4 and 10 July 2012 at BC and on 28 February – 1 March 2013 at BV.

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For both campaigns, the mesocosms were located off-shore in pelagic waters in order to measure primary marine aerosol properties and biogeochemical parameters of the water while minimizing contamination from anthropogenic sources. The mesocosms were reached via ocean kayak or boat. For both campaigns, sampling operations were performed from a mobile plastic platform that was moved via a rope network. The water temperature variances between BC and BV are quite drastic, given the time of year the experiments took place. From conductivity, temperature and depth (CTD) measurements, at BC the water temperature measured nearest to the surface varied from 21.8-25.2°C; at BV, the temperatures ranged from 13.0-13.6°C.

For the experiments described here, we focused on three different mesocosms: control mesocosm C3, and acidified mesocosms P3 and P6. Mesocosm P6 was the most acidified of all mesocosms ($pCO_2$~1250µatm), and P3 was acidified to an intermediate level ($pCO_2$~750µatm). This allowed a range of acidification effects to be analyzed.

## 2.2 Experimental methods

Bubble-bursting experiments were performed using a square glass tank (20l×20w×25h cm$^3$), filled with 3.6L of seawater (water depth of ~10cm), sealed with a stainless steel lid and continuously flushed with particle-free air (11LPM). The tank was constantly slightly over-pressured with particle-free air to ensure the absence of ambient room air. Aerosols were generated by splashing mesocosm seawater through plunging water jets, separated into 8 jets via a flow distributor. The mesocosm seawater was re-circulated using a peristaltic pump; to minimize an increasing temperature of the seawater caused by constant re-circulation, a stainless steel heat exchanger was used on the seawater exiting the pump. The temperature of the water was recorded with a temperature sensor at the beginning and end of each experiment (for the BV campaign). Since no measurements of the bubble size distribution could be performed in such a small device, all water flow characteristics were performed according to the Fuentes et al. (2010a) settings, to reproduce the same bubble size distribution. The water flowrate was set to 1.8LPM, the height of the jets above the water surface was 9cm and the penetration depth of the jets was ~7.5cm. Particle-free air was blown over the seawater (using a j-shaped tube ~1.5cm above the water surface) to mimic the wind blowing effect on the bubble-bursting process. Some of the water samples were also enriched by the addition of an organic rich microlayer from the same mesocosms (average 100mL, range 50-170mL). The enriched mesocosm samples were tested after the un-enriched sample to compare the effect of additional organic species.

Blank measurements were performed during the first ten minutes of each experiment by verifying the aerosol concentration was zero in the particle-free air flushed tank. Between each water sample testing, the aquarium and tubing were rinsed with ultrapure water (>18MΩ), and clean water was re-circulated throughout the experimental setup for 10-15 minutes. Experiments were performed on the mesocosm water in different orders each day to make sure there were no experimental biases.

The aerosol flow was passed through a diffusion drier and was sent through a neutralizer into a differential mobility particle sizer (DMPS) and miniature continuous-flow streamwise thermal-gradient CCN chamber (CCNc) (Roberts and Nenes, 2005) to determine particle CCN activation properties. The neutralizer used was a variable-amplitude corona discharge which charges particles to the equilibrium charge distribution (Stommel and Riebel, 2004, 2005). For the BC experiments, the neutralizer voltage was ~2.8kV and for BV, ~2.0kV.

For the CCNc-DMPS system, aerosol flow passed first through a TSI-type DMA (length 44cm) selecting particle sizes in 26 channels ranging from 10-400nm by stepping the voltage over an integration time of about 8 ½ minutes. Immediately after the DMA, the aerosol flow was split between the CCNc and a TSI CPC model 3010. The DMA sheath flow rate was 9LPM and the sample flow rate was 1LPM in BC; 7.5LPM and 1.35LPM was used in BV, respectively. For the BV campaign, the aerosol flow was split 1LPM for the CPC and 0.35LPM to the CCNc. In the CCNc, a total aerosol flow rate of 100sccm with a sheath-to-aerosol flow ratio of 5 was used. The CCNc operated at specific temperature gradient (dT) settings, testing two different supersaturations (SS). For the BC campaign, a temperature gradient of 6°C (dT6) was used in the column and the top temperature of the column varied as the ambient temperature changed ($T_{top} - T_{amb} = 2°C$); in BV, dT6 and a temperature gradient of 3°C (dT3) were tested and the top temperature of the column was always set at 30°C. The data is plotted as activated fraction vs. particle diameter and fit with a sigmoid curve, from which we obtain the activation diameter at each dT (see Asmi et al. (2012) for more details). The CCNc system was calibrated with atomized $(NH_4)_2SO_4$ and NaCl solutions at the beginning, end and throughout each campaign. The activation diameter of the calibration was then used to calculate the corresponding supersaturation; this supersaturation was then used for all mesocosm experiments. The activation diameters and corresponding supersaturations for each dT for both campaigns are shown in Table 1 (dT6=0.39% SS, dT3=0.08%). The range of SS values used in this work is typical of those reported in natural clouds. Anttila et al. (2009) found cloud SS values from 0.18 to 0.26% for low-level clouds in Northern Finland, Hegg et al. (2009) obtained a SS range from 0.2 to 0.3% for clouds over the California coast, and Asmi et al. (2012) found SS values from 0.1 to 0.3% at the puy-de-Dôme station in Central France.

## 2.3 Seawater parameters

Every day at 8:30 (local time), depth-integrated sampling (0 to 10m) was performed in each mesocosm using 5L Hydro-Bios integrated water samplers. Samples for pigment analyses were filtered (2L) onto GF/F. Filters were directly frozen with liquid nitrogen and stored at -80°C. Measurements were performed on an HPLC from filters extracted in 100% methanol, disrupted by sonication and clarified by filtration (GF/F Whatman). Samples for microbial diversity (2mL) were fixed with 0.5% final concentration glutaraldehyde, frozen in liquid nitrogen, and then transferred to a -80°C freezer. Virus-like particles, heterotrophic and autotrophic prokaryotes abundances were measured with the use of Flow Cytometry (Beckton

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Dickinson FACS Calibur model). Total organic carbon (TOC) was measured instead of dissolved organic carbon (DOC) in order to avoid contamination during filtration. However, the TOC measurement is referred to hereafter as DOC, due to the low concentration of particulate organic carbon in both sites (averaged over all mesocosms and all sampling times, BC: 4.32 ± 0.91 µMol, BV: 11.49 ± 5.50 µMol, which was typically less than 10% of TOC). DOC concentrations were determined on 20mL samples by high temperature oxidation with a Shimadzu 5000A TOC Analyzer. Transparent exopolymeric particles (TEPs) concentrations were measured spectrophotometrically according to a dye-binding assay (Engel, 2009). Samples (250mL) were filtered onto 0.4mm pore size polycarbonate filters under low vacuum (<100mm Hg), stained with 1mL of Alcian blue solution (0.02g Alcian blue in 100mL of acetic acid solution of pH2.5) and rinsed with 1mL of distillate water. Filters were then soaked for 3h in 6mL of 80% sulfuric acid ($H_2SO_4$) to dissolve the dye, and the absorbance of the solution was measured at 787nm, using acidic polysaccharide xanthan gum as a standard.

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## 3. Results and Discussion

In studying the effects of ocean acidification, it was necessary to observe whether changes with biogeochemical processes affected primary marine aerosol emissions and chemical and physical aerosol properties. For many of the parameters studied (e.g. chla concentrations, total prokaryotic cells and virus-like particles abundances), there were no strong discernible differences between the control, C3, or the acidified mesocosms, P3 and P6 along the course of the experiments; however, there were often large differences between the two campaigns due to the pre-bloom and non-bloom conditions. While several studies have shown the effects of ocean acidification on biogeochemical parameters in eutrophic waters (Galgani et al., 2014; Schulz et al., 2013), observations from the MedSea experiment showed no effect of ocean acidification on most of the biogeochemical parameters in these oligo- to mesotrophic areas. These results are discussed more fully in Gazeau et al. (submitted). As a consequence, we did not expect any impact on the primary marine aerosol physical aerosol properties. In the following sections, we will relate trends observed with different biogeochemical parameters to those observed in the primary marine aerosol.

### 3.1 Aerosol Size Distributions and Number Concentration

The marine aerosol size distributions remained fairly stable during a given experiment, which lasted around one hour for each water sample. The aerosol size distribution also remained stable throughout the course of each campaign, with a similar distribution shape. Four lognormal modes were fit to the average size distributions of each campaign, with results summarized in Fig. 1 and Table 2. The average size distributions were taken from 214 size distributions for BC and 182 size distributions for BV, and size envelopes are also included within Fig. 1. In order to investigate the size of the aerosol independently of the concentration, the size distributions were normalized using the total aerosol number concentration. We found that the primary marine aerosol size distributions were best described using the three expected modes: nucleation mode (around 20nm), Aitken mode (around 40nm), and accumulation mode (around100nm); and an additional fourth mode around 260nm. Using only three modes for the fitting procedure could not satisfactorily represent the primary marine aerosol size distribution. A mode at around 300nm was also found by Sellegri et al. (2006) during bubbling experiments for which the effect of wind on the surface breaking bubbles was simulated in a similar experiment set-up. The 300nm mode was interpreted by the authors as the result of a thicker bubble film where the bubbles are forced to break by the wind instead of reaching a natural breaking thickness. The four average lognormal modal diameters determined (18.5±0.6, 37.5±1.4, 91.5±2.0, 260±3.2nm) were present in both BC and BV. The lognormal mode fitting was also used to determine the particle number fraction at each lognormal modal diameter. Looking at the number fractions on a daily temporal scale for SS=0.39%, the lognormal mode number fractions remained relatively constant throughout both campaigns, though differences were noted between the campaigns (Fig. 2, Table 2). Throughout the campaign in BC, the fractions of Modes 1-3 were approximately equal in magnitude (0.297), whereas in BV, the magnitude of the Mode 2 (the Aitken mode) fraction relative to the other modes was dominant (0.48). These same trends were observed for all experiments using SS=0.08% and all the enriched mesocosm samples (Figs. 3-4). When augmenting the bacterial abundance in seawater, Collins et al. (2013) observed an increased particle fraction of the smallest lognormal mode diameter with no change to the shape or magnitude of the size distribution; this was attributed to the replacement of internally mixed salt/organic particle types by insoluble organic type particles. Previous studies have also indicated changing size distributions or mode number fractions with increasing organic material (Fuentes et al., 2010b; Sellegri et al., 2006). In the present study, we will examine which chemical component is linked to the increase of the Aitken mode particles in Section 3.3.

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Many other studies have found different lognormal mode distributions of both artificial and natural seawater samples, though many have similar modal sizes. Differences in the size distribution of laboratory generated primary marine aerosol found in the literature seem to depend on the method used to generate them. Fuentes et al. (2010a) observed 4 modes (modal sizes 14, 48, 124, 334nm) generated from plunging-water jet experiments with artificial seawater. Mode 4 was believed to be linked to splashing water from the jet mechanism. Plunging-water jet experiments were found to most closely mimic the size distribution of ambient primary marine aerosol (Fuentes et al., 2010a) while generating sufficient aerosol for characterization measurements. In a separate study (Fuentes et al., 2010b), 4 modes represented both artificial and natural seawater (modal sizes 15, 45, 125, 340nm) well. Similar to our findings, increasing organic content was found to increase the number fraction of Mode 2 while decreasing the relative fractions of the other modes. In similar experiments with Baltic seawater collected between May and September, Hultin et al. (2011) observed either two lognormal modes (site: Askö, 86, 180nm) or three lognormal modes (site: Garpen, 93, 193, 577nm). Sellegri et al. (2006) tested synthetic sea salt with a weir and observed 3 lognormal modes (4°C: 30, 85, 200nm; 23°C: 45, 110, 300nm). After adding SDS, they noticed an increase in the fraction of particles at the smallest lognormal diameter. In synthetic seawater experiments with sintered glass filters, Mårtensson et al. (2003) observed one submicron lognormal mode (100nm); Tyree et al. (2007) observed a lognormal mode at the same diameter using artificial and natural seawater with pore diffusers. The Mårtensson et al. (2003) and Tyree et al. (2007) studies using sintered glass filters or pore diffusers report relatively different size distributions compared to those obtained by plunging jet experiments, likely due to the bubble formation processes. Collins et al. (2013) observed three lognormal modes in seawater wave channel experiments (~90, 220, 1000nm), with changing number fractions as described in the above paragraph.

Temperature has also been shown to affect size distributions and aerosol number concentrations (Hultin et al., 2011; Mårtensson et al., 2003; Zábori et al., 2012a). The initial and final water temperatures were measured over the course of an experiment (~1hr, BV only); the water temperature was found to increase by 4.6±1.2°C $hr^{-1}$ on average due to the constant water recirculation through the peristaltic pump and an insufficient heat exchange system (encompassing all experiments, water temperatures ranged from ~11.7-26.8°C from the initial to final measurement). This increase is 2-5× times higher than the 1-2°C $hr^{-1}$ temperature increase measured by Zábori et al. (2012a). Even with this large temperature

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range, we did not observe that the increase in the water temperature affected the shape of the size distribution. We were not able to make qualitative statements about the relationship between the number concentration and temperature, with the level of uncertainty in the wind flow stability within these experiments. Acidification had no effect on the aerosol size distribution, as no clear differences were found between mesocosms C3, P3, and P6 within a given field campaign.

## 3.2 Activation Diameter

By testing two temperature gradients, it is possible to look at the hygroscopic properties of different size particles based on the different supersaturations at which they are activated. The activation diameter time series measured at SS=0.39% (dT6) is shown in Fig. 5. In BC, there is little variation temporally between the control and acidified mesocosms tested ($D_{p,50,avg}$=46.47±0.88nm), indicating that acidification does not have a large direct effect on CCN activity. Additionally, the enriched samples showed similar behavior to the non-enriched waters, indicating that the addition of the organic-rich microlayer had little effect on the water uptake for the aerosols. For the experiments incorporating the enriched microlayer, the entire organic-rich volume was added a few minutes before starting the water jet system, rather than being continuously introduced to the tank throughout the entire experiment. This could have led to microlayer depletion over the course of an experiment, explaining why no visible difference was seen between the enriched and un-enriched samples. However, no clear difference was seen between the first (when the microlayer was present) and subsequent size distributions during a given microlayer enriched experiment. In past experiments, the addition of organics to bubbling experiments have shown changes in the size distribution (Sellegri et al., 2006), particle number concentration (Fuentes et al., 2010b; King et al., 2012; Tyree et al., 2007), and CCN activity (Collins et al., 2013; Fuentes et al., 2011). Other experiments have shown no visible change (Moore et al., 2011) from the addition of organics, similar to the experiments performed in this study. In some studies, the concentrations and/or nature of some of the organic surfactants were unrealistic (King et al., 2012; Moore et al., 2011; Sellegri et al., 2006). At BV, the average activation diameter for SS=0.39% over the course of the experiments was $D_{p,50,avg}$= 59.48±1.1nm (Fig. 5), while at SS=0.08% the average activation diameter was $D_{p,50,avg}$= 141.91±10.8nm (Fig. 6). Activation diameters larger than the corresponding salt standards (here, shown as NaCl), indicating higher organic presence, are observed more at BV than BC for SS=0.39% due to the organic pre-bloom conditions, whereas the non-bloom water conditions were very stable at BC. For SS=0.08%, the

**Deleted:** However, there was no discernible clear correlation between the number concentration and average water temperature, in contrast to previous studies (Fig. 5). For any given experiment, the size distribution magnitude and the observed total number concentration increased, decreased or remained constant over the course of the BV campaign, indicating that the temperature effects could have been obscured by the natural variance of the plunging jet bubbling technique.

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activation diameters are very similar to the NaCl standard, which signifies a lower organic fraction for larger particles. Activation diameters for individual mesocosms in both campaigns are shown in Table 3.

There is an anti-correlation of the activation diameter at SS=0.39% with the ambient average air temperature in BV (Fig. 5), though no correlation exists with SS=0.08% (Fig. 6), or in BC (Fig. 5). However, more daily temperature variance was observed in BV than BC, based on the time of year of the campaigns. This anti-correlation could indicate an additional temperature impact on the emission of small particles (~50nm) and their chemical composition, though this effect is unclear and undocumented in the literature.

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We investigated if the observed differences in the activation diameters from BC and BV could be linked to the different operating techniques used for the campaigns. As indicated previously, $T_{top}$ in BC was variable, changing as the ambient temperature changed. As the ambient temperature changed throughout the day, the temperature in the column would also change, leading to possible temperature instabilities throughout the course of an experiment. On the contrary, in BV, $T_{top}$ was fixed at 30°C, a temperature higher than the daily temperature variability. In this way, temperature fluctuations in the column were avoided. However, in observing the measured temperatures throughout the column for both campaigns and all the experiments, the temperatures of the column remained quite stable for both methods of operation, so we believe that these effects are very minor. Additionally, it has been shown that organics can volatilize in the CCN column due to the temperature gradient (Asa-Awuku et al., 2009), biasing observed CCN activity. It is possible that this occurred for both campaigns based on the relatively high measured operating temperatures observed in the column; if organic material was volatilized, the activation diameters would increase from those shown here.

## 3.3 Kappa and Organic Fraction

The hygroscopicity of the aerosol was determined using kappa-Köhler theory (Petters and Kreidenweis, 2007) following Asmi et al. (2012). Using the activation diameter and numerical iteration, the kappa value was determined when the maximum of the saturation curve was equal to the supersaturation in the CCNc, following,

$$S(D_p) = \frac{D_p^3 - D_{p,50}^3}{D_p^3 - D_{p,50}^3(1-\kappa)} \exp\left(\frac{4\sigma_w M_w}{RT\rho_w D_p}\right) \qquad (1)$$

where $S$ is the supersaturation, $D_p$ is the diameter of the droplet, $D_{p,50}$ is the dry diameter, $R$ is the gas constant, $T$ is temperature, and $\sigma_w$, $M_w$, and $\rho_w$ are the surface tension, molecular weight and density of water, respectively. Lower kappa values correspond to more hydrophobic, or organic-like, particles. In BC, the average mesocosm kappa value at SS=0.39% was $\kappa_{avg,BC}$=0.95±0.17. In BV, the average mesocosm kappa values for SS=0.39% and 0.08% are $\kappa_{avg,BV}$=0.45±0.13 and 0.78±0.14, respectively. This indicates that the smaller particles (measured at the higher SS) were higher in organic material. The kappa values obtained at SS=0.08% are more representative of the kappa that would be obtained for a bulk chemical composition, as most of the aerosol mass is comprised in the accumulation mode for submicron particles. Our value then falls well into the suggested range of the kappa average of marine aerosol, $\kappa_{marine}$=0.72±0.24 (Pringle et al., 2010).. Little variance was seen between the control and acidified mesocosms.

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Using the calculated kappa values, we determined the organic fraction using a kappa closure equation,

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$$\kappa_{total} = \varepsilon_{org}\kappa_{org} + (1-\varepsilon_{org})\kappa_{inorg} \qquad (2)$$

where $\varepsilon_{org}$ is the bulk volume fraction of organic material and $\kappa$ is the kappa of the organic or inorganic material. Following Collins et al. (2013), we used $\kappa_{inorg}$=1.25, a good proxy for seawater, and $\kappa_{org}$=0.006. In BC, the organic fraction ranged from -0.21 to 0.46 (average, 0.24±0.14) for SS=0.39%. For BV, the organic fraction ranged from 0.43-0.80 (average, 0.64±0.11) for SS=0.39% and 0.19-0.55 (average, 0.38±0.11) for SS=0.08%. Previous studies have also found mass organic fractions ranging from 30-80% in sea spray aerosol studies of water from the Northern Atlantic, Sargasso Sea near Bermuda, and Pacific water near La Jolla, California (Collins et al., 2013; Facchini et al., 2008; Keene et al., 2007). Negative organic fractions were calculated during the BC campaign due to the sensitivity of Eq. (2) to the value of $\kappa_{inorg}$ over $\kappa_{org}$. We show results here using a $\kappa_{inorg}$ value supported by literature rather than determine non-realistic $\kappa_{inorg}$ values to provide positive organic fractions. Therefore, the values shown in this work can be considered low estimates of the organic fraction. Table 3 shows average kappa and organic fraction values of each mesocosm for both campaigns.

The organic fraction of the Aitken mode particles (obtained from measurements performed at SS=0.39%) is significantly increased during the BV experiment compared to the BC experiment. This indicates that the Mode 2 fraction increase observed in the size distribution is due to the presence of organic matter, in agreement with the observations of Collins et al. (2013)

The ratio of cloud condensation nuclei (CCN) to condensation nuclei (CN) decreased slightly during the pre-bloom period for SS=0.39%: at BC, $CCN/CN_{average}=0.55\pm0.03$ whereas at BV, $CCN/CN_{average}=0.45\pm0.07$. The change between CCN/CN during the oligotrophic and pre-bloom conditions was likely due to the combined effects of a higher organic fraction and higher Mode 2 to Mode 1 ratio during pre-bloom conditions, likely caused by the increasing organic content of the water due to the pre-bloom. For SS=0.08% measured at BV, $CCN/CN_{average}=0.15\pm0.02$.

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## 3.4 Correlations with biological parameters

In a recent study, Rinaldi et al. (2013) showed that chla was the best biological surrogate for predicting organic enrichment in sea spray. Chla parameterizations are currently being used in models to account for the organic content of seawater. We find a strong linear correlation with same-day measurements of organic fraction (from SS=0.39%) and total chla concentrations ($R^2=0.781$, $p<0.00001$) shown in log-log scale in Fig. 7 following

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$$\text{Organic Fraction[\%]} = 42.28 \times \text{(chla)[mg m}^{-3}\text{]} + 22.98 \qquad (3)$$

Similar correlations were also found with a number of pigments: chlorophyll c1+c2 ($R^2=0.783$, $p<0.00001$), 19’-butanoyloxyfucoxanthin ($R^2=0.711$, $p<0.00001$), alloxanthin ($R^2=0.699$, $p<0.00001$), sum carotenes ($R^2=0.773$, $p<0.00001$) and 19’-hexanoyloxyfucoxanthin ($R^2=0.736$, $p<0.00001$) (Fig. 8). Various studies have found linear correlations between the organic fraction of aerosols measured at a receptor site and chla concentrations observed by satellite along the back-trajectory (Langmann et al., 2008; O'Dowd et al., 2008; Rinaldi et al., 2013; Vignati et al., 2010); others have found exponential fittings (Gantt et al., 2011) with the same methodology or a Langmuir functional relationship (Long et al., 2011) using a model with experimental data from Facchini et al. (2008) and Keene et al. (2007). Fig. 7 shows many of the existing chla-organic fraction parameterizations in the literature, including this work. It is clear that many of the parameterizations from the Northern Atlantic Ocean also describe the correlation in the Mediterranean Sea fairly well,

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even though the methodologies for most of them are very different from the one used in this study. The parameterization derived in this work lays at higher organic content when compared to the other parameterizations, even though it does not include secondary organic contributions as do many of the satellite-receptor site studies. This is likely due to the size dependence of the organic fraction that we observed in the BV data. Our parameterization is applicable for Aitken mode type aerosols and would probably shift towards lower organic content for accumulation mode particles. It is also possible that organic components in Mediterranean primary marine aerosol are of multiple origins and not solely linked linearly to chla-rich species. Bacteria have also been observed to affect the organic material in seawater (Gruber et al., 2006; Jiao et al., 2010; Ogawa et al., 2001). We find a correlation with heterotrophic prokaryotes ($R^2=0.476$, $p=1.3\times10^{-5}$), virus-like particles ($R^2=0.161$, $p=0.025$), autotrophic prokaryotes ($R^2=0.499$, $p<0.00001$) and *Synechococcus* abundance ($R^2=0.143$, $p=0.033$), shown in Fig. 9A-D. In a wave channel experiment on natural seawater doped with Zobell growth medium, bacteria and phytoplankton (*Dunaliella tertiolecta*) cultures, Prather et al. (2013) also observed a link between heterotrophic bacteria and organic fraction while no correlation with chla was found, highlighting the necessity to study complex systems of all biological material (phytoplankton, prokaryotes, organic matter) for marine aerosol. Most likely, the observed differences between Prather et al. (2013) and this work have to do with the localized biogeochemical nature of the different experiments, causing variance in the chemical composition and organic fraction of the marine aerosol. An additional correlation ($R^2=0.477$, $p=1.2\times10^{-5}$) exists with TEPs (Fig. 9E), a surface-active complex, variable mixture of organics (Filella, 2014; Passow, 2012). During BC, there is also a sigmoidal correlation between organic fraction and DOC concentrations ($\chi^2=0.411$, $p<0.00003$); data are unavailable for BV (Fig. 9F). Sigmoid fits are also shown in Figs. 8 and 9 for all biological parameters where they could be determined. Sigmoid fits might be more appropriate to use in many cases, to conceptually constrain the organic fraction of the primary marine aerosol to one regardless of the chla concentration. We have included both linear and sigmoid fits, with their respective $R^2$ and $\chi^2$ values for completeness.

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We also wanted to see if correlations existed between different biogeochemical parameters and the temporal relative mode fractions shown in Fig. 2. Relative fractions of Modes 3 and 4 (91.5 and 260nm, respectively) showed no clear correlations to any parameter. However, strong anti-correlations were observed between the Mode 1 (18.5nm) relative fraction and the abundances and concentrations of virus-like particles, heterotrophic prokaryotes and all

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pigments previously discussed, except for alloxanthin, which had a positive correlation (correlations not shown). The relative fraction of Mode 2 (37.5nm) showed strong positive correlations with the abundances and concentrations of virus-like particles, heterotrophic prokaryotes, TEPs and all the pigments discussed, except for alloxanthin, where no correlation was observed (correlations not shown). This further supports the idea of an increase in the Mode 2 (Aitken mode) relative fraction during periods of high biological activity due to the higher concentrations of organic material, at the expense of Mode 1.

The control and acidified mesocosms showed no significant differences in terms of correlations between organic fraction and different biogeochemical parameters. For studies of marine aerosol, this indicates that any acidification effects on these biological parameters impacts the physical and chemical parameters of the aerosol much less than the natural variances caused by organic pre-bloom and bloom periods. It is not yet clear whether this observation can extend beyond the western Mediterranean Sea. However, it is important to note that due to the oligotrophic nature of the Mediterranean, even during the pre-bloom conditions at BV, the chla concentrations and abundances of other parameters are still much lower than could occur in places like the North Atlantic Ocean.

## 4. Conclusions

By performing marine aerosol bubble-bursting experiments over two large-scale campaigns, we were able to compare the effects of ocean acidification during pre-bloom and oligotrophic conditions on physical and chemical properties of Mediterranean Sea aerosol. It is important to note that there are additional effects, such as wind speed, precipitation levels, and temperatures, that could change with future climate change and that these were not included within this analysis; instead, we focused on ocean acidification effects on Mediterranean Sea plankton communities and subsequent effects on primary marine aerosol. Future studies will need to incorporate additional parameters to determine further effects on primary marine aerosol. Ocean acidification had no direct effect on the physical parameters (size distribution, mode diameter and number fraction) measured in either campaign, with similar trends seen for all three differently acidified mesocosms. Additionally, experiments including the enriched sea surface microlayer, which increased organic concentrations, showed no marked difference from the un-enriched mesocosm samples, indicating that enrichment did not influence the water uptake of the primary aerosol at the thermodynamic equilibrium reached in the CCN chamber.

Pre-bloom conditions at BV showed marked increases in the activation diameters and organic fractions (~64%) for all the mesocosms at SS=0.39% compared to non-bloom conditions at BC (~24%). At BV, larger particles (SS=0.08%) had smaller organic fractions (~38%). The organic fraction was strongly correlated with chla and additional pigment concentrations, with weaker correlations observed for heterotrophic and autotrophic prokaryotes, virus-like particles, and *Synechococcus* abundances, and TEPs and DOC concentrations. Many of these correlations corresponded specifically with the increase in Mode 2 (the Aitken mode) and were anti-correlated with Mode 1 during the pre-bloom period. The CCN/$CN_{average}$ ratio also decreased during the pre-bloom period at BV as a probable consequence of the increased organic content during a pre-bloom period. The parameterization of the primary marine aerosol organic fraction as a function of chla derived in the present work is a high estimate compared to the gathered parameterizations from the literature (with a higher organic fraction for a given chla content), which may confirm that species other than chla-rich species contribute to the organic content of marine aerosols in the Mediterranean atmosphere.

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## Author Contribution

K.S., F.G., C.G. designed the experiments and A.N.S., C.R., E.A., K.S. carried them out. Enriched microlayer data were provided by A.E. and W.L.; pigment data were provided by A.S. and F.G.; TEPs data were provided by S.M., M.-L.P., F.I., and S.A.; bacteria and virus data were provided by S.M., M.-L.P., A.T., and P.P; and DOC data were provided by J.L and C.G. A.N.S. and K.S. prepared the manuscript with contributions from all co-authors.

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Table 1. Calibration information at varying temperature gradients for NaCl (35g/L) in tank

| Temperature Gradient | Activation Diameter (nm) | Supersaturation, SS (%) |
|---|---|---|
| dT6 | 42.497±1.82 | 0.39 |
| dT3 | 122.915±8.65 | 0.08 |

Table 2. Modal diameter (nm) and number fraction averages from the size distributions for both campaigns, including data from both supersaturations and microlayer enriched experiments. Lognormal modal diameters and number fractions from Fuentes et al. (2010a) are also shown.

| | BC (SS=0.39% and enriched) | | BV (SS=0.39%+0.08% and enriched) | | Artificial Sea Water Fuentes et al., (2010) | |
|---|---|---|---|---|---|---|
| | Diameter | Fraction | Diameter | Fraction | Diameter | Fraction |
| Mode 1 | 17 ± 1.2 | 0.32 | 20 ± 0.07 | 0.19 | 14 | 0.38 |
| Mode 2 | 38 ± 1.3 | 0.30 | 37 ± 2.5 | 0.48 | 48 | 0.32 |
| Mode 3 | 91 ± 2.1 | 0.27 | 92 ± 3.4 | 0.24 | 124 | 0.17 |
| Mode 4 | 260 ± 2.0 | 0.11 | 260 ± 6.0 | 0.09 | 334 | 0.13 |

Table 3. Average activation diameters, kappa values and organic fractions for both campaigns and supersaturations.

| | | Mesocosm | Activation Diameter (nm) | $\kappa$ | Organic Fraction |
|---|---|---|---|---|---|
| BC | SS = 0.39% | C3 | 47.5 ± 1.6 | 0.88 ± 0.11 | 0.29 ± 0.09 |
| | | C3, enriched | 46.8 ± 4.1 | 0.92 ± 0.08 | 0.26 ± 0.07 |
| | | P3 | 45.8 ± 1.8 | 1.00 ± 0.19 | 0.20 ± 0.16 |
| | | P3, enriched | 48.9 ± 6.1 | 0.81 ± 0 | 0.35 ± 0 |
| | | P6 | 45.7 ± 1.6 | 1.00 ± 0.23 | 0.20 ± 0.18 |
| | | P6, enriched | 46.7 ± 3.4 | 0.93 ± 0.08 | 0.26 ± 0.06 |
| BV | SS=0.39% | C3 | 61.8 ± 2.2 | 0.40 ± 0.09 | 0.68 ± 0.07 |
| | | C3, enriched | 51.9 ± 4.8 | 0.68 ± 0 | 0.46 ± 0 |
| | | P3 | 61.2 ± 2.1 | 0.41 ± 0.12 | 0.67 ± 0.10 |
| | | P6 | 59.1 ± 1.9 | 0.47 ± 0.15 | 0.63 ± 0.12 |
| | | P6, enriched | 53.9 ± 3.6 | 0.61 ± 0.10 | 0.52 ± 0.08 |
| | | Outside | 54.2 ± 3.6 | 0.59 ± 0.14 | 0.53 ± 0.11 |
| | | Outside, enriched | 55.5 ± 3.0 | 0.55 ± 0.07 | 0.56 ± 0.05 |
| | SS= 0.08% | C3 | 146.0 ± 16.6 | 0.72 ± 0.14 | 0.43 ± 0.12 |
| | | C3, enriched | 148.5 ± 37.1 | 0.69 ± 0 | 0.45 ± 0 |
| | | P6 | 137.1 ± 15.5 | 0.87 ± 0.13 | 0.31 ± 0.11 |

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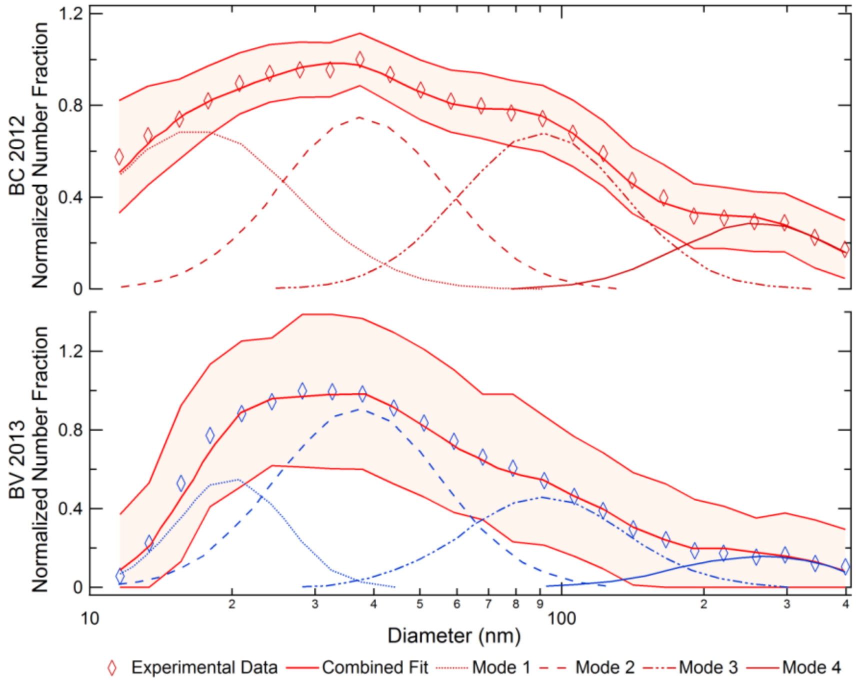

Figure 1. Average size distributions for each campaign (Bay of Calvi, BC, and Bay of Villefranche, BV) fit with 4 lognormal modes. Each campaign average is taken from the supersaturations (SS=0.08% & 0.39%) used for all three mesocosms and includes all enriched samples as well.

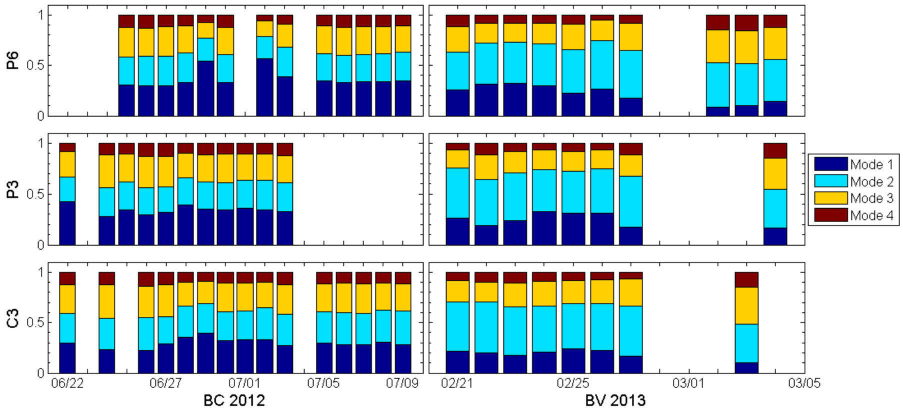

Figure 2. Number fraction of DMPS lognormal modes from all mesocosms (SS=0.39%) at BC and BV.

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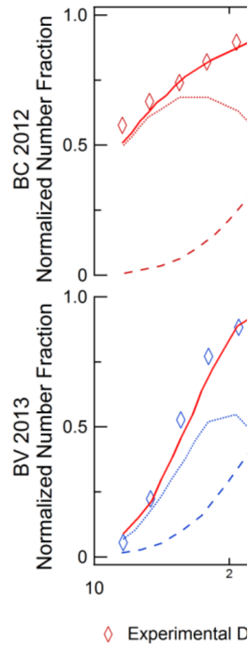


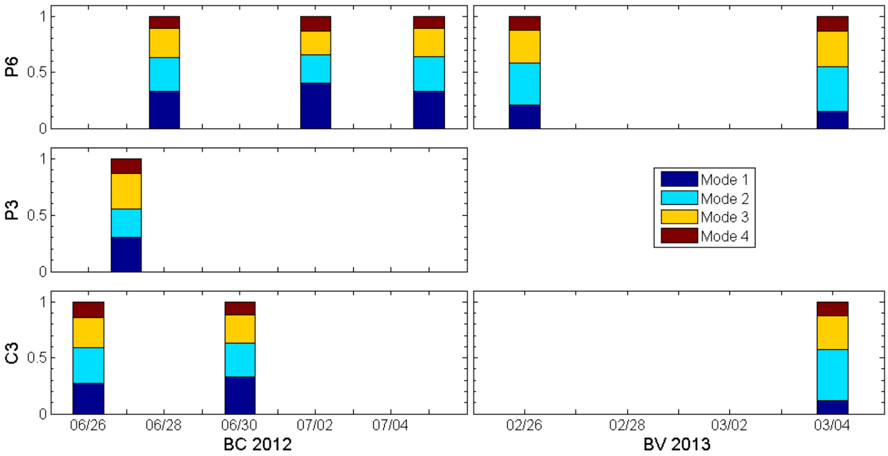


Figure 3. Number fraction of DMPS lognormal modes from microlayer enriched samples (SS=0.39%) at BC and BV.

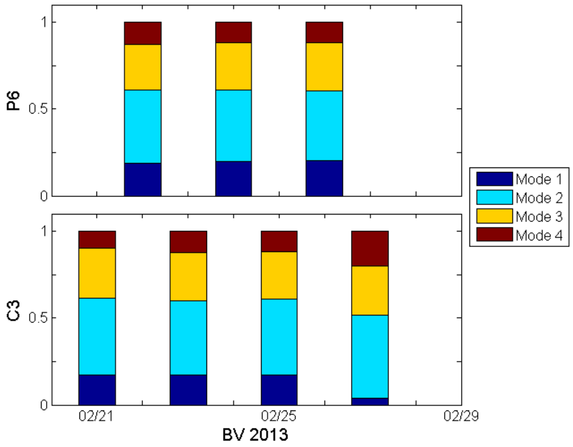


Figure 4. Number fraction of DMPS lognormal modes tested at SS=0.08% for mesocosms C3 and P6 at BV.

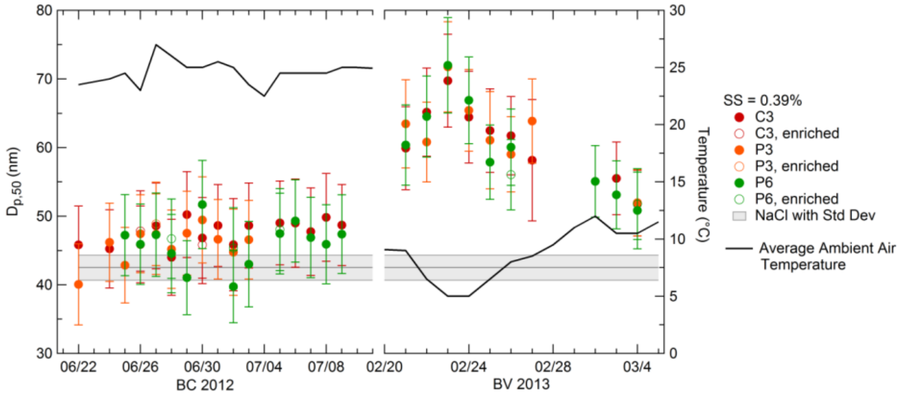


Figure 5. Activation diameter and ambient air temperatures for BC and BV. Data is shown for SS=0.39% (dT6), including the microlayer enriched experiments. The shaded bar indicates the NaCl activation diameter at the given supersaturation.

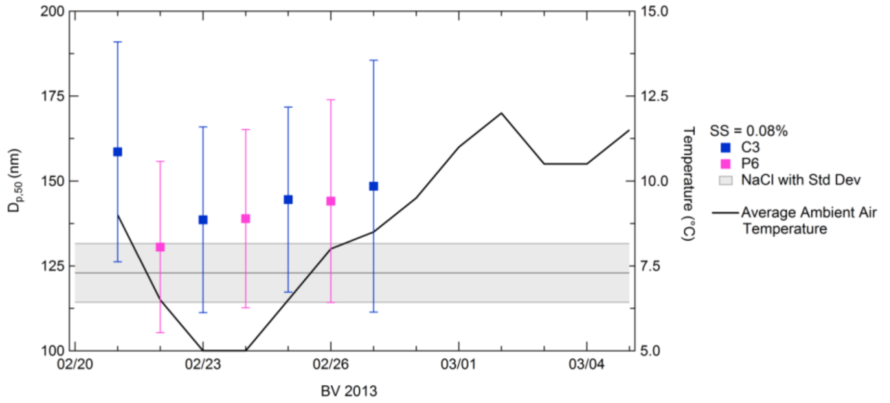
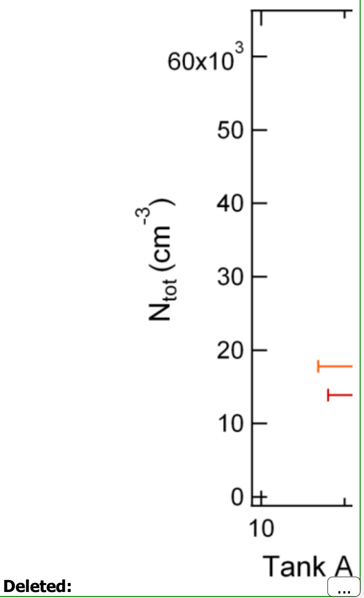


Figure 6. Activation diameter and ambient air temperatures for BV. Data is shown for SS=0.08% (dT3). The shaded bar indicates the NaCl activation diameter.



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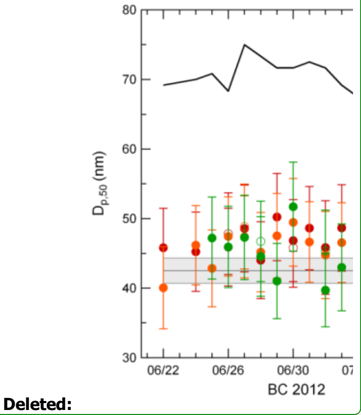

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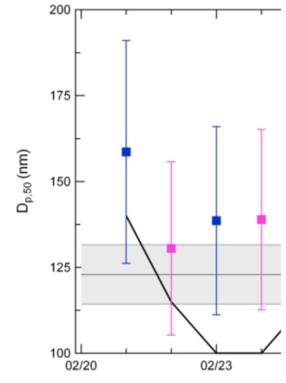

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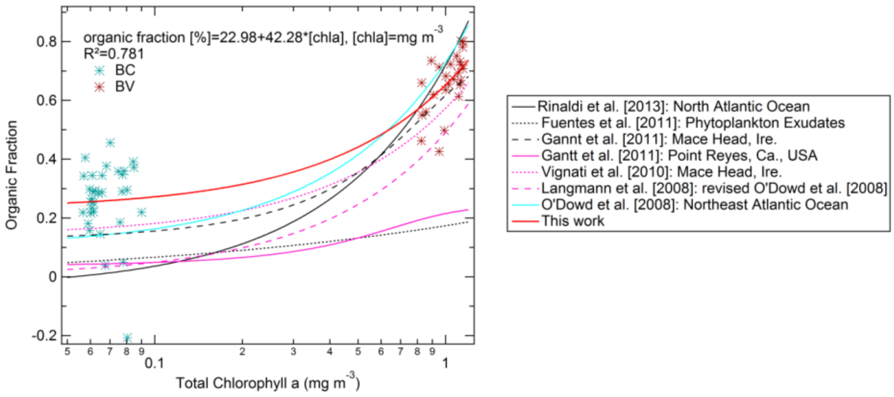

Figure 7. Organic fraction calculated from kappa ($\kappa_{org}$=0.006 and $\kappa_{inorg}$=1.25) at SS=0.39% vs. total chlorophyll-a concentrations (mg m$^{-3}$) for all 3 mesocosms during both BC and BV, fit with published parameterizations of the organic fraction-chla relationship.

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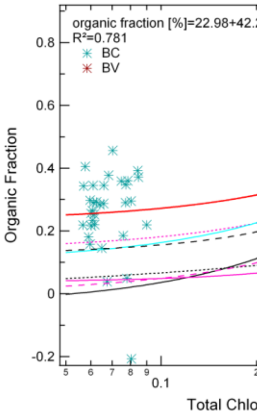

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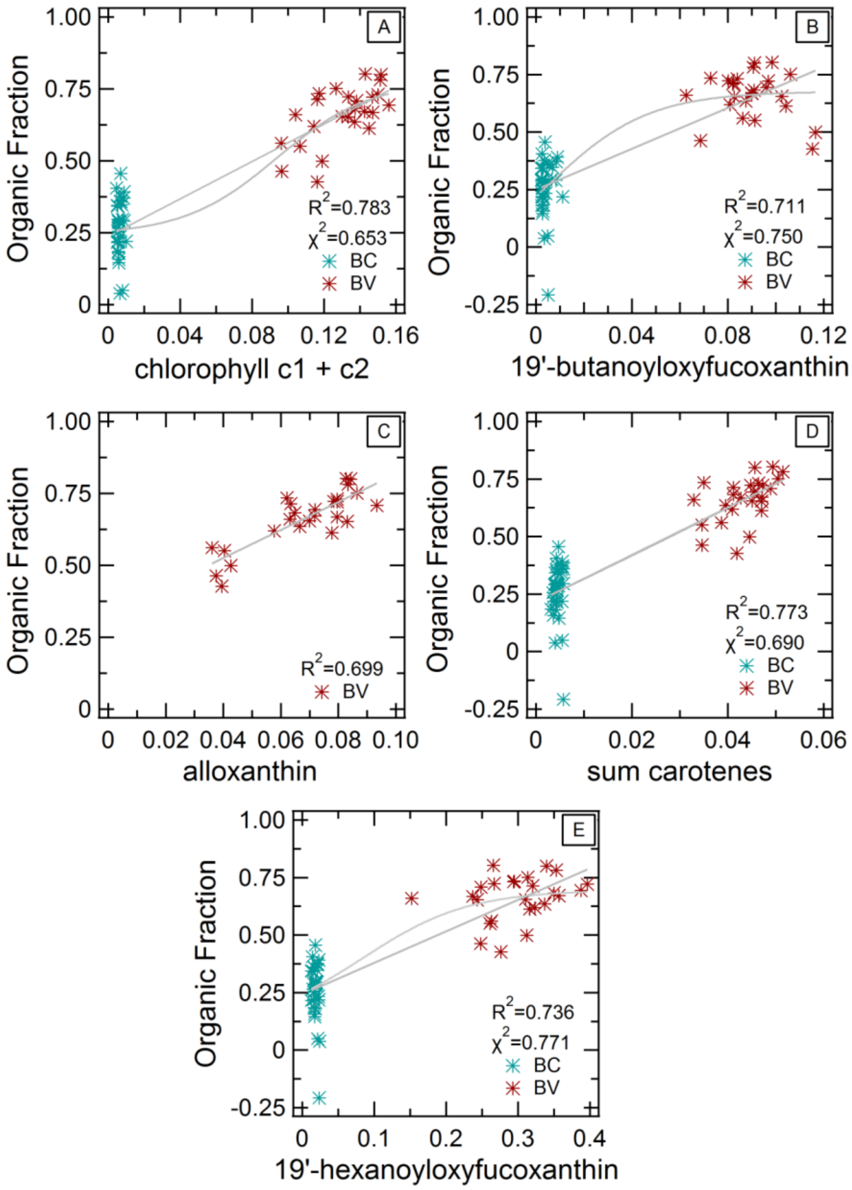

Figure 8. Organic fraction calculated from kappa ($\kappa_{org}$=0.006 and $\kappa_{inorg}$=1.25) at SS=0.39% vs. chlorophyll c1+c2 (A),19'-butanoyloxyfucoxanthin (B), alloxanthin (C), sum carotenes (D) and 19'-hexanoyloxyfucoxanthin (E) concentrations (mg m$^{-3}$) for all 3 mesocosms during both BC and BV. Linear fits with $R^2$ values are shown for all figures, and sigmoid fits with $\chi^2$ values are shown for all panels except for (C).

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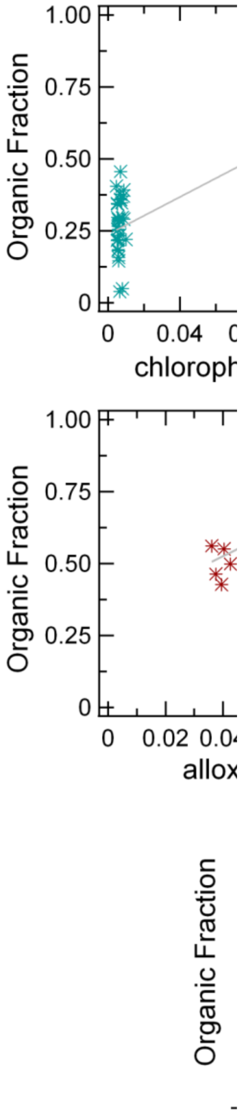

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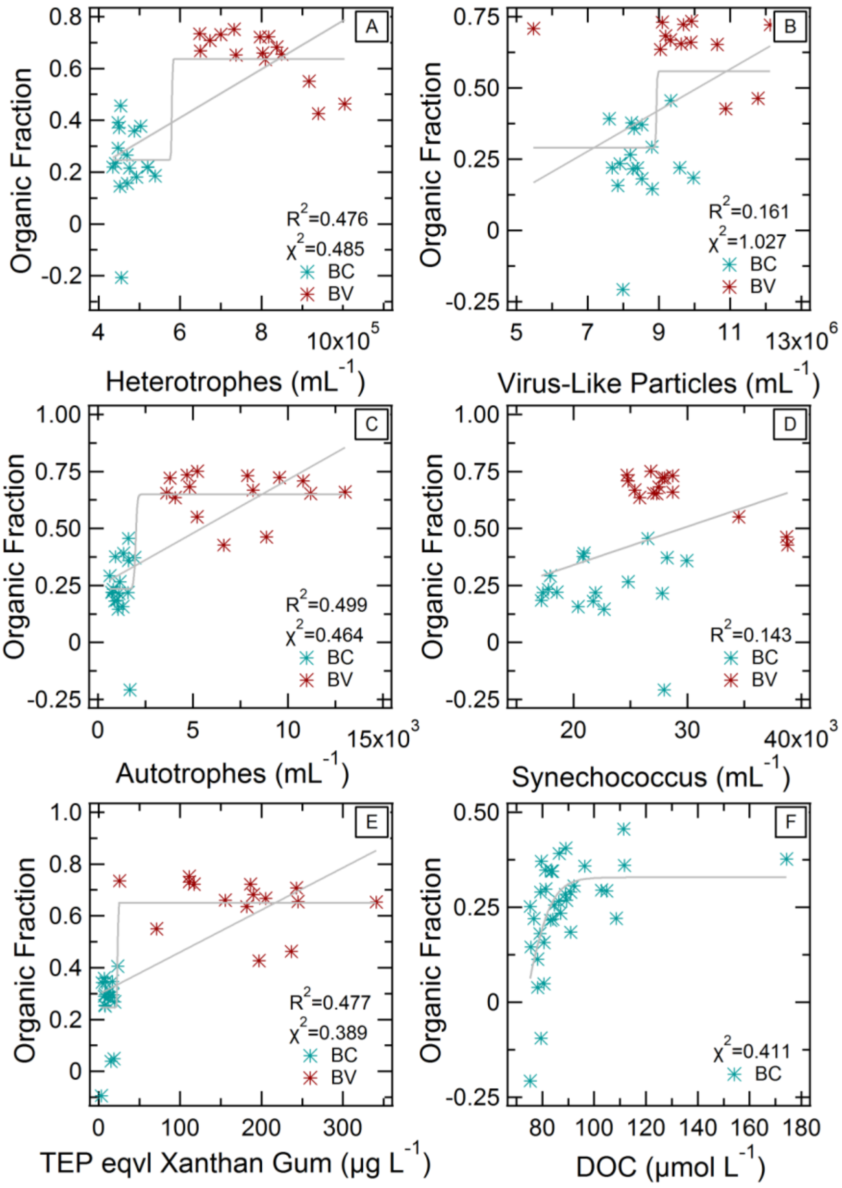
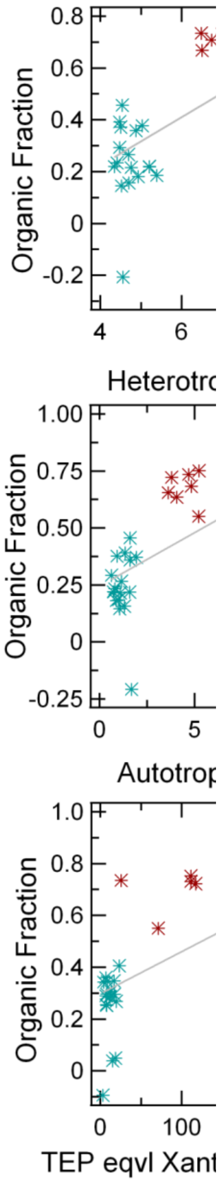


Figure 9. Organic fraction calculated from kappa ($\kappa_{org}$=0.006 and $\kappa_{inorg}$=1.25) at SS=0.39% vs. heterotrophic prokaryotes (A), virus-like particles (B), autotrophic prokaryotes (C), and *Synechococcus* (D) abundances, and TEP equivalent (xanthan gum) (E), and DOC (F) concentrations for all 3 mesocosms during both BC and BV. Linear fits with $R^2$ values are shown for all figures except for (F), and sigmoid fits with $\chi^2$ values are shown for all panels except for (D).



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