Dear Prof. Monks,

The three reviewers provided many thoughtful comments on our ACPD manuscript. We have taken these into account and made substantial revisions to the manuscript in order to fully address the reviewers' comments. We believe the manuscript is greatly improved as a result of these changes. In particular, we have added an initial model-data comparison, since all three reviewers had requested that we show and discuss our model's capability in matching various observations. Because this paper presents only the emissions parameterization and does not include any simulation of atmospheric transport, aerosol microphysics, or chemical processes in the atmosphere, the evaluation is only preliminary, but does give an initial idea of how the model's behavior compares with observations. A thorough evaluation of the resulting atmospheric aerosol distributions is beyond the scope of this paper, and is the intended topic of a future study.

In this document, we enclose our point-by-point responses to the reviewers, a marked-up version of the changes made to the text, and a copy of a new Online Supplement. A complete list of all the changes we have made would be prohibitively long, however, here we provide a short list of the most important changes made in response to the reviewer's comments:

1. Addition of two new figures comparing the model with in-situ observations of aerosol composition (Fig. 13-14).
2. Expansion and improvement of Fig. 11, which now includes all highlighted geographic regions.
3. Addition of panels showing results for the month of May to Fig. 7
4. Several figures were moved to a new Supplement, and additional figures were added to the Supplement for further completeness and so that readers can examine the model results in greater detail.
5. Addition of detailed discussion of the comparison between the model and various observations.
6. Expansion of the discussion of model uncertainties, neglected processes, and future experimental and model development needs.
7. Various minor improvements to the legibility of several figures (including larger font sizes).

Note that figure numbers above refer to the revised manuscript.

We thank you for your consideration of our revised manuscript.

Best regards,
Susannah M. Burrows

Contents of Author Response

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Response to Dr. Brett Gantt

We thank Dr. Gantt for his careful reading and review of our paper. Our specific responses to his comments follow. Reviewer comments are in italic font and our responses are in non-italic font.

Major Comments: *1) Ocean organic concentration: Although the focus of this study is on the air-sea flux of organic compounds, the predictions are largely dependent on the marine biogeochemical modeling. Please show or provide references for the ability of CESM to predict the magnitude and seasonal cycle of the observed organic concentrations in the ocean.*

We agree that the predictions are dependent on, and fundamentally limited by, the predictive capabilities of the underlying ocean biogeochemistry model. Global biogeochemistry models qualitatively and broadly capture many important features of ocean biota and chemical composition, yet they still struggle to accurately reproduce, for instance, the precise location and timing of phytoplankton blooms (Doney et al., 2009), much in the same way that weather prediction models struggle to reproduce the exact location and timing of precipitation events and are nevertheless useful.

We are also actively working toward improving the predictive capability of the CESM biogeochemistry model and have recently submitted a related paper (Ogunro et al., 2014, submitted) that focuses on the oceanic organic concentration.

In response to the reviewers' comments, we have added a sentence to the discussion that points out this limitation and provides a reference for the skill of the CESM ocean biogeochemistry model:

"Additionally, the model's predictive capability is limited by the predictive capabilities of ocean biogeochemistry models, which currently have a limited ability to accurately predict the exact location and timing of phytoplankton blooms (Doney et al., 2009).While the model has some difficulty in exactly reproducing the location and timing of phytoplankton blooms, the patchiness of the active phytoplankton blooms is a realistic qualitative feature. These blooms can be extremely localized, as can also be seen in satellite-derived maps of chlorophyll. This leads to highly localized distributions of the lipid-like class and of OM fraction in our model (Fig. 6 and Fig. 7)."

2) Enrichment: Please describe this process in more detail, including details such as whether the enrichment factor is calculated within the CESM model or offline and whether it is more dependent on the bulk organic concentration or composition. Also, please evaluate the predicted enrichment factor against observations if available.

The enrichment factor is calculated offline in the current study and depends strongly on the composition of ocean organics. The calculation is discussed in detail (Sec. 2.3, Section 3.1 of ACPD manuscript). A revised version of Figure 12 will show in more detail how the total organic mass fraction relates to the lipid vs. the polysaccharide and protein (semi-labile) mass fractions. A new figure will show an initial evaluation of the model's organic mass fraction. A more detailed evaluation will be the subject of a planned future manuscript and is beyond the scope of the current work.

3) Organic fraction: In order to justify the increased complexity of this framework, predictions of the organic fraction of sea spray aerosol and surface organic aerosol concentration must be improved relative to other parameterizations. Please expand Figure 12 to include observed and predicted surface concentration of marine primary organic aerosol and show additional regions for evaluation.

We agree that a more detailed evaluation of this parameterization is necessary, but a full evaluation is beyond the scope of the current paper. However, in response to the comments made by Dr. Gantt and the other reviewers, our revised manuscript includes a new section titled "Comparison with Observations" that includes some initial comparisons of the model with observed organic matter in marine aerosol.

4) Sensitivity simulations: While interesting, these additional tests also increase the length and number of figures of an already complex study. I would recommend combining Figures 13-16 into one supplemental figure with two (or three) columns (enrichment ratio, organic mass fraction, and chlorophyll-a vs organic mass fraction for example).

Following the suggestion of the reviewers, we have combined these figures into a supplemental figure.

Also, please expand Table 3 to give the global marine primary organic aerosol emission rate (in a unit like Tg/yr) for the BASE and sensitivity cases.

In this study, we did not calculate the primary emissions, only the chemical composition of the emitted aerosol. We intend to present results of a fully online emissions simulation in a future publication.

***Minor Comments** (page,line):[2028?]5) 5378,4: "Potential mechanisms for ??? include..."*

Thanks, we have fixed this. The revised sentence reads:

"Potential mechanisms for enrichment of polysaccharides in sea spray include the formation of marine colloidal particles that may be more efficiently swept up by rising bubbles, and cooperative adsorption of polysaccharides with proteins or lipids."

6) 5382,15-28: Provide references for the various description of marine organic com- pounds.

References and detailed explanations are provided in Section 5.2 of the paper. We will add a sentence in this section directing the reader to Sec. 5.2 for further details.

*7) 5397,25: Equation should look something like C1 = 1/3 * SDOC*

Thanks, we have fixed this.

8) 5398,10: Provide a reference to the value of the lower limit of the concentration of processed compounds.

This lower limit was introduced to present unrealistically low or negative concentrations of processed compounds. We have modified the text as follows to clarify this:

"We further apply a lower limit to the concentration of processed compounds in order to prevent unrealistically low or negative concentrations,"

We note that this assumption does not affect the results presented here, since the processed compounds have negligible impact on the aerosol composition in this parameterization.

9) 5400,7: Should read "Although lipids contribute very little..."

Thanks, we have fixed this.

10) 5401,16: Figures need to be numbered in the order they are referred to in the text. See Comment 4 which may help address this issue.

We will check during typesetting of the revised manuscript that the figures appear in the correct order.

11) 5409,5: Should be "inspired".

Thanks, we have fixed this.

12) Figure 6: Please show either the annual average or multiple months representing different seasons

In response to this request and the request of Reviewer 2, we have included similar panel plots for the months of May and November in a packet of supplementary material.

13) Figures: Please increase the font of the figures, especially Figures 6-8 and 10-17.

Following the reviewer's suggestion, we have increased the font size and/or thickness on many of the figures to improve legibility.

14) Figure 12: Please begin x-axis with January. Caption should say "bottom panel"

In response to the request of Reviewer 2, we have added more panels to this plot, which correspond to the remaining geographic regions shown in Figure 9, and we have modified the caption to reflect the new panels. We have also modified the plot so that the x-axis beings at January.

15) Figure 17: Please move x-axis show that it intersects y-axis at 0.1 to improve clarity.

Following Dr. Gantt's suggestion, we have copied the tick-marks on the x-axis to the bottom, so that they now appear both where the x-axis intersects the y-axis and at the bottom of the chart.

References:

Doney, Scott C., Ivan Lima, J. Keith Moore, Keith Lindsay, Michael J. Behrenfeld, Toby K. Westberry, Natalie Mahowald, David M. Glover, and Taro Takahashi. "Skill metrics for confronting global upper ocean ecosystem-biogeochemistry models against field and remote sensing data." *Journal of Marine Systems* 76, no. 1 (2009): 95-112.

O. Ogunro, S. M. Burrows, S. M. Elliott, A. Frossard, R. Letscher, J. K. Moore, L. M. Russell, O. Wingenter. Distribution and Surface Activity of Macromolecules in Offline Simulations of Marine Organic Chemistry, *submitted*, 2014.

Response to reviewer 2

We thank the anonymous reviewer for their careful review and constructive comments on our manuscript. Our responses to individual comments follow. Reviewer comments are in italic font and our responses are in non-italic font.

Specific Comments:

1) It is important to evaluate new models and parameterizations against observations in order to judge their explanatory power. Consequently, the base case simulations of enrichment factor and organic mass fraction shown in Figures 7 and 12, and discussed in the text should be evaluated against organic aerosol observations such as those detailed by Gantt and Meskhidze, 2013 (see their supplementary material and references therein). This should be certainly done for organic mass fraction, and if seawater solution concentrations are available, also for enrichment factor and OM:Na.

We agree with the reviewer that a more detailed evaluation of this parameterization is necessary, but a full evaluation is beyond the scope of the current paper. However, in response to requests made by all of the reviewers, our revised manuscript includes a new section titled “Comparison with Observations” that takes an initial step in this direction. The new section will include figures comparing the model predictions of total OM fraction against the observational series at Mace Head, Ireland (kindly provided by Dr. Matteo Rinaldi and coworkers; Rinaldi et al., 2013), at Point Reyes, California (kindly provided by Dr. Brett Gantt; Gantt et al., 2011), and from several field campaigns (data from the co-authors). Additionally, we have added subsections discussing the observations of Quinn et al. (2014) and the laboratory studies of Keene et al. (2007) in relationship to our model.

2) A more extensive discussion of the spatial variability depicted in Figure 7 is warranted, specifically with regard to how realistic is the patchiness observed in the southern oceans near Antarctica in February? This structure appears to directly mirror the lipid-like seawater concentration map in Figure 6, whose uncertainty from the model is unknown and should be discussed.

Our parameterization is inherently dependent on, and limited by, the predictive capabilities of the underlying ocean biogeochemistry model. In response to the reviewers’ comments, we have added a sentence to the discussion that points this out and provides a reference for the skill of the CESM ocean biogeochemistry model:

“Additionally, the model’s predictive capability is limited by the predictive capabilities of ocean biogeochemistry models, which currently have a limited ability to accurately predict the exact location and timing of phytoplankton blooms (Doney et al., 2009).While the model has some difficulty in exactly reproducing the location and timing of phytoplankton blooms, the patchiness of the active phytoplankton blooms is a realistic qualitative feature. These blooms can be extremely localized, as can also be seen in satellite-derived maps of chlorophyll. This leads to highly localized distributions of the lipid-like class and of OM fraction in our model (Fig. 6 and Fig. 7).”

3) Please add a set of panels to Figure 7 for the month of May so that the reader can observe the structure of the modeled N. Atlantic bloom period as described in the text. This is important because it provides model results in a commonly-studied region upwind of the long-term Mace Head measurement site. Also, include versions of Figure 6 in the supplementary material for May and August so that the reader can compare the ocean concentration maps directly to the organic mass fraction and enrichment maps.

We have included the additional figures suggested by the reviewer in our revised MS.

4) I don’t understand the relevance of the discussion on Pgs. 5401-5403 discussing how the differences in alkane:hydroxyl mass ratio from the polluted to the remote environments translate into a proposed mechanism whereby there are differences in the contribution of surfactants released from phytoplankton disruption vs. standing stock. This section should be revised to better clarify the causality in the proposed mechanism.

We have significantly revised this section in an effort to improve clarity. We have also a subsection headings to clearly separate the portion of the text that considers the effect of anthropogenic pollutants on alkane:hydroxyl ratios.

To reduce confusion, we have removed the more speculative portion of the text that deals with the distinct issue of the differences between North Atlantic and Arctic ecosystems and their possible effect on the organics in sea spray aerosol.

In place of this discussion, we simply note that the ratio of alkane mass to hydroxyl mass may also be affected by ocean biological processes. We have included a supplemental figure displaying the ratios of mean alkane to mean hydroxyl mass, and of OM fraction to Chl-a, over the course of a year for each of the geographic regions selected in the paper. The new figure shows that among these regions in the model, the highest estimated alkane:hydroxyl ratios and the lowest OM-fraction:Chl-a ratios are obtained in the Arctic and the North Atlantic in May and June.

5) In Figure 17, are the model points/error bars global or regional medians? Why do the campaign values extend from lipid adsorptivity:polysaccharide adsorptivity ratios 0.1-100?

In Figure, 17, the error bars for the model are 5%-ile to 95%-ile ranges of all global monthly mean values. The shaded areas are +/- 1 standard deviation uncertainty ranges for the respective field campaigns.

The campaign measurements only have values on the y-axis (alkane mass:hydroxyl mass). In the visual presentation we selected, these values are shown across the entire range of the x-axis that includes the aerosol composition values from the model, because they are intended to be compared to those values. They do not extend to the far left of the figure, where the range of model seawater alkane:hydroxyl mass ratios is presented. This was simply a matter of convenient presentation and has no further significance.

To improve the clarity of the figure, we have removed the x-axis labels and tick-marks to the left of 0.1, since they are not meaningful. We have also revised the caption as follows to improve clarity:

"Fig. 14: Ratio of alkane mass to hydroxyl mass from model macromolecules, and from ship-borne FTIR observations. Points and error bars indicate the model's global median and 5%-ile to 95%-ile range of model estimates for seawater (displayed at the left of the figure) and for emitted submicron SSA in several sensitivity cases. Medians and ranges are calculated from monthly mean grid-box values. For the purpose of this comparison, model macromolecule concentrations were converted to estimated functional group ratios using the values provided in Table 4. Model values are shown as a function of the ratio of the adsorption constants used for lipids and for polysaccharides, in each sensitivity case. Observed alkane:hydroxyl ratios from ship-borne FTIR measurements in several field campaigns are shown as lines and shaded regions. The adsorptivity of the ocean DOC components during each campaign is unknown, therefore the observed alkane:hydroxyl ratio are not associated with particular values on the x-axis. Solid lines indicate averages of data from clean air samples only, i.e., data from air contaminated by anthropogenic pollution have been excluded. The ship-borne observations are from the E-PEACE campaign off the central coast of California (July – August, 2011) (Russell et al., 2013), the ICEALOT campaign in the North Atlantic and Arctic Oceans (March – April, 2008) (Russell et al., 2010), and the VOCALS-Rex campaign, in the Southeast Pacific oligotrophic gyre (October, 2008) (Hawkins et al., 2010). The shaded areas indicate the ± 1 standard deviation uncertainty7 range for VOCALs-Rex (Marine air mass, MAM), ICEALOT (Arctic) and ICEALOT (North Atlantic), respectively."

What are the "differences" meant by the statement on Pg. 5403, Line 1: "An alternative possible explanation is that the differences derive from differences between the phytoplankton communities in the two regions"?

We have revised the unclear sentence to read:

"Another possible explanation for the differences between submicron spray organic composition in the North Atlantic and in the Arctic is that phytoplankton communities in the two regions may produce DOC pools with different chemical compositions as a result of differences in species composition or environmental conditions."

6) In the discussion section (Pg. 5405, Lines 1-10), the manuscript discusses very briefly some sources of model uncertainty related to parameter assumptions and neglect of additional processes. This should be expanded considerably and describe 1) what parameter values are most important *and most uncertain, and 2) over what range of temperatures, salinities, pH, etc. these parameter values need to be constrained. Essentially, what I'd like to see is a wish list that will motivate future laboratory and field experimental studies toward constraining these needed values in order to get the most out of the new model.*

We have taken the opportunity to elaborate on the laboratory and field experimental studies that we think would be most valuable in testing the underlying principles of the model, constraining the uncertain parameters, and improving understanding of the processes we currently believe are the most important missing processes.

Minor Comments:

Pg. 5385, Line 8: Please provide a reference to support the assumption that the bubble film composition is the same as the submicron aerosol composition.

Some support for this assumption can be found in SFG analysis of a wave flume surface and of particles produced from that surface, which were found be surfactant-rich and to have similar SFG spectra, suggesting chemical similarity (Ebben et al., 2013). This assumption is also more generally supported by the observation that submicron spray aerosol is primarily produced from film drops (Blanchard and Syzdek, 1982, 1988; Resch and Afeti, 1992; Spiel, 1998) and that film drops are enriched in organic matter (Macintyre, 1970; Blanchard et al. 1989). Film drops vary in size from less than 0.1 to over 100 um in diameter (Blanchard, 1963; Cipriano and Blanchard, 1981; Resch and Afeti, 1992; Spiel, 1998), whereas most jet drop have diameters much larger than 1 micron (typically hundreds of microns) (Blanchard, 1989; Resch and Afeti, 1992; Spiel, 1994). Even if smaller jet drops do exist, they would be far outnumbered by film drops, since each bursting bubble produces hundreds of film drops and only a few jet drops.

Equating the film drop composition to the submicron spray composition is an approximation, of course. A more complete description would incorporate a representation of composition of the nascent spray as a function of particle size, however, this is beyond the scope of the current paper. The film thickness is an adjustable parameter in the model that controls the overall organic:salt ratio of the aerosol, and it could potentially be replaced with an empirical expression that controls particle composition as a function of particle size.

We will add the following sentence to the revised manuscript:

"This assumption is supported by, e.g., recent studies showing the chemical similarity of a wave flume surface and the particles produced from that surface (Ebben et al., 2013), as well as more generally supported by the observation that submicron spray is produced primarily from film drops (Blanchard and Syzdek, 1982, 1988; Resch and Afeti, 1992; Spiel, 1998)."

Pg. 5397, Line 5: Why does the distribution of lipids reflect the distribution of phy- toplankton primary production, and what is the reference showing the distribution of phytoplankton primary production?

The distribution of lipids is calculated from the product of the phytoplankton concentration, the zooplankton concentration, and a rate constant (Eq. 11). The phytoplankton and zooplankton concentrations are taken from the POP/BEC model within the CESM, as described in sections 5.1 and 5.2. We have added a reference to Eq. 11 here to remind the reader of this.

Pg. 5404, Line 15: Correct misspelling of Arctic.

Thanks, we have corrected this.

Figure 12: Please include panels showing the seasonal variation for the other regions shown in Figure 9.

We have added the additional panels requested by the reviewer.

Figures 13-16: Please combine as suggested by the other reviewer and include the base case simulation maps again in this figure. It is hard to compare the different sensitivity studies when they are all on different pages in different figure layouts.

We have combined these figures and moved them to a package of supplementary material as suggested by the reviewers.

References:

Blanchard, Duncan C. "The electrification of the atmosphere by particles from bubbles in the sea." *Progress in oceanography* 1 (1963): 73-202.

Blanchard, Duncan C., and Lawrence D. Syzdek. "Water-to-air transfer and enrichment of bacteria in drops from bursting bubbles." *Applied and environmental microbiology* 43, no. 5 (1982): 1001-1005.

Blanchard, Duncan C., and Lawrence D. Syzdek. "Film drop production as a function of bubble size." *Journal of Geophysical Research: Oceans (1978–2012)* 93, no. C4 (1988): 3649-3654.

Blanchard, Duncan C. "The ejection of drops from the sea and their enrichment with bacteria and other materials: a review." *Estuaries* 12, no. 3 (1989): 127-137.

Cipriano, Ramon J., and Duncan C. Blanchard. "Bubble and aerosol spectra produced by a laboratory 'breaking wave'." *Journal of Geophysical Research: Oceans (1978–2012)* 86, no. C9 (1981): 8085-8092.

Doney, Scott C., Ivan Lima, J. Keith Moore, Keith Lindsay, Michael J. Behrenfeld, Toby K. Westberry, Natalie Mahowald, David M. Glover, and Taro Takahashi. "Skill metrics for confronting global upper ocean ecosystem-biogeochemistry models against field and remote sensing data." *Journal of Marine Systems* 76, no. 1 (2009): 95-112.

Ebben, Carlena J., Andrew P. Ault, Matthew J. Ruppel, Olivia S. Ryder, Timothy H. Bertram, Vicki H. Grassian, Kimberly A. Prather, and Franz M. Geiger. "Size-Resolved Sea Spray Aerosol Particles Studied by Vibrational Sum Frequency Generation." *The Journal of Physical Chemistry A* 117, no. 30 (2013): 6589-6601.

Gantt, B., N. Meskhidze, M. C. Facchini, M. Rinaldi, D. Ceburnis, and C. D. O'Dowd. "Wind speed dependent size-resolved parameterization for the organic mass fraction of sea spray aerosol." *Atmospheric Chemistry and Physics* 11, no. 16 (2011): 8777-8790.

Keene, William C., Hal Maring, John R. Maben, David J. Kieber, Alexander AP Pszenny, Elizabeth E. Dahl, Miguel A. Izaguirre et al. "Chemical and physical characteristics of nascent aerosols produced by bursting bubbles at a model air-sea interface." *Journal of Geophysical Research: Atmospheres (1984–2012)*112, no. D21 (2007).

Macintyre, Ferren. "Geochemical fractionation during mass transfer from sea to air by breaking bubbles." *Tellus* 22, no. 4 (1970): 451-462.

Resch, François, and George Afeti. "Submicron film drop production by bubbles in seawater." *Journal of Geophysical Research: Oceans (1978–2012)* 97, no. C3 (1992): 3679-3683.

Rinaldi, Matteo, Sandro Fuzzi, Stefano Decesari, Salvatore Marullo, Rosalia Santoleri, Antonello Provenzale, Jost Hardenberg et al. "Is chlorophyll-a the best surrogate for organic matter enrichment in submicron primary marine aerosol?." *Journal of Geophysical Research: Atmospheres* 118, no. 10 (2013): 4964-4973.

Spiel, Donald E. "The sizes of the jet drops produced by air bubbles bursting on sea-and fresh-water surfaces." *Tellus B* 46, no. 4 (1994): 325-338.

Spiel, Donald E. "On the births of film drops from bubbles bursting on seawater surfaces." *Journal of Geophysical Research: Oceans (1978–2012)* 103, no. C11 (1998): 24907-24918.

Quinn, Patricia K., Timothy S. Bates, Kristen S. Schulz, D. J. Coffman, A. A. Frossard, L. M. Russell, W. C. Keene, and D. J. Kieber. "Contribution of sea surface carbon pool to organic matter enrichment in sea spray aerosol." *Nature Geoscience* 7, no. 3 (2014): 228-232.

Response to reviewer 3:

We thank the reviewer for the thorough, thoughtful and constructive comments on our manuscript, which pushed us to think more deeply about certain aspects of the proposed parameterization. Our detailed responses to the reviewer's comments follow. Reviewer comments are in italic font and our responses are in non-italic font.

General Statements: *I think the authors did a good job distilling information regarding compounds considered relevant proxies for ocean surface active material.*

The uncertainties of the method must be truly enormous; and some attempt to convey their bounds is absolutely necessary.

We have already attempted to convey the range of uncertainties in presenting multiple sensitivity cases that address uncertainties in the surface activities of the compound classes. Information about uncertainties in the underlying ocean biogeochemistry model can be gleaned from Doney et al. (2009). However, a detailed exploration of all the uncertainties is a large project that is beyond the scope of the current paper.

To address the reviewers' concerns on this point, we have significantly expanded the discussion of uncertainties in the discussion section, including adding the following text:

"Additionally, our model is limited by the predictive capabilities of ocean biogeochemistry models, which currently have a limited ability to accurately predict the exact location and timing of phytoplankton blooms (Doney et al., 2009). While the model has some difficulty in exactly reproducing the location and timing of phytoplankton blooms, the patchiness of the active phytoplankton blooms is a realistic qualitative feature. These blooms can be extremely localized, as can also be seen in satellite-derived maps of chlorophyll. This leads to highly localized distributions of the lipid-like class and of OM fraction in our model (Fig. 6 and Fig. 7)."

First Major Point: There is growing evidence that the organic mass fraction of nascent aerosol is emphatically not correlated with Chl a, and pointing more towards the hypothesis that the ocean is everywhere capable of saturating the available bubble surface area (i.e. the ocean is surface-area limited), yielding pretty much uniform mass fractions.

1. *Long et al.(2014) showed, using dynamic surface tensiometry, significant surface activity in productive & oligotrophic seawater. This suggests that surface active material is present in large quantities in seawater independent of Chl a or ocean trophic state. For example, as a minimum, using the method of Joos and Rillaerts, (1981), and an approximate diffusion coefficient of 1x10-10 m2s-1, a change in surface tension of -0.4 mN m-1, and a surface age of 4 seconds (thus setting the lower bounds), the theoretical concentration of oleic acid in oligotrophic seawater is on the order of 1 x 10-5 M. While it is recognized that this is unlikely for such a short lived species, this would also imply that the concentration of less surface-active material could be higher. Please let me know if this need to be clarified.*

2. *Both Keene et al.(2007) and Quinn et al. (2014) show enrichment factors & mass fractions above the modeled values in oligotrophic water, and more similar to those predicted by Long et al. (2011).*

These points together suggest that the ocean may be uniformly capable of saturating bubble surfaces regardless of location or biological activity. The main mechanistic effect, as pointed out by this paper, would be in the relative contribution of different chemical species.

We regard highly the work by Quinn et al. (2014) and Long et al. (2014). Both of these studies were published around the time that our ACPD manuscript was submitted or afterwards. We will address each of these in turn, and we will address Keene et al. (2007) later in our response.

Long et al. (2014)

We agree with the comment that "surface-active material is present in large quantities in seawater independent of Chl a or ocean trophic state", and this is reflected in our model.

L14 report that artificial sea spray aerosol production rates during the WACS campaign were higher during daytime than during nighttime for biologically productive waters (high Chl-a), but were constant over the diel cycle (and low) for biologically unproductive waters. However, the total organic mass fraction was similar in both productive and unproductive waters. This suggests that there are differences in the surface chemistry of biologically-productive waters and unproductive waters that can lead to differences in the aerosol production process, even in the absence of changes in the overall organic mass fraction.

Comparison to Quinn et al. (2014)

When looking broadly at published in situ observations of ambient marine aerosol, many studies have found much lower OM fractions observed for fine-mode sea spray aerosol measured in biologically inactive regions and periods compared to the most biologically-active regions and periods (e.g., Barker and Zeitlin, 1972; Hoffman and Duce, 1977; Oppo et al., 1999; O'Dowd et al, 2004; Yoon et al., 2007; Sciare et al., 2009; Ovadaneite et al., 2011; Miyazaki et al., 2011). Since so many studies are in agreement on this point, we feel that ignoring them in favor of the hypothesis that OM fractions in marine aerosol are constant in all times and places equally requires a strong justification.

Instead, we believe that our model offers a mechanism that can satisfactorily explain both sets of observations. In the following, we will show that our model is in agreement with the results of Quinn et al. (2014; hereafter Q14).

The revised manuscript will include several new figures that enable a closer comparison with experimental results: an expanded version of Figure 7 that includes model estimates of the organic mass fraction in May, in addition to the February and August panels already included, an expanded and improved version of Figure 12, including seasonal cycles for all the highlighted ocean regions, and a new figure comparing seasonal cycles in the model with coastal measurements and shipboard measurements (including Q14) in the northwestern North Atlantic, the northeastern North Atlantic, and coastal California and the North Pacific. We will also add a new subsection specifically discussing the Q14 measurements.

The main disagreement between Q14 and our model is that the model predicts that the organic mass fraction is generally higher in regions with higher chlorophyll (ca. 0.2 at the high-Chl-a station and ca. 0.05 at the low-Chl-a station), while Q14 report similar average OM fractions in both regions ([5.6 ± 1.7]% and [5.9 ± 1.9]%, respectively). Given the natural variability of observed mass fraction, however, a larger number of samples would likely be required to detect the relatively small gradient in the organic mass fraction predicted by our model in that region.

On the other hand, the mean enrichment factors during WACS were in fact higher for low-Chl-a samples than for high Chl-a samples, and this difference was statistically significant ($p<0.001$ by a t-test calculated from the values presented in Supplementary Table S1 of Q14), which is consistent with stronger organic enrichment in biologically active waters. Sub-1.1 um enrichment factors in generated aerosol were reported by Q14 to be 1500 ± 460 at Station 1 (high Chl-a) and 2600 ± 900 at Station 2 (low Chl-a); our model predicts enrichment factors in the range 1000–5000 in this region in August (Fig. 7 of ACPD manuscript).

Q14 also presents a second dataset originating from the CalNex field campaign, in coastal waters off the coast of California. Because our model is not designed to simulate coastal processes, and because there may be factors other than ocean biogeochemistry at work, such as runoff from land, and ship pollutants, that field study is less appropriate for comparison with our model.

Nevertheless, we note that our model's predicted OM fraction is within the variability of the CalNex observations, and is similar to the model's prediction in the WACS region (this will be apparent in the new figure comparing model and observations). We also note that the model OM fractions in both the WACS and CalNex regions lack the clear seasonal signal that is present in the model's OM fraction in the North Atlantic and Arctic regions, which are upwind of Mace Head, Ireland.

Second Major Point: While the presence of surfactant material on the water surface does impact bubble residence times, there is extensive literature suggesting that the SML does not exist appreciably behind breaking waves, or at highly energetic sea states.

For example, from Wurl et al. (2011),"For obvious reasons, the SML is temporarily disrupted in the presence of breaking waves, dispersing SML material into the bulk water. In both and field experiments, surface films appear to reform within seconds after disruption."

In the presence of breaking waves, dispersed SML materials adsorb rapidly to the surface of the rising air bubbles, and therefore, bubble plumes may be the most important transport vector for surface-active material to the SML."

I also point the author to the 1st chapter in Donelan et al. (2002) and the references cited therein. These as well as in many other places in Donelan et al. (2002) indicate observation of the SML, or "sea slicks" as they are oft referred, breaking up under conditions of relatively minimal strain. As well, the surface divergence associate with a bubble plume detraining is also sufficient to break apart an SML.

Thus, the active hypothesis in the Atmos. Sci. community that the SML has an appreciable impact on either the process of particle formation or composition is, in my opinion, broadly invalid. Rather – and the author points this out nicely, though without acknowledging the full consequence of the statement – the SML is made up of material generally transported to the surface via bubbles; and that the SML has to regenerate after a wave breaks. I think the appropriate interpretation is that both the SML and particle OM enrichment are nearly independent consequences of interactions between bubbles and surface active material in the ocean.

We agree that the literature shows that the surface microlayer is dynamic, although we do not think that the dynamic nature of the surface microlayer and its disruption by waves necessarily negates the relevance of the SML under relatively calm ocean conditions.

However, our parameterization currently does not require an assumption that the SML exists, it only assumes that the ocean-atmosphere interface is coated by organics to the same extent as bubble interiors. Both the interior and exterior surfaces of the bubble film are assumed to be in equilibrium with concentrations in near-surface waters. The ratio of the coating of the bubble film's exterior surface to its interior surface is controlled by the parameter n_{bub}, which can be appropriately viewed as an adjustable parameter within the model.

We will revise the manuscript to clarify this point, by adding the following text:

"The parameter n_{bub} is an adjustable parameter that represents the number of sides of the bubble film that are covered with the areal fraction j_{bub}. The smallest physically meaningful value, $n_{bub} = 1$, implies that only the bubble interior is coated. We assume $n_{bub} = 2$, which implies that the coverage of the interior and exterior films of the bubble are equivalent (Figure 2). Values of $n_{bub} > 2$ would imply an enriched microlayer, which is possible under calm conditions."

Third Major Point: While it appears that the calculation of 0.05 ms equilibrium time for adsorption by Fuentes et al. (2010) is numerically sound, that time is likely several orders of magnitude too fast. There is some good literature on competitive adsorption equilibrium for surfactant mixtures at much higher concentrations that seem in the ocean, and their results are nowhere near equilibrium (few examples... Fritz and Schlünder, 1981; Mulqueen et al., 2001a, 2001b). It is not clear what the implications for this might be for your model since the time scales for bubble surfaces in the ocean are much greater than 0.05 ms.

But, for competitive adsorption, the use of a thermodynamic equilibrium model is likely insufficient to truly capture the partitioning of individual surfactants on bubble surfaces on the relevant time scales in the ocean. If surfactant-surfactant, or surfactant-ion interaction is important, then the equilibrium model is most definitely insufficient. Given the presence of divalent ions and ionic surfactants in the ocean (e.g. oleic acid, decanol, etc.), and the known tendency of surface active material to form aggregates in seawater, the interactions between surfactants are likely very important. I note that the authors do address this uncertainty in statement, and it is likely outside of our ability to constrain it, given the current body of knowledge.

We concur that surfactant interactions with other molecules, and the formation of aggregates, are significant uncertainties, as we pointed out in the manuscript. We were unable to address these mechanisms within this initial formulation of the parameterization because of the limited current understanding of these processes. However, we are actively working on approaches to incorporate understanding of these processes in the future.

The fundamental question of whether an equilibrium model is an appropriate choice is an important one. Bubble rise times are on the order of tens of seconds, so even if the time scale estimated by Fuentes et al. is four orders of magnitude too fast and the true equilibrium time is 0.5 s instead of 0.05 ms, it would still be much faster than bubble rise times. Krzan et al., (2007) studied the formation of a steady-state adsorption profile on single rising bubbles for several organic surfactants ($C5 - C_{16}$). In most cases, the time to reach equilibrium was less than 1 s, which as noted above is much shorter than typical bubble rise times in the ocean.

Mulqueen et al. 2001a,b is an excellent pair of papers of which we were previously unaware, and we thank the reviewer for bringing them to our attention. These papers show experiments and theoretical analysis of experiments in which, with single surfactants, equilibrium was reached on time scales between 2 – 24 s, but in binary mixtures where the less-surface-active component dominates, it occupies the surface more rapidly, and is only gradually replaced by the more surface-active component as it slowly desorbs, leading to a much slower equilibrium time on the order of 100 s. In the example presented in Fig. 8b of Mulqueen et al. (2001b), assuming that equilibrium was reached after only 10 s (instead of >100 s) would result in a 20% overestimate of the fractional surface coverage (0.48 vs. 0.4). However, it would result in a large error in the partitioning of the surface coverage, which after 10 seconds would be about equal between the two surfactants, whereas at equilibrium the more surface-active component entirely out-competes the less-surface-active component, which is barely present on the surface. This suggests that where the equilibrium assumption is not valid, it will result in greater errors in the chemical speciation at the surface than in the total surface coverage.

However, these experiments were performed for adsorption on a still surface, in a situation where molecular diffusion was the only mechanism for transport to the surface. In the case of a rising bubble plume, molecules can encounter surfaces much more efficiently because the bubble plume itself creates small-scale turbulence that increases the frequency of contact far beyond molecular diffusion alone, so adsorption time scales should be shorter. For larger particles (such as marine colloids) interception and impaction are also important. As a result, time scale analyses from stationary systems are not directly applicable to adsorption in a bubble plume. From both theoretical considerations and experimental evidence, it is clear that the actual kinetics of adsorption on bubble plumes depends in a complex way on the chemical nature and bulk concentration of surfactants, and on the size distribution and rise times of bubbles.

The relevance of the kinetics of adsorption on bubble plumes in this context deserves further study. However, since time scales for surfactants reaching equilibrium on bubble surfaces are frequently shorter than bubble rise times, we believe an equilibrium assumption is a reasonable first approximation, until the limitations of this assumption are more fully understood and a more detailed approach is possible. Furthermore, if equilibrium is approached but not fully achieved, the relationship of surface coverage and bulk concentration may still be approximately represented by a Langmuir isotherm curve (with appropriately adjusted parameters). This is supported, e.g., by calculations of the kinetics of the surface coverage of bubbles with surfactants (transferred to the bubble surface by convective diffusion) as a function of the length of time for which the bubble is exposed to the solution. Results of such detailed kinetic calculations have shown that for bubbles exposed to n-octanol solutions for periods several times shorter than the equilibration time, the relationship between bulk concentration and surface coating is still similar to a Langmuir isotherm, but with a larger value of $C_{1/2}$ (Jachimska et al., 2001). In other words, to a first approximation, assuming equilibrium when the exposure time of the bubble is in fact somewhat shorter than the time required to reach equilibrium would result in the surfactant appearing to be somewhat less strongly adsorbing than it is in reality.

Since bubbles in the ocean span a range of sizes and penetration depths, and ocean surfactants are a complex mixture of species, it will likely not ever be possible to directly simulate the full complexity of these systems in complete chemical detail, but the fidelity of global simulations may ultimately be improved by identifying and incorporating the key processes and variables, particularly those that vary between seasons or ecosystems. We believe our approach offers a path to incorporate a more detailed and mechanistic understanding of the key factors influencing the geographic and seasonal variability of sea spray chemistry, but with a small enough number of variables that it is tractable for implementation in an Earth System modeling context.

To address the reviewer's comment, we will replace the statement that equilibrium is achieved quickly (as estimated by Fuentes et al., 2011) with a short section discussing these issues in more detail:

"It is unclear how rapidly adsorption equilibrium is reached on bubble surfaces in the ocean. Estimates differ widely, for example, Fuentes et al. (2011) estimated an equilibration time scale of less than 0.05 ms for bubbles in a sample of filtered algal exudate, while Krzan et al. (2007) measured adsorption of several organic surfactants on single rising bubbles and observed equilibration to occur in less than 1 s in most cases. The rise velocities in seawater of bubbles with radii greater than 700 μm are in the range 22-35 cm s^{-1} (Patro et al., 2002). Bubble plumes formed by breaking waves penetrate to depths of at ca. 20–30 cm or more (Melville, 1996; Deane and Stokes, 2002), so if equilibrium is reached within less than one second, the exposure time will be sufficient to reach or nearly reach equilibrium for many ocean bubbles. Furthermore, if equilibrium is approached, but not fully achieved, the relationship of surface coverage and bulk concentration may still be represented by a Langmuir isotherm curve (using appropriately adjusted parameters) with fidelity sufficient for application in an Earth System Model. This is supported by calculations of the kinetics of convective-diffusive transport of surfactants to bubble surfaces, and subsequent adsorption (Jachimska et al., 2001).

Because the time scales of surfactant equilibrium in the ocean are similar to or less than bubble rise times in many cases, the assumption of equilibrium is a reasonable and useful first approximation for the purpose of representing bubble adsorption in Earth System models. Further investigation is required to determine under which conditions the assumed Langmuir equilibrium ceases to be a satisfactory approximation, particularly in regards to the equilibrium between competing surfactants (Mulqueen et al., 2001b,a)."

First Minor Point: Is it not precarious to use a model that drives its ocean biology with Chlorophyll as a primary metric to study the potential for Chl a as a proxy for ocean OM? Or am I misinterpreting how the model was employed? Please correct me if I'm wrong.

The POP/BEC ocean model is not driven with chlorophyll, rather, chlorophyll is predicted as a diagnostic variable. Prognostic variables in the model include phytoplankton concentrations and semi-labile DOC. We will improve clarity on this point by adding a sentence to the section "Aims and Approach" (in bold font, with the context reproduced here):

Nevertheless, we will show that this approach – applying a well-established basic surface chemistry theory to marine biogeochemistry model output – is capable of reproducing important features of the observed patterns in the SSA organic mass fraction. In particular, it approximately reproduces the increased OM fraction during strong seasonal blooms associated with high Chl a, e.g., in the North Atlantic. **This is significant because the model chlorophyll is not directly used to calculate the OM fraction, in contrast to other parameterizations of the OM fraction that are computed using chlorophyll.**

Also, to my knowledge, the processes controlling OM composition in the surface ocean are still highly uncertain, and it is unlikely that a climate-model based incantation of the surface ocean is doing an adequate job.

This is in fact one of the major limitations of our approach. In order to improve understanding of processes and to represent the system in more detail than is possible using a single proxy variable, it is imperative to use a process-based model. Global biogeochemistry models qualitatively and broadly capture many important features of ocean biota and chemical composition, yet they still struggle to accurately reproduce, for instance, the precise location and timing of phytoplankton blooms (Doney et al., 2009), much in the same way that weather prediction models struggle to reproduce the exact location and timing of precipitation events and are nevertheless useful.

We are also actively working toward improving the predictive capability of the CESM biogeochemistry model and have recently submitted a related paper (Ogunro et al., 2014, submitted) that focuses on the oceanic organic concentration.

In response to the reviewers' comments, we have added a sentence to the discussion that points out this limitation and provides a reference for the skill of the CESM ocean biogeochemistry model:

"Additionally, the model's predictive capability is limited by the predictive capabilities of ocean biogeochemistry models, which currently have a limited ability to accurately predict the exact location and timing of phytoplankton blooms (Doney et al., 2009)."

Second Minor Point: The authors regularly fail to acknowledge the work by Keene et al. (2007) who clearly demonstrated that high OM mass fractions could be achieved in low-chlorophyll waters. If the authors have some reason for excluding these results, it would be good to provide a justification.

We did not intentionally exclude Keene et al. (2007) from the discussion, but we did focus more on field observations than on laboratory experiments involving sea spray generation. We made this choice in part because laboratory experiments have given contradictory results, and the reasons for this are not yet clearly understood (as summarized in the recent review by Gantt and Meskhidze et al., 2013). However, we are happy to correct this oversight and include K07 in our discussion.

We fully agree that high OM enrichments can be produced from low-chlorophyll waters, and our model is in agreement with K07 on this point. A linear parameterization of OC fraction as a function of chl-a, based on measurements at high-chl-a and at low-chl-a, likely underestimates the amount of OC emitted in intermediate chl-a waters, as was nicely shown by Long et al. (2011) using a Langmuir adsorption-based argument.

To address the referee's comment, we will add a new subsection specifically discussing the K07 measurements, including the following paragraph:

"Keene et al. (2007; hereafter K07) measured the chemical composition of aerosol generated, using a glass frit system, from low-chlorophyll water (Chl-a=0.055) from the Sargasso Sea. The aerosol produced in that had a median enrichment factor for soluble OC of 387, and the OC fraction for the smallest particles produced (0.13 um) was ca. 80%. Using the ``medium'' values of size-resolved aerosol composition reported in K07, we calculate an OC/(OC+inorganics) fraction of 0.26 for 0.75-um particles, and 0.076 for 1.34-um particles. Figure 10 shows that in grid points with Chl-a=0.055, our model predicts submicron OM fractions ranging up to a maximum of about 0.15 (OC fraction = 0.24, assuming OM:OC = 1.8). This value is in reasonable agreement with the K07 results."

Specific Comments:

P5379-L7: Note, the assumption that Chl a was a good proxy for organic aerosol fraction was, in the case of Long et al. (2011), not motivated by observations at tower-based sites. Rather, it was motivated by its potential use as a proxy for surface active material production, and as an observable ocean quantity reflective of microbiology.

In response to the reviewer's comment, we have revised this sentence to:

"Chl a has been used as a basis for global atmospheric model parameterizations primarily because it is a globally available proxy for ocean biological activity. It is also moderately predictive of the organic aerosol fraction at sites ..."

The motivation for the use of Chl a as a proxy for surface active material by Long et al. (2011) has already been pointed out later in the same paragraph (p. 5379, l. 24-26).

P5379-L21-22: This should be reworded to emphasize that DOC is an operationally defined quantity.

Following the reviewer's suggestion, we have reworded this sentence to read:

"Almost all of the marine OC mass is dissolved organic matter (DOM), which is operationally defined as the portion of marine organic matter that will pass through a filter..."

P5382-L27: What is a low concentration for humate? Is this a correct statement? It is my understanding that on continental shelves and in proximity to terrestrial runoff, humate concentrations can be quite high.

This sentence contained an error in which "surface concentration" was erroneously substituted for "surface chemistry". After correcting this error, the sentence reads:

"However, less emphasis will be placed on these classes, because their **surface activity**is generally low."

P5388-L8: It is not clear why Nbub=2 is done. Is it possible to coat two sides of a bubble surface with surfactant? Perhaps if a bubble was created by dilation of a preexisting film, this could happen. If it is the authors' intent to suggest that one side of the film is made of SML material, I point them to the 'Second Major Point' above. If they wish to have a more detailed discussion about this, I will be glad to do so.

It was indeed our intention to suggest that one side of the film is covered with SML material, as discussed in the response to the "second major point". We note that it is not necessary that enriched concentrations of surfactants be present throughout the top 20-100 microns for this to occur. It only requires the formation of a monolayer on the ocean's air-water interface, which should form on timescales that are shorter than many bubble rise times and much shorter than the time between waves under even relatively calm conditions, as noted above. We have revised the text to clarify this.

P5389-L3-5: I think this assertion is far too simplistic. Please see, among others, Lhuissier and Villermaux (2011) and Brenner and Gueyffier, (1999) for a detailed description of the process of film droplet production.

This is indeed a simplification of a very complex process, and we are only asserting that this is a possible partial explanation. However, there is empirical evidence that larger bubbles have thicker films and also produce larger film drops upon bursting from the experiments on film drop production by D. Spiel (1998). We will revise this sentence to make clear the relationship between bubble size, film thickness, and film drop size:

"It may also account in part for the size distribution of the organic mass fraction: since smaller film drop particles are more frequently produced from the thinner films of smaller bubbles (Spiel, 1998), they would be expected to have a higher organic enrichment than larger particles produced from the thicker films of larger bubble (Oppo et al., 1999; Facchini et al., 2008; Gantt et al., 2011).

P5405-L23-28: I disagree with this statement. The observations are quite limited. Also see the statement in the 'First Major Point' above.

This sentence did not clearly reflect our intended meaning.

The original sentence read: "The link between Chl a and surface active DOM has been well-established by observations and experiments."

We will amend this sentence to: "Many studies have identified links between ocean surfactant concentrations and biological activity, which sometimes manifest as a correlation between ocean concentrations of surfactants and Chl a."

Fig 3: Are the units correct for the y-axis? The concentrations of surfactant seem a bit high relative to ocean concentrations.

The units are correct. The strongest surfactants are the lipid-like group, which we assume has concentrations largely below 6 [μmol C] L^{-1}, which equates to about 0.3 μmol L^{-1} or 95 μg L^{-1} oleic acid. The protein-like group has concentrations in the range . The referee notes that surface pressures measured by Long et al. (2014) indicate that "the theoretical concentration of oleic acid in oligotrophic seawater is on the order of 1 x 10^{-5} M". Lipids are not shown directly in Fig. 3, however, since their enrichment is so strong that they would appear far to the right of the figure and including them would render the proteins and polysaccharides difficult to display on the same axis.

Fig. 10: If possible, you might consider adding the error bars for the lines showing Long et al. (2011) results. They were pretty large.

After corresponding with Dr. Long on this point, we have elected not to include this uncertainty range, because it is not readily available in a closed analytical form, and also because it would clutter this figure, which already has a large information density.

Technical comments:

Several of the figures are difficult to read. Primarily, the fonts are blurry unless zoomed in quite a bit. Also, the figures' subtitles are placed in an odd way. Panel labels designating a letter (e.g. in Fig. 4: a) Stearic Acid) should be above the appropriate figure and left justified. I found it a bit confusing otherwise. While I was able to rationalize which figure was referenced, without taking time, I misinterpreted the figures.

Following the reviewer's suggestion, we have worked to improve the readability of the figures' axis labels and subtitles.

The paper wanders a bit in some places. For example, Fig. 17 is cited before Figs. 14, 15 & 16. Also, some of the text is a bit wordy & not clear or easy to follow.

To improve readability and organization of the text, we have added some subsection headings in the Results section. We have also revised the wording in some parts of the paper to improve readability, and corrected the ordering of the figures.

References:

Barker, David R., and Harry Zeitlin. "Metal-ion concentrations in sea-surface microlayer and size-separated atmospheric aerosol samples in Hawaii." *Journal of Geophysical Research* 77, no. 27 (1972): 5076-5086.

Deane, Grant B., and M. Dale Stokes. "Scale dependence of bubble creation mechanisms in breaking waves." *Nature* 418, no. 6900 (2002): 839-844.

Doney, Scott C., Ivan Lima, J. Keith Moore, Keith Lindsay, Michael J. Behrenfeld, Toby K. Westberry, Natalie Mahowald, David M. Glover, and Taro Takahashi. "Skill metrics for confronting global upper ocean ecosystem-biogeochemistry models against field and remote sensing data." *Journal of Marine Systems* 76, no. 1 (2009): 95-112.

Facchini, Maria Cristina, Matteo Rinaldi, Stefano Decesari, Claudio Carbone, Emanuela Finessi, Mihaela Mircea, Sandro Fuzzi et al. "Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates." *Geophysical Research Letters* 35, no. 17 (2008).

Gantt, B., N. Meskhidze, M. C. Facchini, M. Rinaldi, D. Ceburnis, and C. D. O'Dowd. "Wind speed dependent size-resolved parameterization for the organic mass fraction of sea spray aerosol." *Atmospheric Chemistry and Physics* 11, no. 16 (2011): 8777-8790.

Hoffman, Eva J., and Robert A. Duce. "Organic carbon in marine atmospheric particulate matter: Concentration and particle size distribution." *Geophysical Research Letters* 4, no. 10 (1977): 449-452.

Jachimska, Barbara, Piotr Warszynski, and Kazimierz Malysa. "Influence of adsorption kinetics and bubble motion on stability of the foam films formed at< i> n</i>-octanol,< i> n</i>-hexanol and< i> n</i>-butanol solution surface."*Colloids and Surfaces A: Physicochemical and Engineering Aspects* 192, no. 1 (2001): 177-193.

Keene, William C., Hal Maring, John R. Maben, David J. Kieber, Alexander AP Pszenny, Elizabeth E. Dahl, Miguel A. Izaguirre et al. "Chemical and physical characteristics of nascent aerosols produced by bursting bubbles at a model air-sea interface." *Journal of Geophysical Research: Atmospheres (1984–2012)*112, no. D21 (2007).

Krzan, M., J. Zawala, and K. Malysa. "Development of steady state adsorption distribution over interface of a bubble rising in solutions of< i> n</i>-alkanols (C< sub> 5</sub>, C< sub> 8</sub>) and< i> n</i>-alkyltrimethylammonium bromides (C< sub> 8</sub>, C< sub> 12</sub>, C< sub> 16</sub>)." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 298, no. 1 (2007): 42-51.

Long, M. S., W. C. Keene, D. J. Kieber, A. A. Frossard, L. M. Russell, J. R. Maben, J. D. Kinsey, P. K. Quinn, and T. S. Bates. "Light-enhanced primary marine aerosol production from biologically productive seawater." *Geophysical Research Letters* 41, no. 7 (2014): 2661-2670.

Melville, W. K. "The role of surface-wave breaking in air-sea interaction."*Annual review of fluid mechanics* 28, no. 1 (1996): 279-321.

Miyazaki, Y., K. Kawamura, J. Jung, H. Furutani, and M. Uematsu. "Latitudinal distributions of organic nitrogen and organic carbon in marine aerosols over the western North Pacific." *Atmospheric Chemistry and Physics* 11, no. 7 (2011): 3037-3049.

Mulqueen, Michael, Kathleen J. Stebe, and Daniel Blankschtein. "Dynamic interfacial adsorption in aqueous surfactant mixtures: Theoretical study."*Langmuir* 17, no. 17 (2001): 5196-5207.

Mulqueen, Michael, Sammy S. Datwani, Kathleen J. Stebe, and Daniel Blankschtein. "Dynamic surface tensions of aqueous surfactant mixtures: Experimental investigation." *Langmuir* 17, no. 24 (2001): 7494-7500.

O'Dowd, Colin D., Maria Cristina Facchini, Fabrizia Cavalli, Darius Ceburnis, Mihaela Mircea, Stefano Decesari, Sandro Fuzzi, Young Jun Yoon, and Jean-Philippe Putaud. "Biogenically driven organic contribution to marine aerosol."*Nature* 431, no. 7009 (2004): 676-680.

Oppo, C., S. Bellandi, N. Degli Innocenti, A. M. Stortini, G. Loglio, E. Schiavuta, and R. Cini. "Surfactant components of marine organic matter as agents for biogeochemical fractionation and pollutant transport via marine aerosols."*Marine Chemistry* 63, no. 3 (1999): 235-253.

Ovadnevaite, Jurgita, Colin O'Dowd, Manuel Dall'Osto, Darius Ceburnis, Douglas R. Worsnop, and Harald Berresheim. "Detecting high contributions of primary organic matter to marine aerosol: A case study." *Geophysical Research Letters* 38, no. 2 (2011).

Patro, Ranjan, Ira Leifer, and Peter Bowyer. "Better bubble process modeling: Improved bubble hydrodynamics parameterization." *Gas Transfer at Water Surfaces* (2002): 315-320.

Sciare, J., O. Favez, R. Sarda-Estève, K. Oikonomou, H. Cachier, and V. Kazan. "Long-term observations of carbonaceous aerosols in the Austral Ocean atmosphere: Evidence of a biogenic marine organic source." *Journal of Geophysical Research: Atmospheres (1984–2012)* 114, no. D15 (2009).

Quinn, Patricia K., Timothy S. Bates, Kristen S. Schulz, D. J. Coffman, A. A. Frossard, L. M. Russell, W. C. Keene, and D. J. Kieber. "Contribution of sea surface carbon pool to organic matter enrichment in sea spray aerosol." *Nature Geoscience* 7, no. 3 (2014): 228-232.

Yoon, Y. J., D. Ceburnis, F. Cavalli, O. Jourdan, J. P. Putaud, M. C. Facchini, S. Decesari et al. "Seasonal characteristics of the physicochemical properties of North Atlantic marine atmospheric aerosols." *Journal of Geophysical Research: Atmospheres (1984–2012)* 112, no. D4 (2007).

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A physically-based framework for modelling the organic fractionation of sea spray aerosol from bubble film Langmuir equilibria

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Abstract. The presence of a large fraction of organic matter in primary sea spray aerosol (SSA) can strongly affect its cloud condensation nuclei activity and interactions with marine clouds. Global climate models require new parameterizations of the SSA composition in order to improve the representation of these processes. Existing proposals for such a parameterization use remotely-sensed chlorophyll a concentrations as a proxy for the biogenic contribution to the aerosol. However, both observations and theoretical considerations suggest that existing relationships with chlorophyll a, derived from observations at only a few locations, may not be representative for all ocean regions.

We introduce a novel framework for parameterizing the fractionation of marine organic matter into SSA based on a competitive Langmuir adsorption equilibrium at bubble surfaces. Marine organic matter is partitioned into classes with differing molecular weights, surface excesses, and Langmuir adsorption parameters. The classes include a lipid-like mixture associated with labile dissolved organic carbon (DOC), a polysaccharide-like mixture associated primarily with semi-labile DOC, a protein-like mixture with concentrations intermediate between lipids and polysaccharides, a processed mixture associated with recalcitrant surface DOC, and a deep abyssal humic-like mixture.

Box model calculations have been performed for several cases of organic adsorption to illustrate the underlying concepts. We then apply the framework to output from a global marine biogeochemistry model, by partitioning total dissolved organic carbon into several classes of macromolecule. Each class is represented by model compounds with physical and chemical properties based on existing laboratory data. This allows us to globally map the predicted organic mass fraction of the nascent submicron sea spray aerosol.

Predicted relationships between chlorophyll a and organic fraction are similar to existing empirical parameterizations, but can vary between biologically productive and non-productive regions, and seasonally within a given region. Major uncertainties include the bubble film thickness at bursting, and the variability of organic surfactant activity in the ocean, which is poorly constrained. In addition, ~~marine colloids~~ polysaccharides may enter the aerosol more efficiently than Langmuir adsorption would suggest. Potential mechanisms for enrichment of polysaccharides in sea spray include the formation of marine colloidal particles that may be more efficiently swept up by rising bubbles, and cooperative adsorption of polysaccharides with proteins or lipids. These processes may make important contributions to the aerosol, but are not included here.

This organic fractionation framework is an initial step towards a closer linking of ocean biogeochemistry and aerosol chemical composition in Earth system models. Future work should focus on improving constraints on model parameters through new laboratory experiments or through empirical fitting to observed relationships in the real ocean and atmosphere, as well as on atmospheric implications of the variable composition of organic matter in sea spray.

1 Introduction

A growing body of observational evidence shows that the submicron sea-spray aerosol is frequently dominated by organic material, attributable to a primary marine source from sea spray aerosol (SSA) (O'Dowd and de Leeuw, 2007; Facchini et al., 2008; Hawkins and Russell, 2010; Russell et al., 2010). The presence of organic matter in SSA may affect the atmospheric concentrations of cloud condensation nuclei (CCN) in marine air, which in turn affect the radiative properties of clouds, and thereby also climate (Meskhidze and Nenes, 2006). A detailed review of the current state of research on marine organic aerosols can be found in Gantt and Meskhidze (2013).

Analysis of global climate model sensitivities shows that over remote ocean regions, cloud droplet number concentrations and cloud albedo can depend strongly on the simulated sea salt aerosol number concentration and hygroscopicity (Karydis et al., 2012; Moore et al., 2013). Several parameterizations for marine organic aerosol emissions have been proposed, all of which rely on empirical relationships with ocean chlorophyll a concentrations (Chl a) (O'Dowd et al., 2008; Fuentes et al., 2010b; Vignati et al., 2010; Gantt et al., 2011; Long et al., 2011). Thus, a key challenge in modelling the climate impacts of natural aerosols is the development of a process-based model to quantify the organic fraction of SSA (Carslaw et al., 2010). A process-based model will foster advances in understanding of the underlying drivers of marine POA emissions and their interactions with changes in global climate.

Chl a has been used as a basis for global atmospheric model parameterizations primarily because it is a globally available proxy for ocean biological activity. It is also moderately predictive of the organic aerosol fraction at sites such as Mace Head, Ireland (O'Dowd et al., 2004; Rinaldi et al., 2013), Point Reyes, California (Gantt et al., 2011), and Amsterdam Island (in the Southern Ocean) (Sciare et al., 2009), and more reliably so than other satellite-retrieved ocean color products such as dissolved organic carbon (DOC), particulate organic carbon (POC), and colored dissolved and detrital organic material (Gantt et al., 2011; Westervelt et al., 2012; Rinaldi et al., 2013). However, Chl a makes up only a tiny fraction of the available organic matter: Estimates from satellite observations suggest that chlorophyll mass as a percentage of POC ranges from $< 0.1\%$ in ocean gyres to $> 0.4\%$ in biologically productive open ocean regions and reaches a maximum of about two percent in coastal waters (Gardner et al., 2006). We use the terms "productive" and "non-productive~~"~~" to distinguish between ocean regions with and without currently active biological primary production, i.e. phytoplankton blooms, and the term "oligotrophic" to refer to regions where low nutrient availability results in low biological productivity for the entire year. Almost all of the marine OC mass is dissolved organic matter (DOM), ~~i.e., it~~ which is operationally defined as the portion of marine organic matter that will pass through a filter ~~, typically~~ with a pore size of, e.g., 0.2 – 0.7 μm. The mass ratio of DOM:detritus:plankton in surface water is approximately 200 : 10 : 1 (Verity et al., 2000; Nagata, 2008). It has been hypothesized that surface-active materials related to phytoplankton primary production and death drive the relationship between satellite-derived Chl a and sea spray OM (Long et al., 2011); this is supported by a correlation between marine Chl a and surfactant concentrations having been observed in situ during phytoplankton blooms as well as in laboratory phytoplankton cultures (Vojvodić and Ćosović, 1996; Gašparović and Ćosović, 2001; Gašparović and Ćosović, 2003).

Nevertheless, other evidence suggests that the ~~relationship~~ positive correlation between Chl a and marine aerosol fraction observed in bloom regions may not be representative for oligotrophic regions. In shipborne measurements in the North Atlantic, Russell et al. (2010) found a strong positive correlation (0.91) of the submicron OM:Na ratio with wind speed at 18 meters, and a moderate positive correlation (0.46) with Chl a. In the Arctic, they again found a strong positive correlation with wind speed (0.90), but a moderate negative correlation with Chl a (-0.63). Similarly, shipborne measurements during a period of high biological productivity in the open sea of the northeast Atlantic (Hultin et al., 2010) found a mild negative correlation between the marine aerosol organic fraction and chlorophyll a in the water. During a cruise off the California coast, in spray aerosol artificially generated from natural waters, the organic aerosol mass fraction correlated positively with ocean DMS, but not with Chl a (Bates et al., 2012). In a recent laboratory experiment, aerosol organic matter fractions in spray generated from breaking waves in a simulated phytoplankton bloom remained relatively constant during large changes in Chl a concentrations, but SSA hygroscopicity declined simultaneously with increases in heterotrophic bacteria concentrations (Collins et al., 2013; Prather et al., 2013).

These results suggest that empirical relationships with Chl a seasonal blooms are not adequate to predict the OM fraction of SSA, particularly outside of strong seasonal blooms. Indeed, a recent inter-comparison of different parameterizations of the submicron marine organic aerosol found that parameterizations diverged most strongly in their simulation of the organic fraction in chlorophyll-poor regions, yet these regions, because of their large area, contributed the most to total global marine organic sea spray emissions (Albert et al., 2012). A careful reanalysis of the Mace Head measurements recently indicated that while Chl a is a better predictor of OM fraction in filter samples collected at Mace Head than satellite-derived DOM or POM, a time lag of ca. 8 days is observed between peaks in upwind ocean Chl a concentrations and OM enrichment in aerosol, suggesting that the timescales of biological processes in ocean surface waters should be taken into account in order to improve prediction (Rinaldi et al., 2013).

The challenge remains to develop a model framework capable of describing organic SSA enrichment both in regions of active phytoplankton primary production, and in less productive waters, and to explain how ocean chemistry affects enrichment. In this paper, we model the organic fraction of submicron sea spray aerosol as driven by the adsorption of macromolecules on bubble surfaces, mediated by molecular surface activity. At some times and locations, these functional relationships produce strong correlations with Chl a, but under other circumstances the underlying biogeochemistry may differ so that the correlation with Chl a is much weaker, absent, or even negative. These differences highlight the need for incorporating a process-based model of ocean biota rather than relying on a single parameter such as Chl a.

In Section 2, we outline our aims and approach, and review observed patterns and broad ~~trends~~ patterns in the chemical composition and size distribution of sea spray aerosol. In Section 3, we introduce a novel framework for modelling the enrichment of organic matter in the submicron spray aerosol as a Langmuir adsorption process, and discuss possible chemical analogs for marine organic matter. In Section 4, we illustrate the aerosol enrichment predicted by the framework for single model compounds and for two-component mixtures. In Section 5, we combine the framework with distributions of marine organic macromolecules estimated from an ocean biogeochemistry model to generate an emission parameterization that can be applied in GCMs. In Section 6, we further discuss our results, as well as the uncertainties and limitations inherent in this approach. In Section 7, we summarize our main findings and discuss implications for the further development of organic sea spray parameterizations.

2 Effect of chemistry and particle size on enrichment

2.1 Aims and approach

Our aim is to develop a process-based model that can capture broad ~~trends in the geographic and chemical variation~~ geographic patterns in the amount and chemical composition of the organic fraction of marine aerosol using fields simulated by an ocean biogeochemistry model. To this end, it is necessary to partition the marine organic matter into several classes of compounds which may differ in their physical and chemical characteristics. We have chosen five broad classes of macromolecules: a lipid-like mixture associated with labile DOC, a polysaccharide-like mixture associated primarily with semi-labile DOC, a protein-like mixture with concentrations intermediate between lipids and polysaccharides, a processed mixture associated with recalcitrant surface DOC (Hansell, 2013), and a deep abyssal humic-like mixture that is brought to the surface by convective overturning. For brevity, we will refer to these classes as lipids (Lip), polysaccharides (Poly), proteins (Prot), processed (Proc), and humics (Hum), but we recognize that this usage is not a precise classification and further clarification of the chemical nature of the classes will be the subject of future work. For each class of macromolecules, we adopt a single organic molecule as a proxy for the adsorption behavior of each group at the air-water interface. This allows an approximation of the changes in chemical composition that occur as freshly injected DOC is gradually biologically and chemically modified.

Empirical studies of fresh phytoplankton blooms suggest that the approximate distribution of carbon mass in the phytoplankton is 60:20:20 between proteins, polysaccharides and lipids respectively, and this is reflected upon injection (Parsons et al., 1983; Wakeham et al., 1997; Benner, 2002). Because lipids are more quickly removed or altered by chemical and biological processes, their ocean concentrations are much smaller, yet their surface affinity and enrichment is higher than the other groups. Proteins are present in higher concentrations, but are somewhat less strongly enriched than lipids. Polysaccharide concentrations are higher than those of proteins and lipids, but have the lowest adsorption surface affinity. Humics represent abyssal compounds that are mixed into the ocean surface layer during deep overturning. Processed compounds correspond to the recalcitrant portion of DOC, including molecules that have undergone chemical degradation and recombination. However, less emphasis will be placed on these classes, because their surface activity is generally low.

These macromolecule classes are then implemented into a modelling framework that predicts the submicron SSA organic mass fraction by assuming that multiple classes of compounds may compete for bubble surface area and establish equilibrium according to the Langmuir adsorption isotherm. ~~We stress that this framework could equally be applied to a different formulation of the DOC classes , and further~~ The properties of the compound classes and their mapping to variables from an ocean biogeochemistry model will be discussed in detail in Sec. 5.2, but the general outline is as follows.

Further development will be required to ~~refine the approach~~better constrain the model and refine the partitioning of DOC. Nevertheless, we will show that this approach ~~– applying a well-established basic surface chemistry theory to marine biogeochemistry model output –~~ is capable of reproducing important features of the observed patterns in the SSA organic mass fraction. In particular, ~~it~~ the model predicts that OM fractions are relatively constant across most of the globe at most times, but also approximately reproduces the increased OM fraction during strong~~seasonal~~ , highly localized seasonal phytoplankton blooms associated with high Chl a, e.g., in the North Atlantic. Unlike in previous parameterizations, Chl a is not directly used to calculate the OM fraction, and so the model produces strong positive correlations between seasonal cycles in OM fraction and Chl a in certain localized blooms, but these relationships cannot be extrapolated globally. In

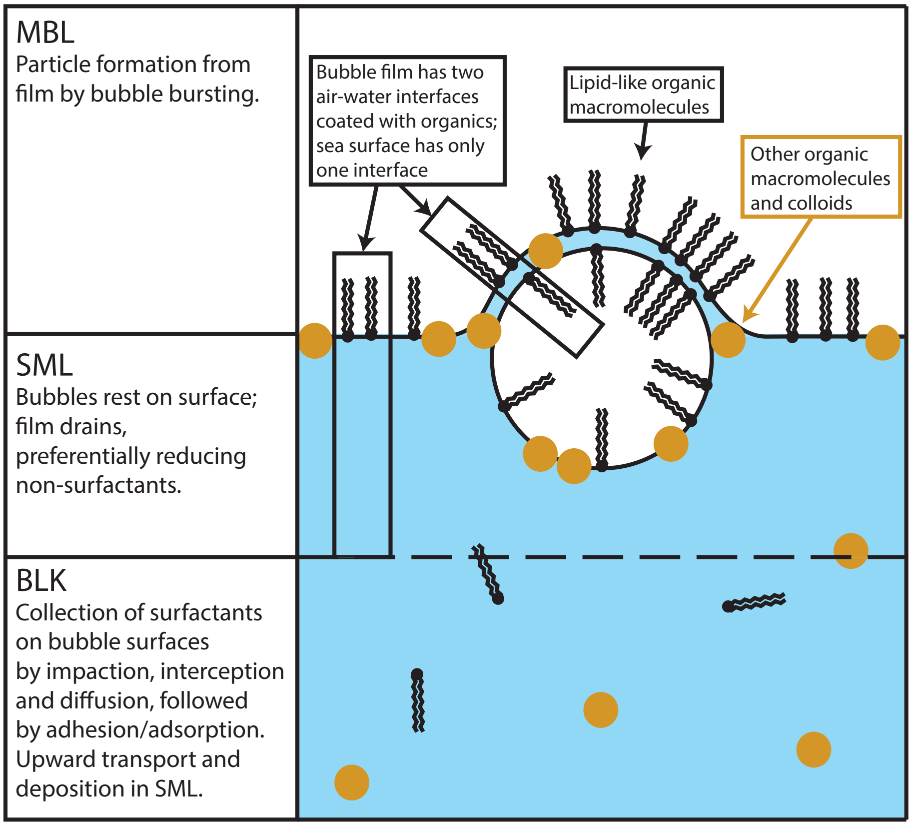


Fig. 1: Conceptual schematic of bulk water (BLK) – sea surface microlayer (SML) – marine boundary layer aerosol (MBL) enrichment processes.

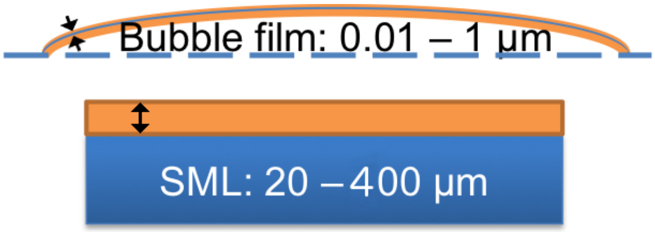


Fig. 2: Cartoon of the slab model used for calculation of the enrichment ratio from surface coverage. The bubble film, when resting at the water surface as suggested by the dashed blue line, is partially coated on both sides with organic surface-active materials, while the SML is partially coated on only one side. Bubble film thicknesses range from about 0.01 – 1 μm (Modini et al., 2013). SML sampling thicknesses depend upon the sampling method and range from 20 – 400 microns (Cunliffe et al., 2012).

addition, ~~it predicts differences between the organic aerosol composition~~ the model predicts differences in the detailed chemical composition of the organic aerosol in the different regions, ~~and~~ which may provide an explanation for observed differences between the organic aerosol composition in the Arctic and the North Atlantic.

In drawing ties between ocean biogeochemistry and atmospheric aerosol chemistry, we utilize notation common in each field. In particular, we draw the reader's attention to the fact that we will express quantities of organic mass (OM) and organic carbon (OC) in different units depending on the context. In the atmospheric context, we will generally use units of mass or mass concentration, which is how organic mass quantities are typically reported in the atmospheric chemistry literature. In the ocean context, we will generally use the molar concentration of carbon atoms in the organic matter (μmol OC L^{-1} or similar), which is the convention of most ocean biogeochemistry observations and models. Mass of OM can be converted to moles of OC by multiplication with the factor ~~$\left(\frac{m_{\mathrm{OM}}}{m_{\mathrm{OC}}}\right)_i \cdot \frac{M_C}{M_i}$.~~ $\left(\frac{m_{\mathrm{OM}}}{m_{\mathrm{OC}}}\right)_i \cdot \frac{M_C}{M_i}$.

2.2 Conceptual overview

In the open ocean, sea spray particles ~~are produced primarily by~~ originate primarily from the bursting of bubbles produced from wave-breaking (Lewis and Schwartz, 2004). As bubbles rise through the water column, surface-active dissolved and particulate materials accumulate on the bubble surface (Blanchard, 1975). ~~Adsorption equilibrium is reached quickly, e.g., in less than 0.05 ms for a sample of algal exudate (Fuentes et al., 2011) .~~

The deposition of collected material at the air-water interface contributes to the formation of the sea-surface microlayer (SML), a chemically distinct film that is enriched in surface-active organic matter relative to the underlying bulk water (Wurl and Holmes, 2008; Wurl et al., 2011; Cunliffe et al., 2012). The SML is disrupted by breaking waves, but reforms within a few seconds and is generally sustained when wind speeds are less than 10 m/s . Bubbles rest on the ~~SML~~ ocean surface for a period of up to a few seconds or more before bursting, which can be prolonged by the presence of soluble surfactant compounds (Garrett, 1967; Johnson and Wangersky, 1987; Modini et al., 2013).

Upon bursting, the film disintegrates into film drops (~~typically up to ca. 20 drops, but potentially many dozens, depending on bubble size)(Blanchard and Syzdek, 1982, 1988; Resch and Afeti, 1992; Spiel, 1998)~~ typically up to ca. 20 drops, but potentially many dozens, d

The film drops make up the majority of the submicron spray aerosol, and because they are drawn form the bubble film, they are enriched in surface-active organic matter (Macintyre, 1970; Blanchard, 1989). A bursting bubble also produces up to about seven jet drops (Spiel, 1994, 1997), the material for which is drawn primarily from the underlying bulk water; jet drops are therefore far less strongly enriched with the organics that coat the bubble surface. A conceptual overview of the processes leading to enrichment of organic matter in aerosol is shown in ~~Figure~~Fig. 1. In the remainder of this paper, we will consider only the composition of the freshly formed film drops, which roughly corresponds to the composition of the submicron sea spray.

The enrichment of organics in the SML and bubble film also will depend on the thickness of the film. SML sampling thicknesses range from 20 – 400 μm depending on the sampling method used (Cunliffe et al., 2012), while bubble film thicknesses range from 0.01 – 1 μm (Modini et al., 2013). In a simple conceptual model in which all organics are partitioned to the surface of a "slab" of saltwater or to both the inner and outer surfaces of a bubble film, the organic enrichment would be significantly higher for the thinner bubble films than for the thicker SML sample. This ~~is~~ would provide a mechanism that would explain the observations indicating that the OC:Na mass ratio is 10^2 – 10^3 higher in the submicron MBL aerosol than in the SML (Russell et al., 2010).

2.3 Enrichment factor

~~1~~ In this paper, we define the enrichment factor $F_{i,j}$ of the i-th chemical component in the j-th mode (SML or bubble film) as:

~~$F_{i,j} = \frac{m_{i,j}/m_{\mathrm{Na},j}}{m_{i,\mathrm{blk}}/m_{\mathrm{Na,blk}}} \approx \frac{m_{i,j}/m_{\mathrm{NaCl},j}}{m_{i,\mathrm{blk}}/m_{\mathrm{NaCl,blk}}}$~~ $F_{i,j} = \frac{m_{i,j}/m_{\mathrm{Na},j}}{m_{i,\mathrm{blk}}/m_{\mathrm{Na,blk}}} \approx$ (1)

where the $m_{i,j}$ [kg kg^{-1}] are the mass mixing ratios of the respective solution constituents, and the subscript "blk" denotes the bulk water~~. We~~ , and the subscript "SS" denotes sea salt. Because the submicron aerosol is primarily drawn from film drops, we assume that the bubble film fraction is predictive of the organic fraction in submicron nascent spray. ~~Note that~~ This assumption is supported by, e.g., recent studies showing the chemical similarity of a wave flume surface and the particles produced from that surface (Ebben et al., 2013) , as well as more generally supported by the observation that submicron spray is produced primarily from film drops (Blanchard and Syzdek, 1982, 1988; Resch and Afeti, 1992; Spiel, 1998 Note that sea salt mass may be altered during atmospheric transport, e.g., due to chlorine depletion by acid substitution in MBL aerosol, the ratio of Na:Cl mass in marine aerosol can be several times higher than in seawater (Pszenny et al., 1993; Keene et al., 1998; Buseck and Posfai, 1999; Lewis and Schwartz, 2004), but the equality should hold for nascent spray. Oxidation of organic matter may also occur in the atmosphere, increasing the organic mass content.

Reported enrichment factors for organic matter in marine aerosol vary over a range greater than 10 – 1000 (Burrows et al., 2013) and are generally not directly comparable, due to the lack of a standardized definition. However, a few general trends can be observed:

1. Surfactants that are enriched in the SML are also further enriched in the aerosol (Kuznetsova et al., 2004, 2005; Russell et al., 2010), and experimental evidence indicates that the transport of surfactants from seawater to the aerosol is linearly related to the transport to the seawater surface (Tseng et al., 1992) . This suggests that the same chemicophysical properties underlie both enrichment steps.

2. SML enrichment is strongest when bulk surfactant concentrations are low; when bulk surfactant concentrations are comparatively high, additional increases in bulk concentrations result in proportionally smaller increases in surface coverage (Marty et al., 1988; Hultin et al., 2011; Wurl et al., 2011). This is consistent with a surface saturation effect: as concentrations increase, more molecules compete for a smaller available surface area.

3. At high enrichment, adsorbing molecules compete for surface area at the air-water interface, with the most

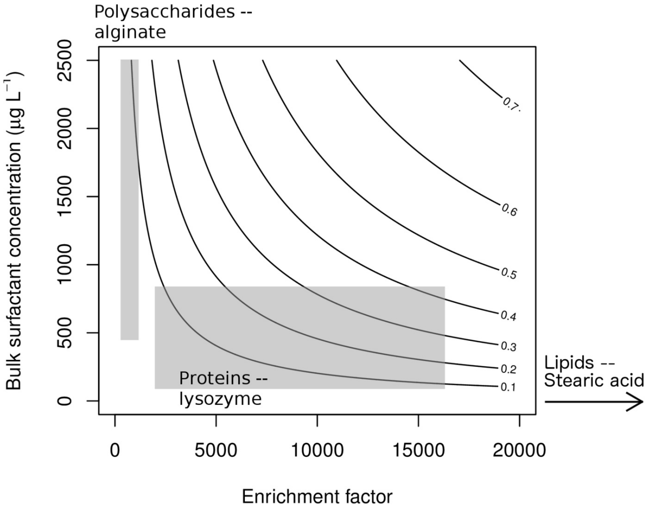


Fig. 3: Organic mass fraction in dry aerosol (OM:(NaCl+OM) mass ratio), as a function of enrichment factor and ocean organic mass. Approximate ranges of mass and enrichment factors for polysaccharides and proteins, as defined in Sect. 3.2 and Sect. ~~??~~5.2, are indicated as grey shaded regions. Lipids would appear far to the right of the figure, near the bottom.

surface-active compounds crowding out less surface-active molecules (Jarvis et al., 1967; Garrett, 1968; Harper and Allen, 2007).

4. Within a single homologous chemical group, enrichment of the particulate fraction is typically stronger than enrichment of the dissolved fraction (Marty et al., 1988; Kuznetsova and Lee, 2002; Kuznetsova et al., 2005). This is likely because bubbles more efficiently scavenge larger particles due to their larger radius and inertia (Sutherland, 1948; Weber et al., 1983; Dai et al., 1998, 2000).

3 Competitive Langmuir adsorption model

3.1 Model equations

To represent the saturation effect and the chemical and physical specificity of enrichment, we model the ~~enrichment~~ surface coverage as a competitive Langmuir adsorption equilibrium (Langmuir, 1918):

$$\theta_i = \frac{\Gamma_{i,eq}}{\Gamma_{i,\infty}} = \frac{\alpha_i C_i}{1+\sum_{i'}\alpha_{i'}C_{i'}}, \tag{2}$$

where the subscript i indicates the i-th component of the mixture, θ_i is the fractional surface coverage, C_i is the molar concentration, α_i is the Langmuir coefficient, $\Gamma_{i,eq}$ is the equilibrium surface excess and $\Gamma_{i,\infty}$ is the saturation surface excess.

Substantial experimental evidence supports the application of the Langmuir isotherm to the adsorption of surfactants onto the surface of bubbles ascending through the water column, and at the air-water interface ~~e.g., Skop et al., 1994; Giribabu and Ghosh, 2007; Schmitt-Kopplin et a~~ Fuentes et al. (2010a) have applied the Langmuir isotherm to fit laboratory measurements of surface-area tension relationships for phytoplankton exudate samples used to generate laboratory aerosol. Long et al. (2011) used a Langmuir-based equation in a global model parameterization of the organic fractionation of sea spray, but with a different formulation than we propose here, and using Chl a as the driving variable.

Potential interactions between molecules at the surface, e.g., cooperative adsorption (Baeza et al., 2005), are neglected. Importantly, this implies that Langmuir coefficients can be linearly combined: we can define an effective bulk Langmuir coefficient, α_{eff}, as a concentration-weighted average of the α_i:

$$\sum_i \theta_i = \frac{\alpha_{\mathrm{eff}}C_{\mathrm{tot}}}{1+\alpha_{\mathrm{eff}}C_{\mathrm{tot}}}, \tag{3}$$

$$C_{\mathrm{tot}} = \sum_i C_i, \tag{4}$$

$$\alpha_{\mathrm{eff}} = \frac{\sum_i \alpha_i C_i}{C_{\mathrm{tot}}}. \tag{5}$$

In other words, if the enrichment of each member of a group of compounds is described by the competitive Langmuir isotherm (Eq. 2), it follows that the enrichment of the entire group can also be described by the Langmuir isotherm (Eq. 5). This justifies the simplification of representing a complex mixture of compounds as a single class.

The Langmuir isotherm allows for three of the effects observed in enrichment of the SML and aerosol (Sect. 2.3): stronger enrichment of more surface-active molecules, saturation, and competition between constituents. The fourth effect, stronger particulate enrichment can be added as a simple extension by using a higher value of α_i for particulates than for dissolved matter.

To calculate the organic mass fraction of the ~~SML and the~~ bubble film, we treat the surface as a slab of seawater of thickness l_{bub} ~~or l_{SML}, respectively, which~~ that is partially coated with surfactants with fractional surface coverage ~~θ_i~~ $\theta_{i,\mathrm{bub}}$ with molar mass M_i and specific area a_i (Figure 2). The mass enrichment factor is then:

$$F_{\underline{i,j,\mathrm{mass}}\,i,\mathrm{bub},\mathrm{mass}} = \left[\underline{\frac{n_j\frac{\theta_{i,j}M_i}{a_i}}{\rho_{\mathrm{SW}}\cdot l_j\cdot s}}\;\frac{n_j\frac{\theta_{i,\mathrm{bub}}M_i}{a_i}}{\rho_{\mathrm{SW}}\cdot l_j\cdot s}\right]\left[\frac{s}{m_{i,\mathrm{blk}}}\right], \tag{6}$$

where ~~n_j represents the number of surfaces covered,~~ $s = 0.035\,\mathrm{kg\,kg^{-1}}$ is the ocean salinity, and $\rho_{\mathrm{SW}} = 1.025\,\mathrm{kg\,L^{-1}}$ is the approximate density of seawater.

We ~~use $n_{\mathrm{SML}} = 1$ and $n_{\mathrm{bub}} = 2$ to account for the two coated surfaces of the bubble film (interior and exterior; Figure 2), and~~ have assumed that the concentration of the organic material in the bulk is negligible, and neglected effects of bubble curvature. The parameter n_{bub} is an adjustable parameter that represents the number of sides of the bubble film that are covered with the areal fraction θ_{bub}. The smallest physically meaningful value, $n_{\mathrm{bub}} = 1$, implies that only the bubble interior is coated. We assume $n_{\mathrm{bub}} = 2$, which implies that the coverage of the interior and exterior films of the bubble are equivalent (Figure 2). Values of $n_{\mathrm{bub}} > 2$ would imply an enriched microlayer, which is possible under calm conditions.

The dry mass fraction in the nascent aerosol is given by:

$$\left(\frac{m_{i,j}}{m_{i,j}+m_{\mathrm{NaCl}}}\right)=\frac{n_j\frac{\theta_{i,j}M_i}{a_i}}{n_j\frac{\theta_{i,j}M_i}{a_i}+\rho_{\mathrm{SW}}\cdot l_j\cdot s}\cdot\left(\frac{m_{i,\mathrm{bub}}}{m_{i,\mathrm{bub}}+m_{\mathrm{NaCl}}}\right)=\frac{n_j\frac{\theta_{i,\mathrm{bub}}M_i}{a_i}}{n_j\frac{\theta_{i,\mathrm{bub}}M_i}{a_i}+\rho_{\mathrm{SW}}\cdot l_j\cdot s} \tag{7}$$

For the SML, the layer thickness is the sampling thickness, which ranges between 20 and 400 μm for sampling devices in use today (Cunliffe et al., 2012). For the bubble film, we take the mean film thickness to be ~~0.5~~0.1 μm. ~~This is likely an overestimate for bubbles that have significant surfactant coverage:~~ Because soluble surfactants can stabilize the bubble cap (Garrett, 1967; Johnson and Wangersky, 1987), ~~such that bubbles~~ bubbles with high surfactant coverage persist longer and more drainage occurs before bursting. Stabilized bubbles can be as thin as 0.1 μm, while clean bubbles can have thicknesses of up to a few microns, depending on bubble diameter (Spiel, 1998; Modini et al., 2013).

The slab model can account to a large extent for the fact that enrichment factors observed in the atmospheric aerosol are typically 5 – 20 times higher than in the SML (Kuznetsova et al., 2004, 2005). It may also account in part for the size distribution of the organic mass fraction: ~~if smaller~~ since smaller film drop particles are more ~~often produced from thinner bubble films , then~~ frequently produced from the thinner films of smaller bubbles (Spiel, 1998) , they would be expected to have a higher organic enrichment than larger particles produced from ~~thicker films (Oppo et al., 1999; Facchini et al., 2008; Gantt et al., 2011) .~~ the thicker films of larger bubble (Oppo et al., 1999; Facchini et al., 2008; Gantt et al., 2011) . Experiments with radio-labeled lipids in artificial seawater have also shown that smaller bubbles transport surfactants to the air more efficiently than larger bubbles (Tseng et al., 1992) .

We illustrate the relationship between the organic mass fraction and enrichment ratio in Figure 3, which shows the organic mass fractions in the nascent film aerosol (after subtracting water mass), calculated as a function of marine bulk OC concentrations and bulk:MBL OC enrichment factors.

Bulk OC:NaCl ratios of 10^{-4} to 10^{-3} (Ittekkot, 1982; Carlson et al., 2000; Lomas et al., 2001), combined with organic mass fractions of ca. 0.2 – 0.3 in the submicron aerosol over the remote open ocean, imply that enrichment factors for the submicron SSA are about 10^2 to over 10^3 (Russell et al., 2010). Much higher organic mass fractions (up to ca. 0.8) have been observed for the smallest particle sizes at Mace Head ~~during~~ downwind of seasonal blooms (O'Dowd et al., 2004; Facchini et al., 2008; Gantt et al., 2011). However, the enrichment factor is highly sensitive to the size fraction selected: integrating the size distribution of the organic fraction from artificially-generated aerosol (Gantt et al., 2011) across a canonical sea spray size distribution (Lewis and Schwartz, 2004) results in an organic mass fraction of ca. 60% for $D_p < 0.5$ μm, but only ca. 15% for $D_p < 1$ μm and 3% for $D_p < 2$ μm.

The model requires that the following physical parameters be specified for each of the components: Langmuir coefficient α_i, specific area a_i, and molecular mass M_i. In addition, it requires specification of the bubble film thickness l_{bub} for the calculation of the enrichment ratio, and n_{bub}, which controls the fractional coating of the exterior surface relative to the interior surface. These parameters can be estimated either from laboratory experiments on individual model compounds or empirically fitted to observations of observed organic mass fractions.

3.2 Selected model compounds and their chemical properties

3.2.1 Overview of data reviewed

~~The physical chemistry literature contains a range of organic and polymer~~ A large number of experiments have been published that include adsorption data at the air-water interface under a variety of conditions (e.g., Adamson and Gast, 1997). Most ~~reported data are from experiments~~ of these experiments were conducted at room temperature, which may not be representative for remote situations, particularly for cold temperatures in polar regions. Salinity varies between experiments but ~~is~~ was lower than the ~~seawater salinity~~ salinity of seawater in most cases. Nevertheless, a substantial number of studies report the adsorption behavior of organic macromolecules under conditions approximating the marine surface environment~~, which we have collected~~ . We have summarized these studies in Table 1.

For each of the organic classes in our study, we have selected ~~analogs on the basis of their representativeness as well as the quality of available~~ representative analog moleculess for which measurements of adsorption behavior at the air-water interface ~~. For each analog, we report~~ are available. Based on the literature we reviewed, we select order-of-magnitude estimates of the Langmuir half-saturation and surface excess parameters ~~based on the reviewed literature~~for each analog molecule (Table 1).

Table 1: Marine and laboratory model compounds selected to represent the ocean macromolecules, along with reference half-saturation concentrations $C_{1/2}$ and carbon surface excess Γ_{max}. Except as stated in the text, data are for room temperature and low ionic strength. Concentrations and surface densities are given in moles per liter carbon and then atoms per square angstrom. Parenthetical values were estimated based on others in the same class. We use the following abbreviations in the table (1) Proteins (Prot), (2) polysaccharides (Poly), (3) lipids (Lip), (4) humic acid and related compounds (Hum).

Structure	Ocean Analogs	Laboratory Analogs	$C_{1/2}$	Carbon Γ_{max}	References
Prot	Generic enzymes	Lysozyme	10^{-4}	1.0	F97, GP79b
	Denatured strands	Casein	10^{-5}	0.5	BM85, DR03, GP79b
Poly	Soluble starch	Maltodextrin	$> 10^{0}$	(10-100)	SB07, VW83
	Alginate	Natural alginate	10^{-1}	10-100	B00, VW83, Z81
	Generic glucans	Pectin	10^{-1}	Close packing	F97, NB06, RB00, P11
		Gum Arabic	10^{-2}	50	DR03, G91, NB06
Lip	Commercial surrogate	SDS	10^{-2}	0.2	CT52, L98, T70, T07
	C18 fatty acids	Stearic and oleic	$< 10^{-6}$	1.0	B12, CD68, H70, G70, L91
	Sterols	Cholesterol	$< 10^{-6}$	0.7	A86, BM85, MB78, P88, P05
Hum	Fulvic acid	Riverine Standard	10^{-1}	1.0	A89, D06, S06, T07, VW83
	Humic acid	Commercial	10^{-1}	1.0	M90, T07, TC04

General abbreviations: BSA - Bovine Serum Albumin, SDS - Sodium Dodecyl Sulfate

Reference abbreviations: A86 - Alexander et al. (1986); A89 - Averett et al. (1989); B00 - Babak et al. (2000); B12 - Brzozowska et al. (2012); BM85 - Barger and Means (1985); CD68 - Christodoulou and Rosano (1968); CT52 - Cook and Talbot (1952); D06 - Dinar et al. (2006); DR03 - Damodaran and Razumovsky (2003); F97 - Frew (1997); G70 - Garrett (1970); G91 - Gaonkar (1991); H70 - Heikkila et al. (1970); L91 - Lindsley et al. (1991); L98 - Li et al. (1998); M90 - Malcolm (1990); MB78 - McGregor and Barnes (1978); NB06 - Nilsson and Bergenståhl (2006); P88 - Parrish (1988); P05 - Parra-Barraza et al. (2005); P11 - Perez et al. (2011); RB00 - Rosilio and Baszkin (2000); S06 - Svenningsson et al. (2006); SB07 - Shogren and Biresaw (2007); T70 - Tajima et al. (1970); T07 - Tuckermann (2007); TC04 - Tuckermann and Cammenga (2004); VW83 - Van Vleet and Williams (1983); Z81 - Ẑutić et al. (1981)

~~Nonlinear~~ The maximum surface excess Γ_{max} can be obtained by nonlinear curve fitting to the Langmuir-Szyskowski ~~relation (Lan et al., 2001; Svenningsson et al., 2006) additionally permits the derivation of Gibbsian Γ_{max}, the upper limiting surface excess, which~~ equation (Lan et al., 2001; Svenningsson et al., 2006) . Γ_{max} can be approximately understood as the inverse of the area occupied per unit of substance, when the surface is saturated. Surface excess is less variable than the Langmuir adsorption parameter, for our model compounds. Although the geometric arrangement and orientation of molecules on the surface can differ widely between molecules, variations in Γ_{max} rarely exceed an order of magnitude within a homologous series (Graham and Phillips, 1979a,b; Damodaran and Razumovsky, 2003; Tuckermann, 2007).

We now discuss in detail the adsorption property recommendations for each class of macromolecule.

3.2.2 Proteins

We include two example proteins: a globular protein, lysozyme, composed of 100 amino acid residues, and casein, as example of a disordered protein that is highly surface-active (Adamson and Gast, 1997; Damodaran and Razumovsky, 2003). These model compounds are representative of a range of surface activities that are observed in marine phytoplankton blooms (Ẑutić et al., 1981; Barger and Means, 1985). We consider lysozyme and BSA to represent freshly released enzymes, which should temporarily retain their structure after injection into the water column. Casein, on the other hand, is taken to be representative of the surface behavior of a denatured protein (Lehninger, 1975; Benner, 2002). The proteins adsorb by training monomeric sequences along the interface with hydrophobic groups rotated into the vapor phase, then looping as necessary, with the result that disordered and denatured proteins tend to have a stronger surface affinity than structured, globular proteins (Graham and Phillips, 1979a; Adamson and Gast, 1997; Baeza et al., 2005).

3.2.3 Polysaccharides

Soluble starches are traditionally considered the representative model for carbohydrates emerging from phytoplanktonic cells (Van Vleet and Williams, 1983; Frew, 1997). Naturally-occurring polysaccharides are typically water-soluble and not surface active (Stephen, 1995). We adopt pectin as the primary polysaccharide model compound. A structural component of cell walls in fruit, it provides a well-studied example of natural, intermediate amphiphilicity (Nilsson and Bergenståhl, 2006; Perez et al., 2011). The marine derivative alginate may be purified from brown algae such as *Macrocystis*. It is commercially available and although it is actually a coastal derivative, its surface activity is similar to that of pectin (Babak et al., 2000). As a third and final analog, we select the synthetic oligomer maltodextrin (Shogren and Biresaw, 2007). It consists of only about 10-20 glucose subunits linked by regular glycosidic bonds and has very limited surface activity.

3.2.4 Lipids

Atmospheric aerosol chemists have frequently used sodium dodecyl sulfate (SDS) as a proxy for natural lipids. However, SDS is more soluble and has lower affinity for the air-water interface than representative lipids found in the environment, such as the analogs we have selected: stearic acid, oleic acid, and cholesterol. Multiple lines of experimental evidence indicate very high surface activity of these compounds. Diffusion from surface films into the bulk phase is slow (Sebba and Briscoe, 1940; Heikkila et al., 1970). For oleic and stearic acid, results from theory describing polymer dissolution (Ter Minassian-Saraga, 1956; Brzozowska et al., 2012) and measurements of diffusion coefficients for long aliphatic chain molecules justify a very high estimate of surface activity, with $C_{1/2} < 10^{-6}$ (Wilke and Chang, 1955; Sallee and Dietschy, 1973; Weisiger and Zucker, 2002).

This is consistent with the extremely low solubility measured for long-chain lipids (Vorum et al., 1992). Cholesterol is likewise highly surface-active and sparingly soluble (Sebba and Briscoe, 1940; McGregor and Barnes, 1978; Alexander et al., 1986).

3.2.5 Processed compounds

The processed and mixed organics include those resulting from biogeochemical aging of the other groups, i.e., they represent the recalcitrant portion of DOC. Some of the freshly produced polymers hydrolyze after being released via cell disruption into seawater, and they are further degraded by enzymes, bacteria, and photolysis (Tranvik and Kokalj, 1998). Fragments may recombine into new molecules with a heterogenous mixture of functional groups (Amon and Benner, 1996; Benner, 2002).

The identity and surface adsorption behavior of these processed compounds is poorly characterized. Lacking better information, we take them to be most similar to the humics and apply the same adsorption parameters.

3.2.6 Humics

The reviewed literature values for humics refer primarily to material derived from riverine and coastal sources and sometimes available commercially as a set of standard substances, e.g., Suwanee Riverine fulvic acid or European counterparts (Van Vleet and Williams, 1983; Averett et al., 1989; Tuckermann and Cammenga, 2004; Svenningsson et al., 2006). Langmuir adsorption parameters are fairly consistent across these studies, so that some confidence can be attached to the values in Table 1.

4 Box model calculations

To illustrate the concepts developed here, we performed box model calculations for individual compounds and two-component systems. We use parameters as specified in Table 2, which we designate as the BASE case. Organic enrichments are computed over the approximate ranges of surface ocean OC molar concentrations for the respective macromolecule class. The ranges are taken from the ocean biogeochemical model results for the respective macromolecule class, which will be described in detail in Section 5.

4.1 Single model compounds

In Figure 4, we show the organic mass fraction resulting from each of several model macromolecules, and illustrate its sensitivity to bulk concentrations of the macromolecule, and to variations in the Langmuir adsorption parameter. The compounds shown here are a representative lipid (stearic acid), protein (lysozyme), polysaccharide (alginate) and humic compounds (Suwannee River fulvic acid).

Among the macromolecules shown in Figure 4, only stearic acid and lysozyme are sufficiently surface-active to contribute significantly to the mass fraction of the film. Stearic acid contributes the most, despite the fact that it is present in lower concentrations than the other macromolecules, because of its strong affinity for the air-water interface. By contrast, humics (Suwannee river fulvic acid) can be present in much higher concentrations in the bulk ocean water, but contribute negligibly to the film. Polysaccharides would contribute negligibly using alginate as the model compound, but other models such as casein have stronger surface activity.

4.2 Two-component model

We now illustrate the effect of competitive adsorption in a two-component model consisting of a lipid (stearic acid) and

Table 2: Coefficients used to calculate box model and global organic enrichment, BASE case. Values are derived from model compounds as described in Table 1: lysozyme, natural alginate, stearic acid, fulvic acid.

Compound class	OM:OC ratio	$C_{1/2}$ [mol C L^{-1}]	α_i [m^3 mol^{-1}]	M_i [g mol^{-1}]	a_i [Å^2 molec.$^{-1}$]	M_i/a_i [mg m^{-2}]	References
Polysaccharides	2.3	0.1	9.0	250000	300	140	B00, F01, SB07, P11, TL01
Proteins	2.2	1.0×10^{-4}	22000	66463	4400	2.5	B02, F01, GP79a
Lipids	1.3	1.0×10^{-6}	18000	288	18	2.6	B12, H70, TL01
Humics	1.8	0.1	0.40	732	34	3.6	A89, M90, S06
Processed	1.8	0.1	0.40	732	34	3.6	A89, B00, M08, S06

Reference abbreviations: A89 - Averett et al. (1989); B00 - Babak et al. (2000); B02 - Benner (2002); B12 - Brzozowska et al. (2012); F01 - Fraga (2001); GP79a - Graham and Phillips (1979a); H70 - Heikkila et al. (1970); M90 - Malcolm (1990); M08 - Moore et al. (2008); P11 - Perez et al. (2011); S06 - Svenningsson et al. (2006); SB07 - Shogren and Biresaw (2007); TL03 - Turpin and Lim (2001).

a protein (lysozyme or casein), with properties as specified in Table 1 and Table 2. The model representations of lysozyme and casein differ only in the value of α_i, which is ten times greater for casein than for lysozyme.

Stearic-acid-like lipids dominate the surface adsorption when they are present in a mixture with globular, lysozyme-like proteins (Figure 5a). Disordered, casein-like proteins have higher surface activity. While still less adsorptive than stearic acid, they are highly competitive as a result of their higher marine concentrations (Figure 5b).

5 Ocean biogeochemical model

5.1 Description of simulations

Marine biogeochemical systems models now incorporate major processes determining the distribution of organic material in the ocean. These include the release and transport of labile and semi-labile dissolved organic carbon (DOC) (Moore et al., 2001, 2004; Hansell et al., 2012), which have e-folding lifetimes in surface waters of approximately 10 days and 100 days, respectively, before being removed by microbial processes (e.g., consumption by heterotrophic bacteria, (Christian and Anderson, 2002)) or transformed by photochemical reactions (Tranvik and Kokalj, 1998).

We used the Parallel Ocean Program (POP; Maltrud et al., 1998) to simulate the general circulation and its biogeochemical elemental cycling routines (BEC; Moore et al., 2004) to simulate marine biogeochemistry. Both are components of the Community Earth System Model (CESM; www.cesm.ucar.edu, Hurrell et al., 2013). Calculations were performed using the CESM 1.0 beta release 11. Biogeochemistry variables calculated in BEC include several classes of nutrients, phytoplankton, and zooplankton, in addition to dissolved inorganic carbon (DIC), alkalinity, particulate organic carbon (POC) and semi-labile dissolved organic carbon (DOC). Biogeochemical tracers are transported, and their concentrations are updated in each time step by a tendency that includes source, removal, advection, and diffusion terms as in Gregg et al. (2003); Sarmiento and Gruber (2006); Elliott et al. (2011):

$$\frac{\partial}{\partial t}T_k = \nabla \cdot (D \nabla T_k) - \mathbf{V} \cdot \nabla T_k \\ - w_T \frac{\partial}{\partial z} T_k + S_T(\mathbf{T}) - R_T(\mathbf{T}), \quad (8)$$

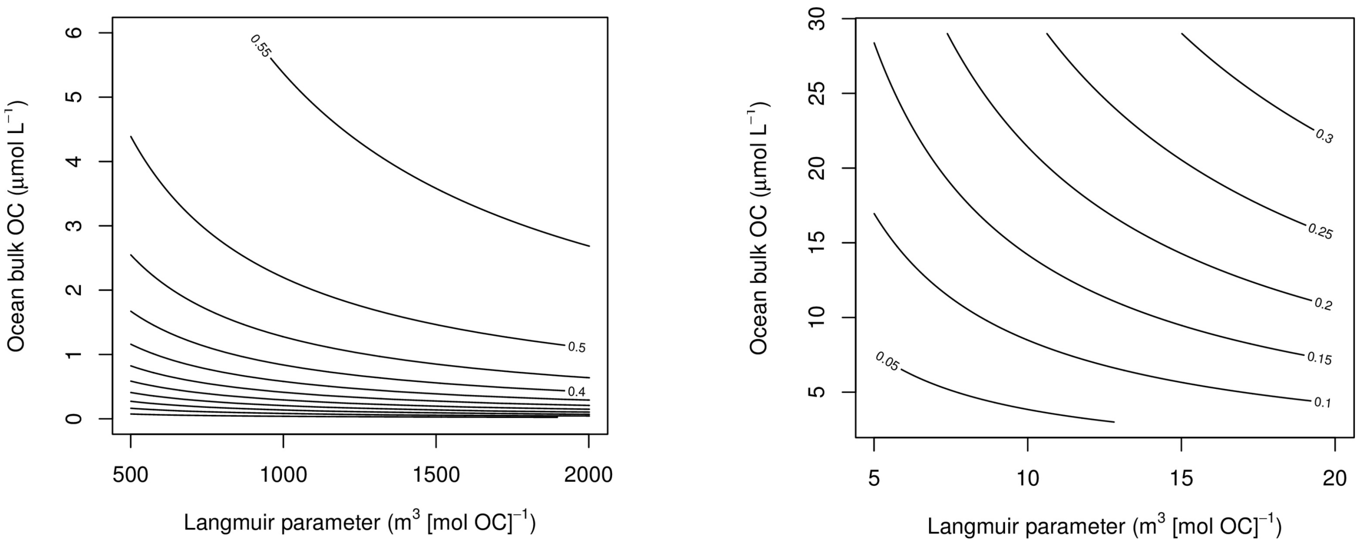
where T_k is the concentration field of the k-th tracer; $\mathbf{T}$ is the vector field of all tracer concentrations, D is the eddy diffusivity coefficient, $\mathbf{V}$ is the three-dimensional ocean current field, w_T is a supplementary particle-driven vertical motion, and $S_T(\mathbf{T})$ and $R_T(\mathbf{T})$ are the local rate of production (source) and loss (removal) as functions of $\mathbf{T}$. The additional vertical term includes movement associated with sinking of particles, e.g., calcium carbonate or silicate hard parts from large phytoplankton (Armstrong et al., 2001), or alternatively buoyant rise associated with TEP (transparent exopolymeric particles; Azetsu-Scott and Passow, 2004).

The labile portion of DOC is removed instantaneously during CESM simulations because it is low in mass and computational emphasis is usually placed on carbon budgeting. By contrast, all semi-labile carbon is treated as a single aggregate tracer with a 100-day lifetime (Moore et al., 2004).

5.2 Mapping of macromolecules to marine biogeochemical variables

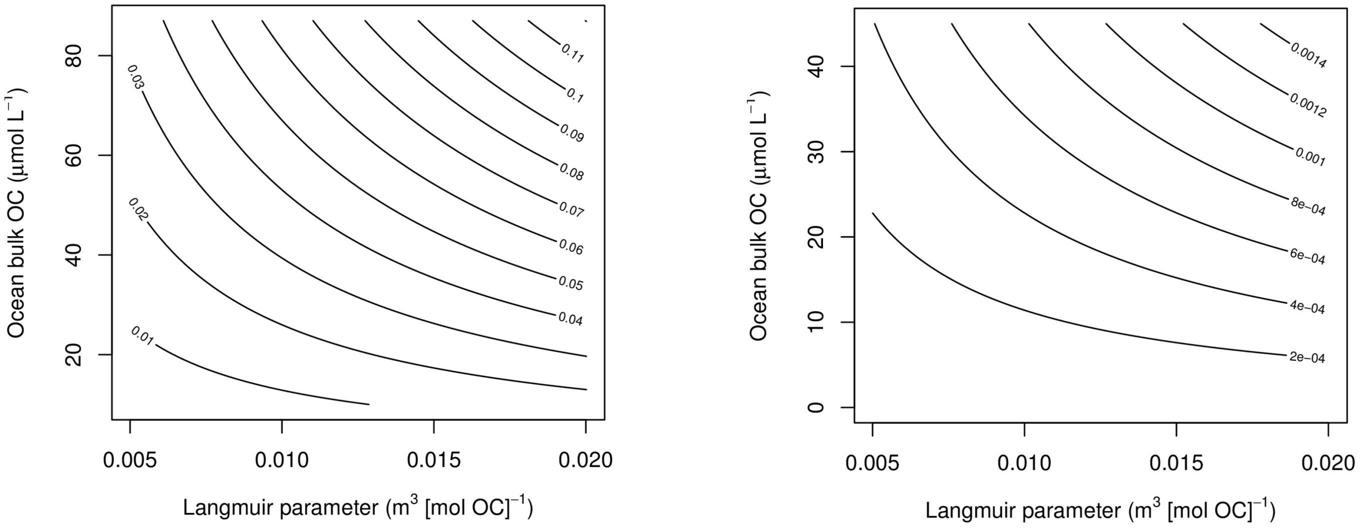
The development of the macromolecule distributions begins from the premise that the major source of marine DOC is cell lysis, i.e. the disruption of cell exteriors resulting in the release of organic components to the water (Kujawinski et al., 2002). This can follow from viral attack, graz-

(a) Stearic acid **(b) Lysozyme**



~~Stearic acid~~ ~~Lysozyme~~

(c) Alginate **(d) Suwannee River fulvic acid**



~~Alginate~~ ~~Suwannee River fulvic acid~~

Fig. 4: Organic mass fraction in dry aerosol (OM:(NaCl+OM) mass ratio), predicted organic mass fractions for model compounds as a function of Langmuir parameter α_i [m^3 (mol OC)$^{-1}$] and OC molar concentration. Ranges of OC concentration (vertical axis) are estimated for classes of molecules from ocean biogeochemical model output, as described in Section 5 and chemical parameters are as indicated in Tab. 2. Ranges of Langmuir parameters (horizontal axis) are obtained by varying α_i between 0.5 and 2 times the respective model compound value from the BASE case.

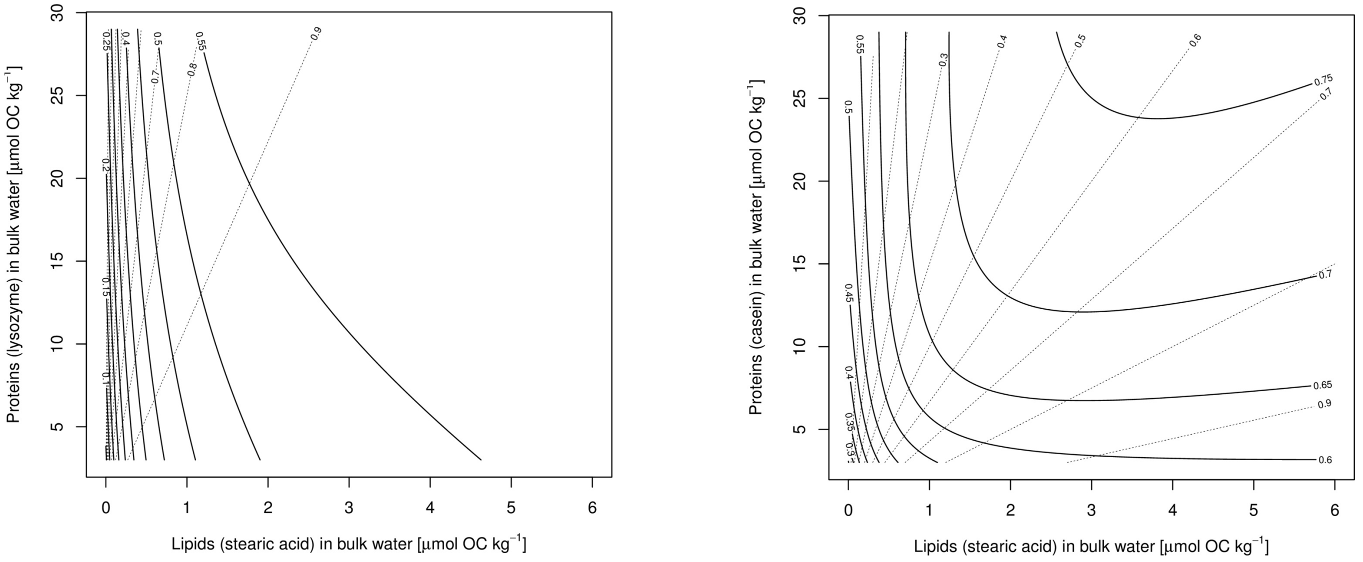
ing by larger zooplankton, or simply senescence, i.e., aging. ~~Phytoplanktonic exudation~~ Phytoplankton exudate is a smaller, but still important source of DOC (Carlson, 2002).

We apportion DOC among five classes of organic compounds (with abbreviations in parentheses): (1) Proteins (Prot), (2) polysaccharides (Poly), (3) lipids (Lip), (4) humic acid and related compounds (Hum), with the remainder assigned to (5) geochemically aged and mixed compounds (Proc). We summarize these four classes of compounds in the carbon concentration vector field $\mathbf{C}$:

$$\mathbf{C} = (\mathrm{Prot}, \mathrm{Poly}, \mathrm{Lip}, \mathrm{Hum}, \mathrm{Proc}). \tag{9}$$

The model species we have chosen as chemical representatives of these classes are discussed in detail in Section 3.2 and also in parallel work focused on the marine surfactant chemistry (Elliott et al., 2013).

The analysis strategy is as follows: first, calculate the distributions of the freshly produced compounds offline based


(a) Stearic acid and lysozyme **(b) Stearic acid and casein**

~~Stearic acid and lysozyme~~ ~~Stearic acid and casein~~

Fig. 5: Organic mass fractionation in a two-component model including stearic acid and either lysozyme or casein (with properties as specified in Table 1 and Table 2) and over a range of OC concentrations estimated from ocean biogeochemical model as described in Sect. 5. Dark solid lines show total organic mass fraction of film aerosol. Thin dashed lines show fraction of organic mass that is contributed by stearic acid.

on POP/BEC results - proteins, polysaccharides and lipids deriving from DOC. Second, calculate the distribution of the remaining “processed” compounds. Third, calculate the additional humic compounds resulting from deep overturning in the winter at high latitudes.

Lipids are extremely short-lived (Parrish, 1988; Parrish et al., 1992), so we treat them as existing in a local steady state determined by rates of phytoplankton production and disruption with a lifetime of 10 days:

$$C_3 = S_3 \cdot \tau_3, \tag{10}$$

where S_3 is the production rate of lipids and $\tau_3 = 10$ days is the assumed lifetime of lipids in ocean surface water. The source term S_3 assumed to be proportional the product of the phytoplankton carbon concentration C_{phyto} and the rate of phytoplankton disruption by zooplankton:

$$S_3 = 0.2 \cdot k_{\text{dirupt}} \cdot C_{\text{phyto}} \cdot \frac{C_{\text{zoo}}}{\overline{C_{\text{zoo}}}} \tag{11}$$

where C_{zoo} is the zooplankton carbon concentration with geographic mean value $\overline{C_{\text{zoo}}}$, and k_{dirupt} is a pseudo-rate constant, set to a value of $1/300$ day^{-1}. The factor 0.2 reflects the assignment of 20% of freshly produced DOC from phytoplankton spillage to the lipids.

The distribution of lipids (Fig. 6a) reflects the distribution of phytoplankton primary production (~~Figure 6a~~Eq. 10). S_3 is taken to be 20% of dissolved carbon flow computed from BEC. Our method of reconstructing the C flux is similar to that introduced by Elliott (2009) for the injection of organosulfur compounds into the water column during global DMS simulations. However, since the macromolecules are not present solely in the cytosol, allowance is made for conversion to ~~zooplanktonic~~ zooplankton and particulate mass.

Polysaccharides are the longest-lived among the freshly produced compound classes (Kaiser and Benner, 2009), and they are presumed here to be identical with the POP semi-labile dissolved organic carbon (SDOC):

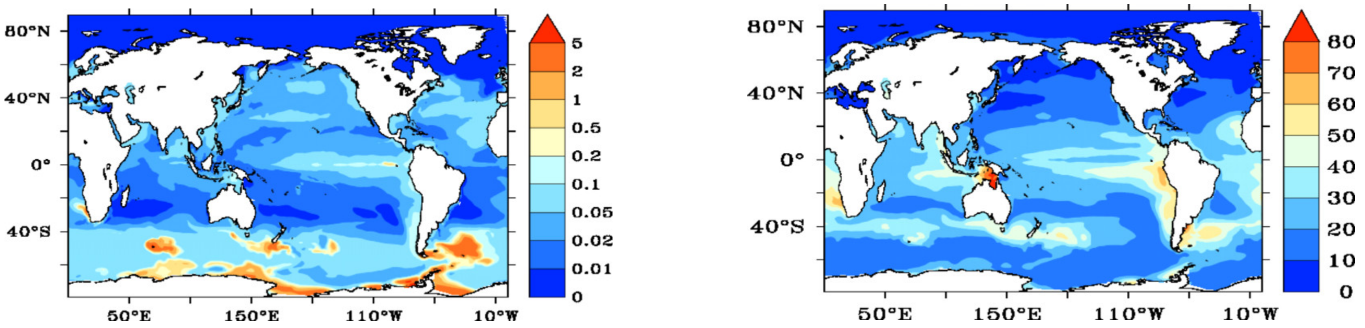
$$C_2 = \text{SDOC}. \tag{12}$$

Proteins are of intermediate lifetime and are observed to contribute a fraction of the marine organic matter that lies between that of lipids and of polysaccharides (Tanoue, 1992; Hubberten et al., 1994; Kuznetsova et al., 2004; Kaiser and Benner, 2009). We thus estimate the protein concentration as one-third of the SDOC:

$$C_1 = \frac{1}{3} \cdot \text{SDOC}. \tag{13}$$

As shown in Figure 6b and Figure 6c, polysaccharides and proteins are present in broad regions associated with higher marine biological activity.

We assign the remaining surface DOC to the class “processed carbon.” Processed carbons and humic materials represent the recalcitrant portion of DOC, with lifetimes ranging from decades to tens of thousands of years (Hedges et al., 2001; Benner, 2002; Hansell et al., 2012). Annual average DOC was approximated as a function of latitude consistent with climatological data (Hansell et al., 2012), with

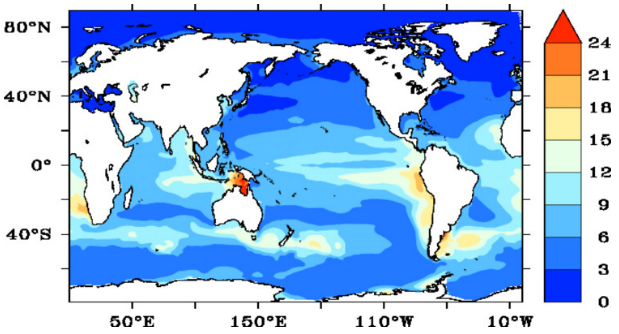


(a) Lipid-like mixture

(b) Polysaccharide-like mixture

~~Polysaccharide-like mixture~~

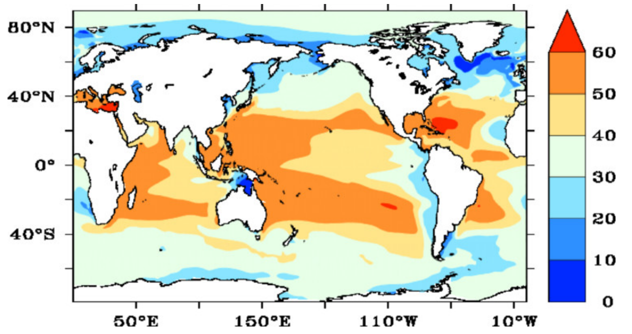
(c) Protein-like mixture



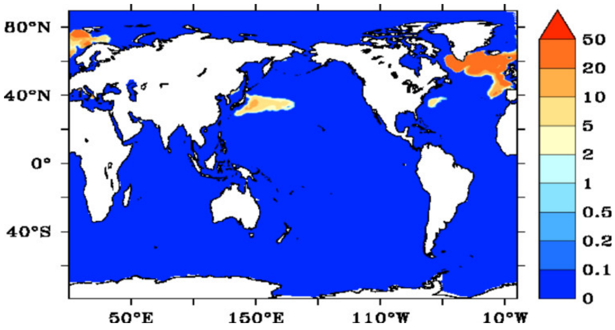
~~Protein-like mixture~~

~~Lipid-like mixture~~

(d) Processed mixture



(e) Deep abyssal humic-like mixture



~~Deep abyssal humic-like mixture~~

Fig. 6: ~~Processed mixture~~Ocean surface concentration of each compound class [μmol L^{-1}], February. ~~Ocean concentration of each compound class μmol L^{-1}, February.~~

fine structure and seasonality filtered then re-injected from the POP SDOC. The other surface macromolecules were then subtracted, leaving behind the mixed, processed polymers (Benner, 2002; Kaiser and Benner, 2009). We further apply a lower limit to the concentration of processed compounds in order to prevent unrealistically low or negative concentrations, $C_{5,min} = 3\ \mu\text{mol C}^{-1}$. This processed carbon is then:

$$C_5 = \max\left[\left(\text{DOC}_\text{total} - \sum_{i=3}^{3} C_i\right), C_{5,\text{min}}\right] \tag{14}$$

The distribution of processed carbon is shown in Figure 6d. Processed carbon constitutes the vast majority of the DOC, particularly in oligotrophic zones.

Humics include abyssal carbon carriers and are estimated based on the timing and depth of convective turnover. Convection is parameterized in POP by the KPP non-local vertical mixing scheme (Large et al., 1994), which predicts the eddy diffusivity D as a function of water column stability and generates turnover below typical mixed layer depths in high latitude winter. For the purposes of this analysis, we assume that overturning occurs when the mixed-layer depth exceeds a threshold value. We further assume that prior to overturning, lipids, proteins, polysaccharides, and processed compounds are initially well-mixed from the surface to the mixed-layer depth h_ML (specified as 200 m) and that humics are initially well-mixed in a layer extending from h_ML to the depth of convective mixing, h_{conv}. The mixed-layer concentration of the surface organic classes is the vector C_ML:

$$C_\text{ML} = \{C_1, C_2, C_3, 0, C_5\} \tag{15}$$

The pre-overturning concentration of deep humic substance below the mixed layer is set to 50 μM C, representative of a global average abyssal carbon concentration (Benner, 2002; Dittmar and Kattner, 2003; Hansell et al., 2012):

$$C_\text{deep} = \{0, 0, 0, 50, 0\} \tag{16}$$

Where overturning is triggered, it is assumed to result in instantaneous, homogeneous mixing from the surface to h_conv. Concentrations after overturning are then:

$$\mathbf{C} = \mathbf{C}_\text{ML}(h_\text{ML}/h_\text{conv}) + \mathbf{C}_\text{deep}((h_\text{conv} - h_\text{ML})/h_\text{conv}) \tag{17}$$

As shown in Figure 6e, this has the effect of focusing humic activity in well-understood zones of deep turnover (Longhurst, 1998; Oliver and Irwin, 2008).

5.3 Results: Global geography of the Langmuir adsorption of macromolecules

~~North Atlantic~~

~~Southeast Pacific~~

~~Monthly mean values from BASE case in two ocean regions (Apr – Mar). Green: POP-simulated Chl a mg m^{-3}. Note that Chl a is divided by five in left panel to improve legibility of seasonal trends. Black: total submicron SSA dry organic mass fraction. Blue: lipid mass fraction. Magenta: polysaccharide + protein mass fraction.~~

~~Effective mass enrichment ratio~~

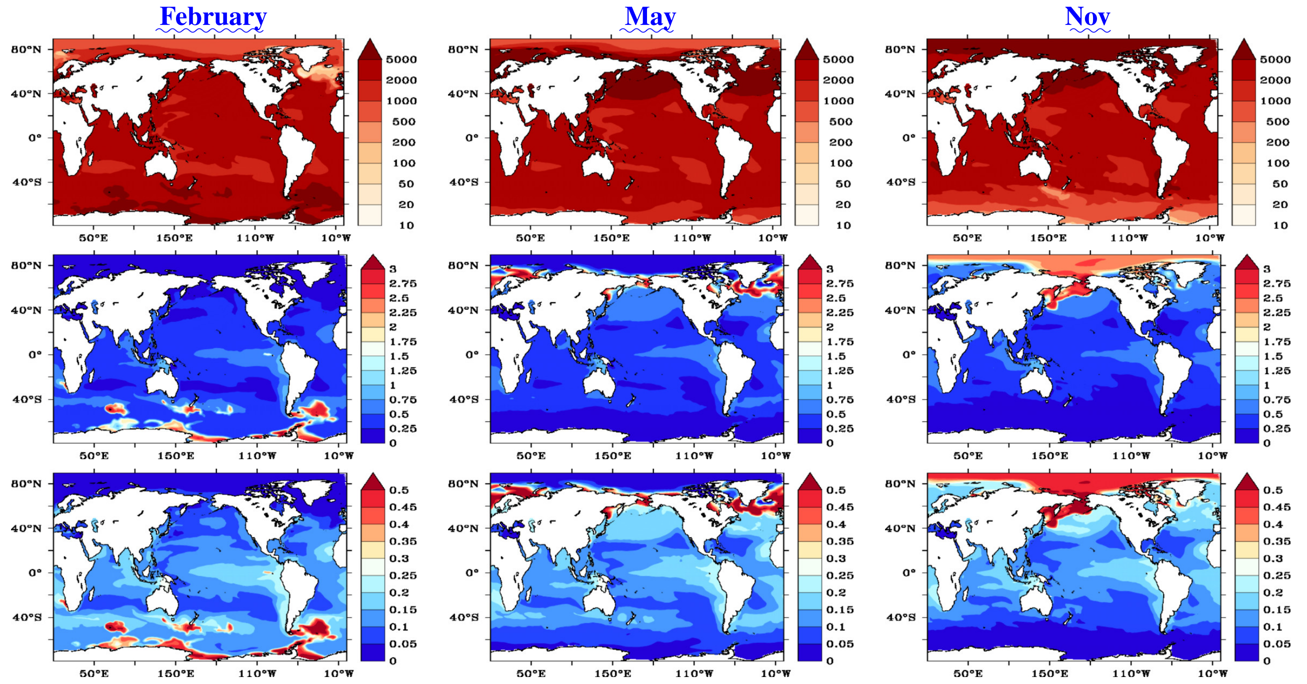
~~Organic mass fraction~~

~~Global estimates of effective enrichment and organic mass fractions. Case LOW-LIP: using model compounds as described in Table 1, but with α_lip decreased by a factor of ten; February.~~

~~Effective mass enrichment ratio~~

~~Organic mass fraction~~

~~Global estimates of effective enrichment and organic mass fractions. Case FILM-0.5: using model compounds as described in Table 1, but with $l_\text{bub} = 0.5\,\mu$m; February. Global estimates of effective organic mass fractions – February. Case EXUDATE: using empirical constants derived from phytoplankton exudates (Fuentes et al., 2011) , with the same physical constants applied to all five compound classes. Left: Organic mass fraction. Right: Organic mass fraction vs. POP Chl a. Global estimates of organic mass fraction in nascent film drops – sensitivity cases (February). Left: Case HIGH-PROT: using model compounds as described in Table 1, but with α_prot for casein (ten times larger value). Right: Case HIGH-HUM: using model compounds as described in Table 1, but with $\alpha_\text{humic} \times 10^4$. Mean mass fractions predicted for each region as defined in Fig. 9 and globally for different sensitivity cases. FEB MAY AUG NOV North Atlantic 0.04 0.31 0.19 0.12 Arctic 0.02 0.36 0.19 0.07 Northeast Pacific 0.10 0.14 0.12 0.12 Southeast Pacific 0.18 0.17 0.15 0.17 Southern Ocean 0.20 0.13 0.08 0.15 GLOBAL 0.14 0.14 0.14 0.13 GLOBAL - $l_\text{bub} = 0.5$ 0.03 0.04 0.04 0.03 GLOBAL - LOW-LIP 0.09 0.09 0.09 0.09 GLOBAL - HIGH-PROT 0.33 0.33 0.32 0.33 GLOBAL - HIGH-HUM 0.16 0.15 0.15 0.14 Ratio of alkane mass to hydroxyl mass from model macromolecules, and from ship-borne FTIR observations. Points and error bars indicate median and 5%-ile to 95%-ile range of model estimates for seawater and for emitted submicron SSA, calculated from global monthly grid-box mean values. For the purpose of this comparison, macromolecule concentrations were converted to estimated functional group ratios using the values provided in Table 4. Solid lines indicate averages of data from clean air samples only, i.e., data from air contaminated by anthropogenic pollution have been excluded. The ship-borne observations are from the E-PEACE campaign off the central coast of California (July – August, 2011) (Russell et al., 2013) , the ICEALOT campaign in the North Atlantic and Arctic Oceans (March – April, 2008) (Russell et al., 2010) , and the VOCALS-Rex campaign, in the Southeast Pacific oligotrophic gyre (October, 2008) (Hawkins et al., 2010) . The shaded areas~~


February

May

Nov

Fig. 7: Global estimates of effective enrichment and organic mass fractions. Case BASE: using model compounds as described in Table 1. Top: Effective mass enrichment ratio. Middle: OM:Na mass ratio in nascent film drop aerosol. Bottom: Organic mass fraction in nascent film drop aerosol. Left: February. Center: May. Right: August.

~~indicate the ± 1 standard deviation uncertainty range for VOCALs-Rex (Marine air mass, MAM), ICEALOT (Arctic) and ICEALOT (North Atlantic), respectively. Conversion from moles carbon per macromolecule class to the mass associated with FTIR-observable functional-groups (g of the functional group/ moles carbon of macromolecule).~~[a] ~~alkane hydroxyl carboxyl amine Lipids~~[a] ~~10.11 0.85 0 0 Polysaccharides~~[a] ~~7.0 19.17 0 0 Proteins~~[a] ~~6.18 1.35 18.53 6.47 Processed~~[a] ~~7.0 19.17 0 0 Humics 7.0 19.17 0 0~~

We apply selected surface activity and physical properties to predict the bubble surface coverage and thereby the film organic mass fraction (Tab. 1, Tab. 2; Elliott et al., 2013). Results are shown in Fig. 7. Predicted organic mass fractions are between 10% and 20% in most regions, and exceed 50% in regions of high biological productivity. Mass enrichment factors are in the range 1000–2000 over much of the globe. Because the OM:Na ratio is more strongly conserved than the OM:NaCl ratio (due to chlorine depletion in the atmosphere), it is also presented in the middle panels; values range from less than one over most of the globe to more than 2.5 in phytoplankton blooms. For comparison, typical OM:Na mass ratios measured during the ICEALOT campaign in the Arctic and North Atlantic in March were around 0.7 – 0.8 (Russell et al., 2010). Predicted organic mass fractions of the nascent film drops are shown in the lower panels, and range up to about 0.5. In tropical upwelling zones, e.g., in the equatorial Pacific, the model predicts very similar organic enrichment in February and in August, reflecting the limited seasonality of nutrient and light availability near the equator. The highest organic enrichments are predicted in the locations with active seasonal blooms, e.g. the Labrador Sea in August and the Antarctic Sea in February. Spring blooms are not shown in the interest of space but are also represented, e.g. the North Atlantic bloom reaches a peak around May.

Figure 8 shows the mass fractions of the dry submicron SSA that are contributed by of each the four organic compound classes polysaccharides, proteins, lipids, and humics (processed compounds are not shown because their contribution is negligible). Although lipids contribute ~~only~~ very little of the ocean DOC (Figure 6a), they contribute the majority of the aerosol OC in regions of high productivity (Figure 8c). In less-productive waters, organic mass is primarily contributed

---

[a] ~~Molar mass associated with a functional group is assumed to include half the mass of the carbon atom if single-bonded and the full mass of the carbon atom if double-bounded, e.g., C-H mass is 7 g mol^{-1} (including half the mass of the carbon atom), and COOH mass is 45 g mol^{-1} (including the full mass of the carbon atom). Functional group distribution per macromolecule class (moles functional group/ moles carbon) is estimated based on model compounds as indicated.~~

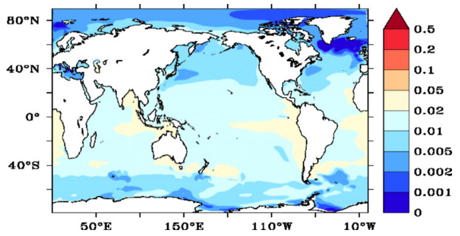
[a] ~~Functional group mass distribution of cholesterol.~~

[a] ~~Functional group mass distribution characteristic of simple sugars.~~

[a] ~~Characteristic functional group mass distribution of a mixture of amino acids present in seawater.~~

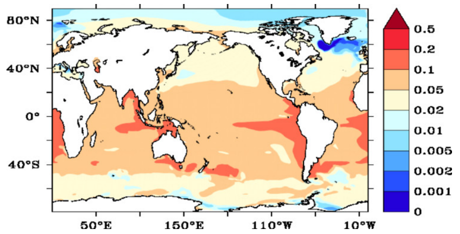
[a] ~~Same as for polysaccharides.~~

(a) Polysaccharides



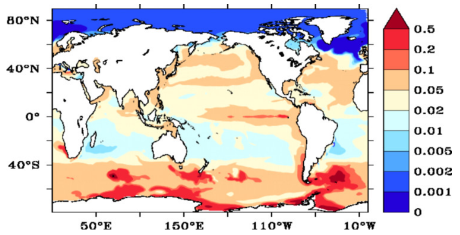
~~Polysaccharides~~

(b) Proteins



~~Proteins~~

(c) Lipids



~~Lipids~~

Fig. 8: Submicron SSA dry mass fraction from each compound class, February, BASE case. Fractions of processed and humic classes (not shown) are negligible.

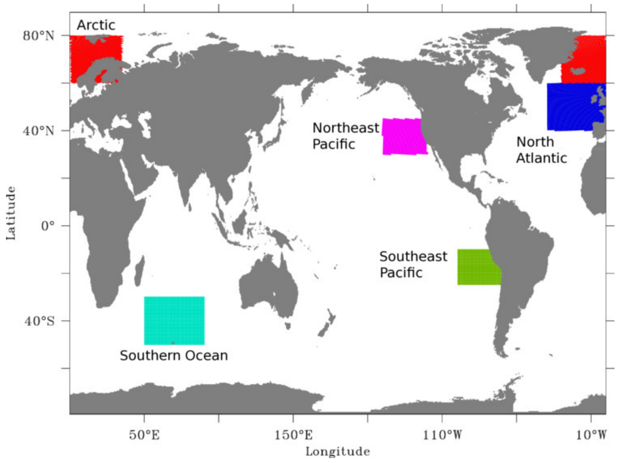


Fig. 9: Geographic regions as ~~used~~ defined in this paper.

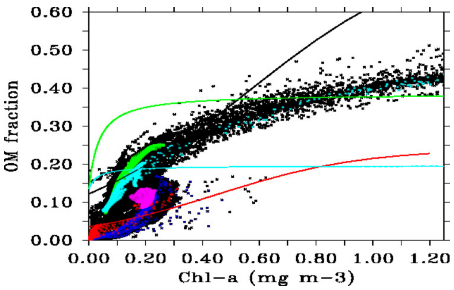
by proteins, and polysaccharides are also a significant contributor (Figure 8b and Figure 8a).

~~For comparison~~

5.4 Chl-a:OM relationship and comparison with previous parameterizations

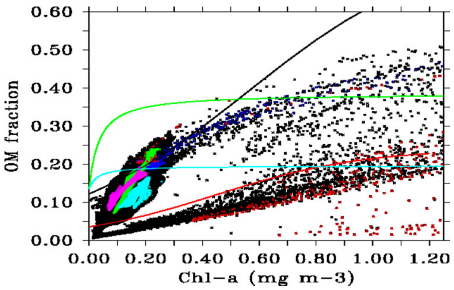
In the presentation of some of the remaining results, we have chosen to highlight several geographic regions that are of interest as locations for field campaigns, or to highlight differences between ocean ecosystems. These regions are defined in Fig. 9. To compare our model with existing Chl a-based parameterizations, we show the predicted relationship between chlorophyll concentration as predicted by the Parallel Ocean Program (POP) and the sea spray organic mass fraction in February, May, August and November, visually highlighting points from each of the selected greographic regions (Fig. 10). ~~Data from individual regions are highlighted in colors corresponding to the map in the upper panel; black points indicate the rest of the world.~~ The functional shape of the (Chl a)-(OM fraction) relationship resembles empirical relationships derived by other authors and largely falls within observational constraints (Gantt et al., 2011; Long et al., 2011). Organic mass fractions increase rapidly at lower chlorophyll concentrations, and then begin

(a) February



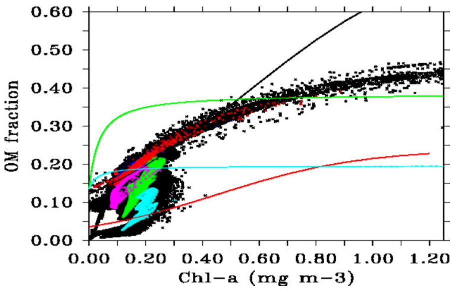
~~February~~

(b) May



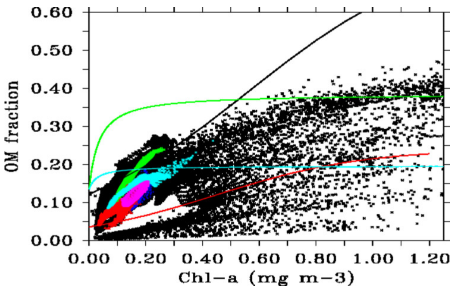
~~May~~

(c) August



~~August~~

(d) November



~~November~~

Fig. 10: POP-simulated Chl a vs. submicron SSA dry organic mass fraction, with model output from five geographic regions highlighted, BASE case. Colored points are data in the regions shaded in corresponding colors in Fig. 9, i.e., red: Arctic; dark blue: North Atlantic; magenta: northeast Pacific; green: southeast Pacific; cyan: Southern Ocean. Black points indicate rest of world. Black and red lines indicate empirical fits to observations from Mace Head, Ireland ($D_p < 1.5\,\mu$m), and Point Reyes, California ($D_p < 2.5\,\mu$m), respectively (Gantt et al., 2011). Blue and green lines show the parameterization of Long et al. (2011) for particle diameters of 0.8 and 0.5 μm, respectively.

~~BASE case~~

~~LOW-LIP case~~

~~Correlation between POP-simulated monthly mean Chl a~~

to flatten out at higher chlorophyll concentrations, as surfaces approach saturation. However, the predicted Chl a-OM relationship varies depending on region and season. For example, in May, for the same values of Chl a, predicted OM fractions are significantly higher in the North Atlantic than in the Arctic, consistent with observations (Russell et al., 2010).

5.5 Seasonal cycles in Chl a and OM

Although global mean concentrations are relatively constant throughout the year (Tab. 3), certain regions have a strong seasonal cycle in average OM fraction. For the geographic regions defined in Fig. 9, the regionally-averaged seasonal cycles of total OM fraction, lipid fraction, the total of protein and polysaccharide fraction, and Chl a are shown in Figure 11, and the regional mean values of OM fraction are compared in Tab. 3. Regions characterized by strong seasonal blooms such as the Arctic, North Atlantic and Southern Ocean display strong seasonal cycles in the total OM fraction, while in the northeast Pacific and southeast Pacific, the seasonal cycle is far more muted. The relative contriutions of the lipids and the semilabile classes (proteins and polysaccharides) also vary seasonally and between regions. In the North Pacific, the total OM fraction remains relatively constant, but the relative contriutions of lipids versus proteins and polysaccharides vary over the course of the year.

To better understand the seasonality of the Chl a-OM relationship, we calculated the correlation between monthly mean POP-simulated Chl a and monthly mean aerosol organic fraction (Figure 12). Areas with strong seasonal blooms, such as the North Atlantic, exhibit strong positive correlations (compare Figure 6a and Figure 8c for locations of simulated blooms in Southern Hemisphere summer; seasonal cycle is shown in Figure ~~??~~11). In regions such as the Southeast Pacific, spring blooms are weaker, and semi-labile DOM accumulates over the course of the spring and summer season, approaching its peak as Chl a declines (Figure ~~??~~11). In these regions, monthly mean Chl a and SDOC can be anti-correlated, and SDOC contributes significantly to estimated aerosol organic mass (polysaccharides and proteins). This produces the anti-correlation between Chl a and OM fraction evident in our model in some regions.

Because the values of the model parameters are highly uncertain, we ~~show the effect of varying~~ explore some of the ~~parameters~~ uncertainties in a small set of sensitivity tests. Some of the figures referenced in this section are available in the online supplementary material. This is indicated by the figure number being prefixed with "S-". Summary results are presented in Tab. 3.

5.5.1 Low lipid adsorptivity

First, because lipids drive much of the variability in predicted OM enrichment, we show a case in which the lipid adsorp-

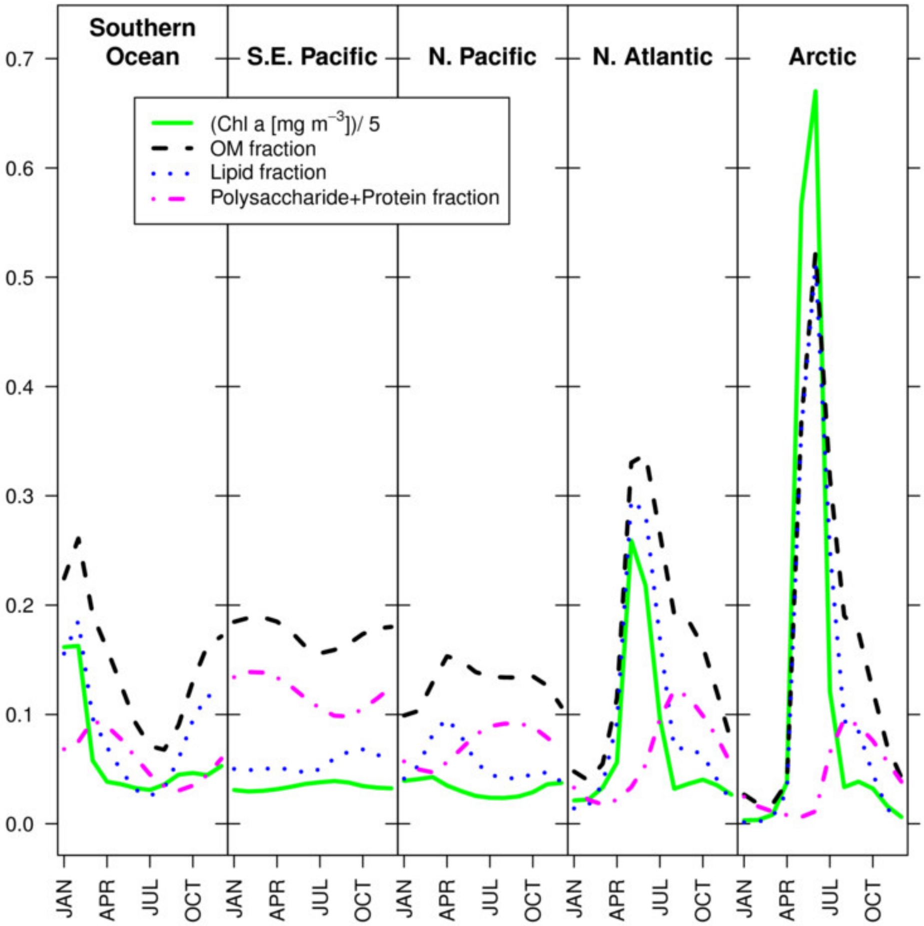


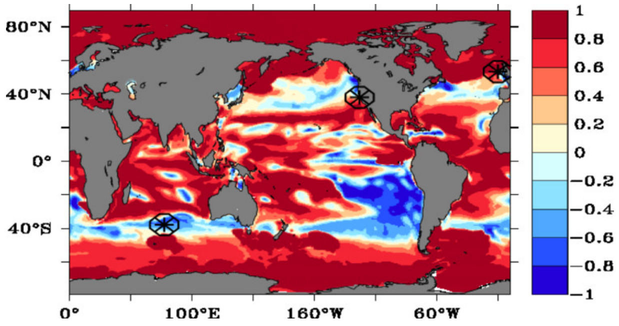
Fig. 11: Monthly mean values from BASE case for ocean regions indicated in Figure 9. Green solid line: POP-simulated Chl a [mg m^{-3}] / 5 – Note that Chl a is scaled to improve legibility of seasonal trends. Black dashed line: total submicron SSA dry organic mass fraction. Blue dotted line: lipid mass fraction. Magenta dot-dash line: polysaccharide + protein mass fraction.

tivity α_{lip} has been reduced by a factor of ten (LOW-LIP; Fig. ~~??~~S-4; middle row). In this scenario, the maximum OM fraction in bloom regions is ca. 0.3, compared to > 0.5 in the BASE case. By contrast, in the midlatitude oceans, e.g., in the southeastern Pacific, the OM fraction is dominated by the SDOC-associated polysaccharides and proteins and changes little between the BASE and LOW-LIP cases. Because the influence of lipids on the aerosol OM is reduced in the LOW-LIP case, the SDOC-dominated regions with a negative correlation of Chl a and aerosol OM fraction expand for this case (Fig. 12b).

~~One potential approach to constrain these parameters is to use field observations of the chemical composition. In Figure 15, we show that the estimated ratio of the mass associated with C-H bonds (alkane mass) increases relative to that associated with C-OH groups (hydroxyl mass) as the ratio of lipid adsorptivity to polysaccharide adsorptivity increases. Conversion of the macromolecular classes to functional group-associated mass was performed using the weights presented in Table 4. Higher alkane:hydroxyl ratios indicate an aerosol that is more lipid-like and dominated by long aliphatic chains. Lower alkane:hydroxyl ratios indicate an aerosol that is more oxidized and more carbohydrate-like.~~

~~We compare the model estimates in Figure 15 with mean values from FTIR measurements of submicron sea spray collected during several ship-based field campaigns. The campaigns shown here span all four of the major ocean biomes delineated by Longhurst (1998) , and thus are affected by very different ocean ecosystem processes and plankton communities. Differences in alkane:hydroxyl ratios could be driven by either differences in the composition of the source organic matter, or in the chemical processing to which molecules are exposed before emission, both of which can be expected to differ systematically between ocean biomes. The lowest observed alkane:hydroyl ratios are from clean marine samples collected during E-PEACE (0.24), off the central coast of California (Coastal biome), in the presence of high chlorophyll. These are followed by samples from the ICEALOT campaign (marine air mass:~~

(a) BASE case



(b) LOW-LIP case

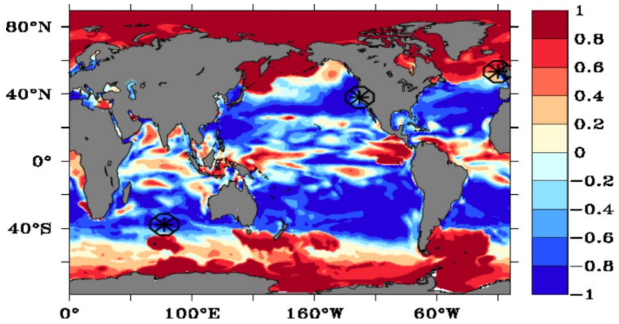


Fig. 12: Correlation between POP-simulated monthly mean Chl a and predicted monthly mean organic mass fraction for one simulated year, for the BASE case and LOW-LIP case. Stars indicate the locations of Mace Head, Ireland; Point Reyes, California; and Amsterdam Island (Southern Ocean).

Table 3: Regional seasonal mean mass fractions for each region as defined in Fig. 9.

	FEB	MAY	AUG	NOV
BASE case – regional mean values				
North Atlantic	0.04	0.31	0.19	0.12
Arctic	0.02	0.36	0.19	0.07
Northeast Pacific	0.10	0.14	0.12	0.12
Southeast Pacific	0.18	0.17	0.15	0.17
Southern Ocean	0.20	0.13	0.08	0.15
GLOBAL	0.14	0.14	0.14	0.13
Global mean values – sensitivity cases				
GLOBAL - $l_{\mathrm{bub}} = 0.5$	0.03	0.04	0.04	0.03
GLOBAL - LOW-LIP	0.09	0.09	0.09	0.09
GLOBAL - HIGH-PROT	0.33	0.33	0.32	0.33
GLOBAL - HIGH-HUM	0.16	0.15	0.15	0.14

~~1.95; all: 2.05), which transected the North Atlantic bloom (Westerlies biome) and the Arctic Sea (Polar biome). The highest alkane:hydroxyl ratios in clean marine air were obesrved during the VOCALS-Rex campaign (1.95), located in the Southeast Pacific (Coastal biome and Trade wind biome). In all cases, the average alkane:hydroxyl ratio is lower in the clean-air samples than the average of all samples from the respective campaign, suggesting that anthropogenic pollutants are associated with a higher proportion of long aliphatic chains and perhaps a lower oxidation state relative to primary marine organic aerosol emissions.~~

~~We tentatively propose a mechanism that can explain the divergence of behivor between the Arctic and North Atlantic SSA organic matter, both in our model (Fig. 10, Fig. 15) and in obervations (Russell et al., 2010) , with (1) higher alkane:hydroxyl ratios in the Arctic than in the North Atlantic, and (2) higher OM fraction for the same value of Chl a in the Arctic than in the North Atlantic. Our explanation hinges on differences between ocean ecosystems. Our model posits that the strongly surface-active molecules that contribute most to the marine organic aerosol are produced from phytoplankton disruption. Chl a is an indicator of phytoplankton standing stock, which is typically equivalent to about one-half to three days ocean primary productivity or consumption; however, this ratio varies regionally. At steady state, the ratio of the phytoplankton standing stock (and Chl a) to the rate of phytoplankton productivity, is several times higher in the polar ocean biome than elsewhere, about one to five days (Longhurst, 1998, , Fig. 3.1). This implies that for the same values of Chl a, loss rates are comparatively lower in the Arctic, including losses to disruption and the concomitant spillage of surface-active molecules. This can explain both the lower OM fraction and the lower alkane:hydroxyl ratio in the Arctic. An alternative possible explanation is that the differences derive from differences between the phytoplankton communities in the two regions.~~

~~The simulated ratios of different macromolecular classes in the aerosol are highly sensitive to the assumed adsorptivity constants within the large range of uncertainty explored here. However, chemically-resolved observations of the sea spray aerosol can help to constrain the values of these parameters. Specifically, the LOW-LIP+HIGH-POLY case is in better agreement with FTIR measurements of submicron marine aerosol composition than are the other adsorptivity cases (BASE and LOW-LIP).~~

~~The~~

5.5.2 Sensitivity to assumed bubble film thickness

The bubble film thickness is another important uncertain parameter. Changing the bubble film thickness from 0.1 μm to 0.5 μm results in a significant decrease in the organic mass fraction (FILM-0.5; Fig. ~~??~~S-4; bottom row). Film thickness can be as small as ca. 0.01 μm for bubbles with high concentrations of soluble surfactants, and as large as ca. 1 μm for bubbles in clean water (Modini et al., 2013). In additional tests (not shown), we varied the film thickness across this range as a function of bubble surface coverage. Because we used $l_{\mathrm{bub}} = 0.1\,\mu$m when bubble surface coverage exceeded a threshold value, the organic enrichment remained the same in the regions with the highest enrichment, but decreased somewhat in regions of lower enrichment.

5.5.3 Test assuming uniform adorptivity of DOC

In a third sensitivity test (“EXUDATE”; Fig. ~~??~~S-5; top row), we applied the same properties to all four compounds: the average properties of filtered exudate from four phytoplankton species, measured by Fuentes et al. (2011), with OM:OC ratio from the mean stoichiometry of phytoplankton biomass (Fraga, 2001). The surface activity of the filtered exudate is insufficient to generate substantial enrichment of the bubble film (Fig. ~~??, left panel~~S-5). Furthermore, by treating all DOM as chemically identical, it is impossible to produce patterns of (~~Chl-*a*~~Chl *a*) : (OM fraction) resembling observations from strong seasonal blooms (Fig. ~~??, right panel~~S-5; top row).

We conclude that these filtered exudates can not be considered representative for marine organic material in general and in particular for enrichment associated with a phytoplankton bloom. One possible explanation is that the surface activity of the marine phytoplankton exudate may have been significantly reduced by filtration (Žutić et al., 1981). Furthermore, marine ecosystem processes (e.g. attack of phytoplankton by zooplankton and recycling of organic matter by heterotrophic bacteria) and photochemistry may modify the surface activity of DOM.

5.5.4 Tests with high adsorptivity of proteins and humics

Results from two additional tests are shown in Fig. ~~??~~S-5 (top row). In one test (HIGH-PROT; Fig. ~~?? left panel~~S-5; middle row), we use casein, rather than lysozyme, as the model protein, i.e., we increase the value of α_{prot} by a factor of ten. This results in organic mass fractions exceeding 0.2 and enrichment factors ~~(not shown)~~ exceeding 5000 over most of the globe. In a final test (HIGH-HUM; Fig. ~~?? right panel~~S-5; bottom row), we increase α_{humic} by a factor of 10^4, which produces increased enrichment in confined regions of strong seasonal upwelling.

5.5.5 Summary of sensitivity cases

We summarize the gloal organic mass fractions predicted for different ~~regions and~~ sensitivity cases in Tab. ~~??~~3. In all the sensitivity cases, the global mean is very constant across the seasons. ~~However, certain regions have a strong seasonal cycle, i.e., the North Atlantic, the Artic, and the Southern Ocean. In the Northeast Pacific and southeast Pacific, the seasonal cycle is far more muted.~~

Comparing the sensitivity cases, it can be seen that the overall OM fraction exhibits the largest relative change with the factor of five increase in the bubble film thickness, decreasing by nearly a factor of five in response. A decrease in the lipid adsorptivity by a factor of ten results in only a ca. 35% decline in the global mean OM fraction relative to the BASE case. An increase in the protein adsorptivity by a factor of ten results in an approximate doubling of the global mean OM fraction. This is consistent with recent findings that the total marine OM emissions simulated by global model parameterizations ~~is~~ are more sensitive to the emissions in oligotrophic regions than to the emissions in strong blooms (Albert et al., 2012). Finally, a large perturbation ($\times 10^4$) ~~the the~~ to the adsorptivity of the abyssal humic-like compounds results in only a small change in the global mean OM fraction, because changes are confined to small regions of winter convective overturning (Fig. ~~??; right panel~~S-5; bottom row).

6 ~~Discussion~~

5.1 Comparison with field observations

Although we have introduced a parameterization for the OM fraction, simulations of atmospheric transport, microphysics, and chemical transformations in the atmosphere are beyond the scope of this work. Here we present a brief initial comparison of the parameterized OM fraction and functional group ratios with observations from field campaigns and coastal sites. While these comparisons give initial insights into the performance of the emissions parameterization, it should be noted that there are important limitations. Because we have not yet treated atmospheric transport or simulated interannual variations in this initial development work, at this stage we compare observations only with monthly mean predictions of the composition of emitted aerosol, averaged over a region including the field campaign location, or over a region upwind of coastal locations where samples were collected. Unless otherwise stated, all comparisons are with the BASE simulation. Simulations that include effects of atmospheric transport, microphysics, and chemical aging, as well as detailed comparisons with in situ observations, are the planned topics of a future publication.

5.1.1 Comparison of total OM fraction with ship-board and coastal observations

We first compare the total OM fraction with ship-board and coastal observations. The observations presented include the water-insoluble OM fraction (WIOM) observed at coastal stations (Gantt et al., 2011; Rinaldi et al., 2013) and observations of OM fraction in ambient aerosol from ship campaigns (Russell et al., 2010, 2013) , and in aerosol generated in-situ by bubbling air through seawater during ship campaigns (Quinn et al., 2014) . All observations of ambient aerosol have been screened for marine conditions with little anthropogenic pollution, but each

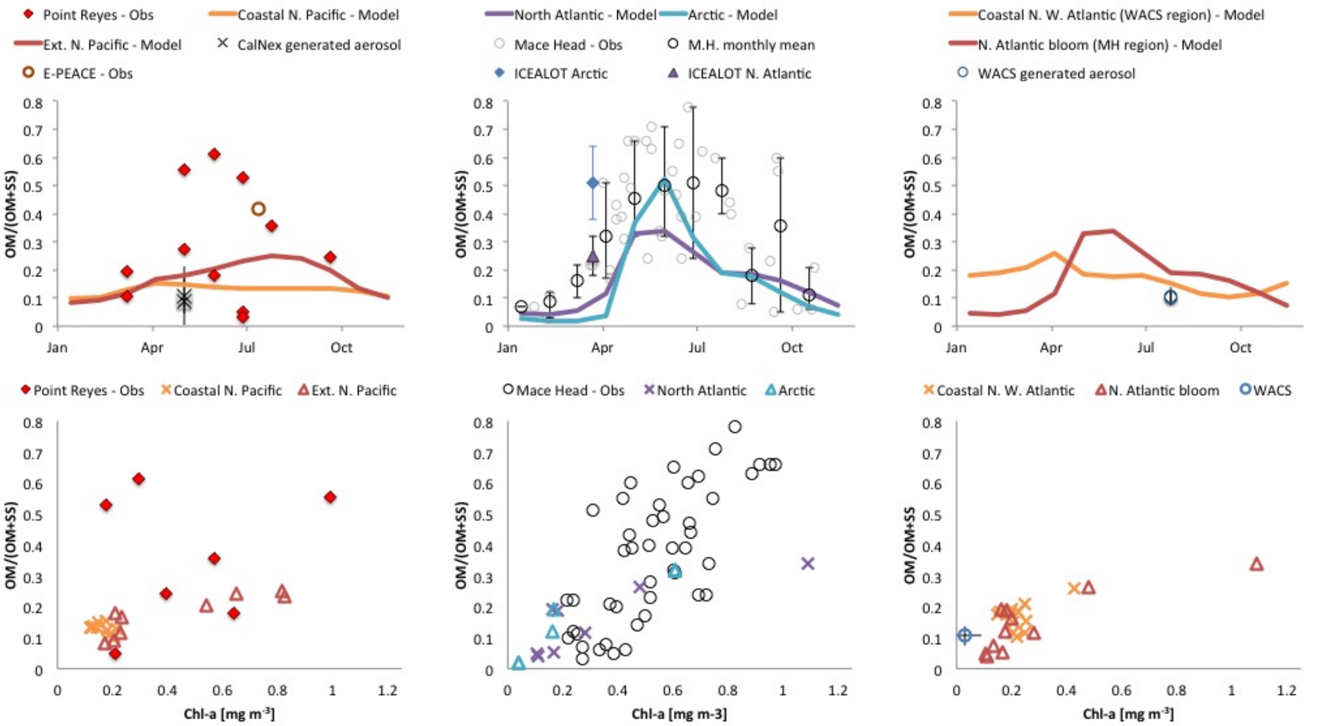


Fig. 13: Observed OM or WIOM fraction and modelled OM fraction in three regions: Left: coastal California and North Pacific, compared with Point Reyes and E-PEACE campaign; Middle: North Atlantic bloom region and Arctic, compared with Mace Head and ICEALOT campaign; Right: northwest North Atlantic, compared with WACS campaign. Top: seasonal cycle; Bottom: relationship with observed or modelled Chl *a*. Point Reyes observations (N=10) are compared with model OM fraction averaged over a coastal North Pacific region (Fig. 9) and an extended region covering most of the North Pacific (20°N – 40°N; 120°W – 210°W). Mace Head observations (N=42) are compared with model composition averaged over the North Atlantic and Arctic regions (Fig. 9). Error bars for WACS and CalNex are 95% confidence intervals (by a t-test), error bars for VOCALS and ICEALOT are one standard deviation; error bars for monthly mean Mace Head observations are the range of observed values in the calendar month.

investigator has used different criteria for screening. For the coastal observations, paired values of upwind Chl *a* have been used, consistent with previous studies (Gantt et al., 2011; Rinaldi et al., 2013) .

~~This framework represents an initial step towards representation of~~ The top panels of Figure 13 compare the model predictions of the seasonal cycle with observations. Each comparison is shown for three geographic regions: coastal California (left), the north Atlantic bloom region upwind of Mace Head (middle), and the coastal region of the northwestern North Atlantic (right). Because each ambient aerosol measurement may have been influenced by emissions from a large region upwind of the measurement location, for the purposes of this comparison, we have averaged the model OM fraction over larger regions as indicated in Fig. 9, or as otherwise indicated.

The model is in reasonably good agreement with the seasonal cycle at Mace Head, falling within the range of observations for most months. The underestimation of the OM fraction in March, April, and August may be caused by the winter overturning, which may removing surfactants too effectively in the model (Sec. 5). At Point Reyes, the ~~effects of ocean surface organic matter composition on sea spray aerosol composition. Sources of uncertainty related to our implementation of the Langmuir adsorption framework include uncertainties in~~ few available observations indicate a relatively constant seasonal cycle without a strong peak, behavior which is qualitatively reproduced by the model.

The bottom panels of Fig. 13 show the Chl *a* vs. OM fraction relationships in the same three regions, for Chl *a* values in the range 0–1.25 mg m^{-3}. Note that the model values presented here represent the regionally-averaged Chl-a and OM fraction and as such, do not reflect the full range of variability of the model, shown in Fig. 10. Observations indicate a much stronger dependence of OM fraction on Chl *a* in the North Atlantic / Artic region influencing Mace Head, Ireland than in the Pacific region influencing Point Reyes, however, this is at least in part due to the different particle size fractions observed at those two stations. The model's regionally-averaged monthly mean

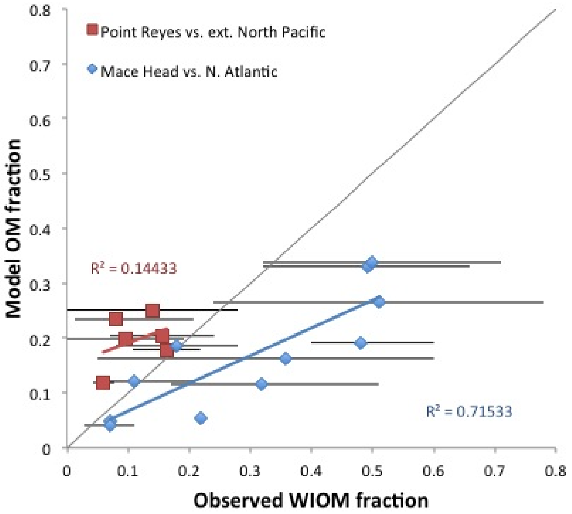


Fig. 14: Observed monthly mean WIOM/(WIOM+SS) vs. modelled monthly mean OM SSA fraction, averaged over a region upwind of the respective measurement location. Observations shown are: (1) sub-1.5-μm WIOM fraction from a coastal site at Mace Head, Ireland (N=42 filters collected during the years 2002-2009), filtered for clean marine conditions (as described in Rinaldi et al., 2013) and (2) sub-2.5-μm WIOM fraction from a buoy located near Point Reyes, California (N=10 filters collected during the years 2000-2007), during clean conditions as determined by low BC concentrations (as in Gantt et al., 2011) . Observations have been grouped into month-of-year means for appropriate comparison with model results. Error bars show the range of observations for each month. Model OM fractions are calculated over the North Atlantic region (as indicated in Fig. 9) and extended North Pacific region, respectively. Linear regressions and their corresponding R^2 values are shown for each data set. The 1:1 line is indicated in grey.

values do not approach the highest OM fractions observed at Mace Head, but are mostly within the range of the observations for Chl $a < 1$ in both regions. In the coastal northwest Atlantic, the ~~values of the chemical parameters, and the neglect of certain processes.~~

~~We have primarily used adsorption parameters obtained under typical laboratory conditions , i. e., at room temperature, low salinity (ionic strength)and neutral pH, but we have applied these values across divergent conditions.At least for some relevant studies, errors resulting from this approximation may be minimal.For example, for the suite of proteins reviewed here , the observed temperature dependence of the surface coverage is small at temperatures between room temperature and~~ WACS generated aerosol is within the range of low-chl-a observations.

In Fig. 14, we compare regionally-averaged monthly mean OM fractions from our emissions parameterization with climatological monthly means of observed WIOM from the same two sites. The comparatively lower WIOM fractions at Point Reyes compared to Mace Head are at least partially attributable to the different size fractions measured at the two sites (sub-1.5-μm at Mace Head and sub-2.5-μm at Point Reyes). Since we have not corrected here for the particle size fraction observed, it is not surprising that our model underpredicts the Point Reyes observations while simultaneous overpredicting the Mace Head observations.

5.1.2 Comparison of estimated functional group composition with FTIR measurements

Table 4: Conversion from moles carbon per macromolecule class to the mass associated with FTIR-observable functional-groups ([g of the functional group] / [moles carbon of macromolecule]).[a]

	alkane	hydroxyl	
Lipids[b]	10.11	0.85	0 ~~°C (Graham and Phillips,~~
Polysaccharides[c]	7.0	19.17	
Proteins[d]	6.18	1.35	
Processed[e]	7.0	19.17	
Humics[e]	7.0	19.17	

[a] Molar mass associated with a functional group is assumed to include half the mass of the carbon atom if single-bonded and the full mass of the carbon atom if double-bounded, e.g., C-H mass is 7 g mol^{-1} (including half the mass of the carbon atom), and COOH mass is 45 g mol^{-1} (including the full mass of the carbon atom). Functional group distribution per macromolecule class ([moles functional group] / [moles carbon]) is estimated based on model compounds as indicated.

[b] Functional group mass distribution of cholesterol.

[c] Functional group mass distribution characteristic of simple sugars.

[d] Characteristic functional group mass distribution of a mixture of amino acids present in seawater.

[e] Same as for polysaccharides.

In this section, we compare the model estimates with mean values from FTIR measurements of submicron SSA collected during several ship-based field campaigns in Figure 15. For the purpose of this comparison, the macromolecular classes have been converted to functional group-associated mass using the weights presented in Tab. 4. Higher alkane:hydroxyl ratios indicate an aerosol that is more lipid-like and dominated by long aliphatic chains. Lower alkane:hydroxyl ratios indicate an aerosol that is more oxidized and carbohydrate-like.

~~Several processes have been neglected that may prove important to marine organic enrichment.Perhaps most importantly, we have neglected the role of marine colloids~~

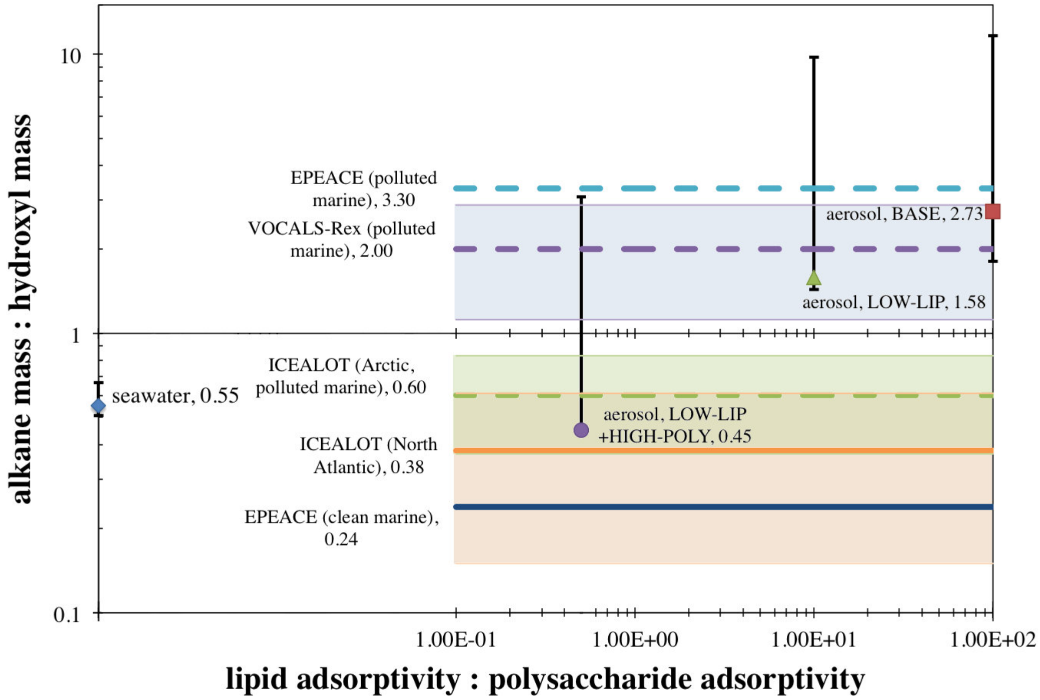


Fig. 15: Ratio of alkane mass to hydroxyl mass from model macromolecules, and from ship-borne FTIR observations. Points and error bars indicate the model's global median and 5%-ile to 95%-ile range of model estimates for seawater (displayed at the left of the figure) and for emitted submicron SSA in several sensitivity cases. Medians and ranges are calculated from monthly mean grid-box values. For the purpose of this comparison, model macromolecule concentrations were converted to estimated functional group ratios using the values provided in Table 4. Model values are shown as a function of the ratio of the adsorption constants used for lipids and for polysaccharides, in each sensitivity case. Observed alkane:hydroxyl ratios from ship-borne FTIR measurements in several field campaigns are shown as lines and shaded regions. The adsorptivity of the ocean DOC components during each campaign is unknown, therefore the observed alkane:hydroxyl ratio are not associated with particular values on the x-axis. Solid lines indicate averages of data from clean air samples only, i.e., data from air contaminated by anthropogenic pollution have been excluded. The ship-borne observations are from the E-PEACE campaign off the central coast of California (July – August, 2011) (Russell et al., 2013) , the ICEALOT campaign in the North Atlantic and Arctic Oceans (March – April, 2008) (Russell et al., 2010) , and the VOCALS-Rex campaign, in the Southeast Pacific oligotrophic gyre (October, 2008) (Hawkins et al., 2010) . The shaded areas indicate the ± 1 standard deviation uncertainty range for VOCALs-Rex, ICEALOT (Arctic) and ICEALOT (North Atlantic), respectively.

~~aggregates (Facchini et al., 2008) in driving interfacial adsorption. However, colloids can be easily added within the framework when an estimate of their geographic distributions and properties has been developed. We have also neglected interactions between groups of molecules at the bubble surface. For example, some polysaccharides that do not adsorb on their own may do so in cooperation with proteins (Baeza et al., 2005) . And we have not accounted for the stronger adsorption of~~ The lowest observed alkane:hydroxyl ratios are from clean marine samples collected during E-PEACE (alkane:hydroxyl=0.24), off the central coast of California, in the presence of high chlorophyll. These are followed by samples from the ICEALOT campaign, which transected the North Atlantic bloom (alkane:hydroxyl=0.38) and the polluted marine samples from the Arctic Sea (alkane:hydroxyl=0.60). Alkane:hydroxyl ratios were higher in polluted marine air during the VOCALS-Rex campaign (alkane:hydroxyl=2.00), located in the Southeast Pacific. In all cases, the ~~particulate phase relative to the dissolved phase (Marty et al., 1988) .~~ average alkane:hydroxyl ratio is lower in the clean-air samples than in polluted samples, suggesting that anthropogenic pollutants are associated with a higher proportion of long aliphatic chains and perhaps a lower oxidation state relative to primary marine organic aerosol emissions. The alkane:hydroxyl ratio may also be affected by ocean biological processes: the model suggests it will be highest during strong seasonal blooms (Fig. S-6).

~~The link between Chl~~We compare the observations with the mean and range of estimated alkane-to-hydroxyl ratios from the model's BASE case and two sensitivity cases: LOW-LIP (10x lower lipid adsorptivity) and LOW-LIP+HIGH-POLY (10x lower lipid adsorptivity and 20x higher polysaccharide adsorptivity). Results from clean marine conditions are in better agreement with the LOW-LIP+HIGH-POLY case.

5.1.3 Comparison with Quinn et al. (2014) (Q14)

Quinn et al. (2014) (hereafter Q14) present measurements of the organic carbon fraction of sea spray aerosol from the WACS field campaign in the northwestern North Atlantic and Sargasso Sea region (August, 2012). The organic enrichments observed by Q14 are in the same range as the OM predicted by our model in the same region in August, which range from about 0.05 in the Sargasso Sea to about 0.2 near the coast (Fig. 8, Fig. 13). While our model predicts that the organic mass fraction is somewhat higher in regions with higher chlorophyll, Q14 shows similar average OM fractions at both a high-Chl a location and a low-Chl a location. However, the number of data points in the Q14 samples is too small to draw firm conclusions (N=9 and N=7 at the high-Chl a and ~~surface active DOM has been well-established by observations and experiments. Field~~ low-Chl a station, respectively). On the other hand, the mean enrichment factors during WACS were higher for low-Chl a samples than for high Chl a samples, and this difference was statistically significant ($p<0.001$ by a t-test calculated from Supplementary Table S1 of Q14), which is consistent with the understanding that organic enrichment tends to be higher in biologically active waters. Q14 also includes results from the CalNex campaign (coastal California, May 2010), which are consistent within uncertainty bounds with the model (Fig. 13).

5.1.4 Comparison with Keene et al. (2007) (K07)

Keene et al. (2007) (hereafter K07) measured the chemical composition of aerosol generated, using a glass frit system, from low-chlorophyll water (Chl a=0.055) from the Sargasso Sea. The aerosol produced in that had a median enrichment factor for soluble OC of 387, and the OC fraction for the smallest particles produced (0.13 μm) was ca. 80%. Using the "medium" values of size-resolved aerosol composition reported in K07, we calculate an OC/(OC+inorganics) mass fraction of 0.26 for 0.75-um particles, and 0.076 for 1.34-um particles. Fig. 10 shows that in grid points with Chl a=0.055, our model predicts submicron OM fractions ranging up to a maximum of about 0.15 (OC fraction = 0.24, assuming OM:OC = 1.8). This value is in reasonable agreement with the K07 results.

6 Discussion

This framework represents an initial step towards representation of the effects of ocean surface organic matter composition on sea spray aerosol composition. Many studies have identified a link between surface active DOM concentrations and ocean biological activity, which sometimes manifests as a correlation between ocean concentrations of surfactants and Chl a. For example, field studies in the northern Adriatic have found significant positive correlations between bulk surfactant activity in the SML and independent measurements, at the same stations, of Chl a concentration, phytoplankton primary production, pH and oxygen saturation (Žutić et al., 1981). These studies have also identified a seasonal cycle in surfactant concentrations, with the highest concentrations appearing in spring and summer (Gašparović and Ćosović, 2001). In phytoplankton cultures, surfactant activity has been found to increase in proportion to biomass, until leveling out at high surfactant concentrations, and observational studies have concluded that the largest source of surfactants in the SML is phytoplankton exudates and their degradation products (Žutić et al., 1981; Gašparović et al., 1998; Sekelsky and Shreve, 1999). Similarly, in an iron fertilization experiment in the Southern Ocean, concentrations of surface-active substances increased strongly during the bloom, reaching their highest concentrations at the end of the bloom (Croot et al., 2007). An important source of surfactants is the lysis of phytoplankton and spillage of their constituents into the water. This may explain results of a recent field study off the coast of California, in which the organic mass in spray aerosol generated with an in situ particle generator did not correlate with chlorophyll, but did correlate with the concentration of DMS in the ocean, indicating a possible relationship with cell lysis (Bates et al., 2012).

All of these observations support the interpretation that the correlation of the organic fraction of the spray aerosol with Chl a ~~is~~ that is sometimes observed is driven by underlying ocean chemistry: specifically, by the high concentrations of strong surfactants in productive waters. More productive waters also have a greater proportion of larger particles (Buonassissi and Dierssen, 2010), which can further enhance the organic mass in the ~~spray. The model framework proposed here makes explicit the link between~~ SSA. The parameterization proposed here is the first to explicitly link the physical surface chemistry of ocean bubbles and organic enrichment of the SSA.

6.1 Sources of uncertainty and priorities for future experiments

In this section, we discuss some of the main sources of uncertainty, currently neglected processes, and inherent limitations of our approach.

6.2 Equilibrium assumption

It is unclear how rapidly adsorption equilibrium is reached on bubble surfaces in the ocean. Estimates differ widely, for example, Fuentes et al. (2011) estimated an equilibration time scale of less than 0.05 ms for bubbles in a sample of filtered algal exudate, while Krzan et al. (2007) measured adsorption of several organic surfactants on single rising bubbles and observed equilibration to occur in less than 1 s in most cases. The rise velocities in seawater of bubbles with radii greater than 700 μm are in the range 22-35 cm s^{-1} (Patro et al., 2002) . Bubble plumes formed by breaking waves penetrate to depths of at least ca. 20–30 cm or more (Melville, 1996; Deane and Stokes, 2002) , so if equilibrium is reached within less than one second, the exposure time will be sufficient to reach or nearly reach equilibrium for many ocean bubbles. Furthermore, if equilibrium is approached, but not fully achieved, the relationship of surface coverage and bulk concentration may still be represented by a Langmuir isotherm curve (using appropriately adjusted parameters) with fidelity sufficient for application in an Earth System Model. This is supported by calculations of the kinetics of convective-diffusive transport of surfactants to bubble surfaces, and subsequent adsorption (Jachimska et al., 2001) .

Because the time scales of surfactant equilibrium in the ocean are similar to or less than bubble rise times in many cases, the assumption of equilibrium is a reasonable and useful first approximation for the purpose of representing bubble adsorption in Earth System models. Further investigation is required to determine under which conditions the assumed Langmuir equilibrium ceases to be a satisfactory approximation, particularly in regards to the equilibrium between competing surfactants (Mulqueen et al., 2001b,a) .

6.2.1 Effects of particle size and wind speed

Our model does not yet include the effects of two important physical parameters, particle size and wind speed, on submicron SSA OM fraction. The fraction of organic matter in nascent sea spray increases dramatically for smaller particles (Oppo et al., 1999; Keene et al., 2007; Facchini et al., 2008) Although the exact mechanisms driving the functional relationship between OM fraction and size of nascent particles are not fully understood, empirical functions can be used in order to implement the parameterization into an atmospheric model (Gantt et al., 2011) . Some researchers hypothesize that the formation of the SML under very calm conditions may result in higher organic enrichment being observed at low wind speeds (Gantt et al., 2011) . Laboratory experiments in which organic aerosol is produced from generated waves under different wind speed and wave state conditions could aid in testing this assumption.

6.2.2 Adsorption parameters and neglected adsorption processes

We have utilized adsorption parameters obtained primarily at room temperature, but we have applied these values globally across a range of sea surface temperatures. This assumption is justified to a certain extent by laboratory measurements. For example, for the proteins reviewed here, the observed dependence of the surface coverage on temperature is small between room temperature and 0° C (Graham and Phillips, 1979a,b,c) . However, it is not clear whether the adsorption constants of marine biomolecules are, in general, sensitive to sea-surface temperature. Laboratory constraints on adsorption parameters for a variety of marine biomolecules or proxies across the entire temperature range 0° C – 30° C will be needed in order to understand how temperature affects the emission process, particularly in polar oceans.

In addition to parameter uncertainties, several processes have been neglected that may prove important to marine organic enrichment. Perhaps most importantly, we have neglected the role of marine aggregates (Facchini et al., 2008) in driving interfacial adsorption. Further study is needed to derive a parameterization of the colloid formation process appropriate for inclusion into a global model.

We have also neglected interactions between groups of molecules at the bubble surface. For example, some polysaccharides that do not adsorb to the air-water interface on their own may do so in cooperation with proteins (Baeza et al., 2005) . Laboratory studies examining the interactions of appropriate marine proxy molecules at the air-water interface may help to advance understanding and provide quantitative constraints on this process.

Finally, we have not yet accounted for the observed greater enrichment of the particulate phase relative to the dissolved phase in the SML (Marty et al., 1988; Kuznetsova and Lee, 2002; Kuznetsova et al., 2005) This phenomenon may be driven by chemical adsorption processes, or by the more efficient scavenging of larger particles from the water column due to bubble impaction. (Sutherland, 1948; Weber et al., 1983; Dai et al., 1998, 2000) .

6.2.3 Observational constraints needed from field studies

Currently, only very limited observations of organic matter are available from field studies, and these observations are frequently not easily intercomparable, due to differences in the experimental methods used. An ideal tool for model evaluation would be a long-term, consistent database of observations of the organic composition of submicron aerosol, sea-surface microlayer, and subsurface water across a variety of ocean ecosystems. Methods that provide more detailed but also quantitative chemical information can increase the ability to distinguish between different chemical classes of organic matter and help to advance understanding of the underlying processes that determine the distribution and composition of marine organic matter. While complete molecular characterization may not be possible, measurement of functional group composition (e.g., by FTIR as shown here) can begin to provide clues into chemical processes. Several measurement techniques for studying the organic composition of amient marine aerosol particles have recently been reviewed and directly compared by (Frossard et al., 2014) .

One geographic region that is a traditional focus of field campaigns is the North Atlantic basin. Additional observations there, during the peak of the spring bloom, may prove essential to resolving the apparent contradiction between the view that the organic mass fraction of submicron aerosol is essentially constant (Quinn et al., 2014) and the view that it dramatically changes over the coarse of a strong bloom (O'Dowd et al., 2004; Rinaldi et al., 2013) .

Finally, SFG measurements of the detailed surface chemistry of natural and artificial ocean surfaces and sea spray particles (Ault et al., 2013; Ebben et al., 2013; Laß et al., 2013) are an emerging approach that is very intriguing. Further such studies could prove valuable in identifying important marine surfactants and distinguishing their role in ocean biochemical processes as well as their molecular interactions and orientations at the ocean surface and particle surfaces.

6.2.4 Uncertainties in the underlying ocean biogeochemistry simulations

The model's predictive capability is inherently limited by the underlying ocean biogeochemistry model. Global ocean biogeochemistry models currently have a limited ability to accurately predict the exact location and timing of phytoplankton blooms (Doney et al., 2009) . While the model has some difficulty in exactly reproducing the location and timing of phytoplankton blooms, the patchiness of the active phytoplankton blooms is a realistic qualitative feature. These blooms can be extremely localized, as can also be seen in satellite-derived maps of chlorophyll. This leads to highly localized distributions of the lipid-like class and of OM fraction in our model (Fig. 6a and Fig. 7).

Active development of the ocean biogeochemistry model is underway, and it is hoped that the model's skill may improve in the future. Additionally, it should be considered whether more sophisticated metrics can be applied to assess the skill of ocean biogeochemistry simulations. Because of the highly localized nature of phytoplankton blooms, approaches such as object-based verification or fuzzy verification could be considered, which are used in verification of hurricane and precipitation forecasts. These approaches may produce a more meaningful assessment of the model's ability to simulate realistic blooms if their location or timing is slightly mis-matched.

7 Conclusions

In this study, we have introduced a novel framework for the parameterization of the organic fraction of SSA.

The framework predicts the mass of mixtures of organic components with different surface activity (Langmuir coefficient α_i), molecular mass M_i, and surface packing (maximum surface excess $\Gamma_{i,\infty}$), in competitive equilibrium with each other. This framework represents an initial step towards linking information available in ocean biogeochemical models to emissions parameterizations for global atmospheric chemistry and climate models. Because the enrichment behavior is dominated primarily by two macromolecule classes, lipids and proteins, a two-component model may prove sufficient to capture one important dimension of the geographic variation in ocean biogeochemistry: the differences between regions of high and low biological productivity.

We have reviewed evidence that organic enrichment in the SML and in sea spray aerosol are chemically specific in consistent ways, and that there is a selectively stronger enrichment of larger particles in the SML. Using a conceptually straightforward model, we have emphasized that high organic mass fractions in the submicron aerosol can be obtained only when strongly adsorbing materials are present in sufficiently high concentrations. By contrast, the concentration of weakly or non-adsorbing organic matter in the bulk ocean plays only a minor or negligible role in determining total OM concentrations in nascent sea spray.

Using output from an ocean biogeochemistry model, we derived estimates of the distributions of five classes of macromolecules, and selected a model compound to represent the physical and chemical properties of each class. This allows us to simulate global patterns in OM fractions. Predicted OM:~~Chl-*a*~~ Chl a relationships at high Chl a levels resemble existing empirical parameterizations derived from observations at coastal sites, but are derived independently using ocean biogeochemistry model output fields. Further observations are needed to better-constrain the spatial and seasonal variability in these relationships, particularly outside of strong seasonal plankton blooms.

The simulated ratios of different macromolecular classes in the aerosol are highly sensitive to the assumed adsorptivity constants within the large range of uncertainty explored here. Chemically-resolved observations of the sea spray aerosol may help to constrain the values of these parameters, although contradictions currently exist with the limited set of measurements examined here. Specifically, FTIR measurements from the Southeast Pacific agree best with the BASE case estimate while FTIR measurements from the North Atlantic and Arctic agree best with the

LOW-LIP+HIGH-POLY case. These discrepancies deserve further investigation.

Because concentrations of surface-active compounds correlate with Chl a during strong phytoplankton blooms, our model shows that adsorption-driven enrichment of organic matter in sea spray is correlated with chlorophyll concentrations during blooms. However, the same Chl a concentration may correspond to different film OM fractions in different regions and seasons. Parameterizations of the spray aerosol organic fraction that rely solely on chlorophyll are likely to underestimate organic enrichment in regions where chlorophyll is low, but moderately surface-active compounds with intermediate biogeochemical lifetimes are still present. Our model suggests that in regions where aerosol OC is dominated by semi-labile compounds rather than labile compounds, the seasonal cycle in the OM fraction may actually be anti-correlated with Chl a, because peak SDOC concentrations occur a few months later than peak Chl a concentrations.

Prediction of ocean and aerosol organic films is also of potential interest for several further reasons in the context of global change. When organics make up a large fraction of the aerosol mass, under some conditions the organic molecules may form a solid or semi-solid layer covering the aerosol surface, kinetically delaying water uptake by reducing either the mass accommodation coefficient (Takahama et al., 2010) or the bulk diffusion coefficient within the aerosol particle (Shiraiwa et al., 2013). Ocean films can inhibit the exchange of gases across the air-sea interface, in particular, they can slow ocean uptake of carbon dioxide (Frew et al., 1990; Frew, 1997; Tsai and Liu, 2003; Wanninkhof et al., 2009). Furthermore, the thickness of ocean interfacial films may influence the size distribution of sea spray. For example, soluble surfactants can stabilize bubble surfaces, such that greater film drainage and thinning occurs prior to bursting (Spiel, 1997; Oppo et al., 1999; Russell et al., 2010; Modini et al., 2013).

We conclude that variations in the concentration of highly surface-active compounds associated with primary production and possibly marine particle size, rather than bulk TOC concentrations, drive a portion of the spatial and temporal variability of the submicron sea spray organic mass fraction. Future work should focus on improving constraints on the impacts of marine surface chemistry on SSA production through laboratory experiments and empirical fitting to field observations. The dependence of SSA composition on particle size and wind speed should be investigated. Atmospheric implications should be explored, including impacts on CCN activity.

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References

Adamson, A. W. and Gast, A. P.: Physical chemistry of surfaces, Wiley Interscience, New York, 1997.

Albert, M. F. M. A., Schaap, M., Manders, A. M. M., Scannell, C., O'Dowd, C. D., and de Leeuw, G.: Uncertainties in the determination of global sub-micron marine organic matter emissions, Atmospheric Environment, 57, 289–300, 2012.

Alexander, D. M., Barnes, G. T., McGregor, M. A., and Walker, K.: The penetration of monolayers by surfactants, vol. 311 of *ACS Symposium Series*, chap. 10, pp. 133–142, American Chemical Society, Washington, DC, doi:10.1021/bk-1986-0311.ch010, ed.: J. Scamehorn, 1986.

Amon, R. M. W. and Benner, R.: Bacterial utilization of different size classes of dissolved organic matter, Limnology and Oceanography, 41, 41–51, 1996.

Armstrong, R. A., Lee, C., Hedges, J. I., Honjo, S., and Wakeham, S. G.: A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals, Deep Sea Research Part II: Topical Studies in Oceanography, 49, 219–236, 2001.

Ault, A. P., Zhao, D., Ebben, C. J., Tauber, M. J., Geiger, F. M., Prather, K. A., and Grassian, V. H.: Raman microspectroscopy and vibrational sum frequency generation spectroscopy as probes of the bulk and surface compositions of size-resolved sea spray aerosol particles, PCCP Phys. Chem. Ch. Ph., 15, 6206, 2013.

Averett, R. C., Leenheer, J. A., McKnight, D. M., and Thorn, K. A.: Humic substances in the Suwanee River, Georgia: Interactions, properties, and proposed structures, Tech. Rep. Open-File Report 87-557, U. S. Geological Survey, Denver, Colorado, 1989.

Azetsu-Scott, K. and Passow, U.: Ascending marine particles: Significance of transparent exopolymer particles (TEP) in the upper ocean, Limnol. Oceanogr., 49, 741–748, 2004.

Babak, V., Skotnikova, E., Lukina, I., Pelletier, S., Hubert, P., and Dellacherie, E.: Hydrophobically associating alginate derivatives: surface tension properties of their mixed aqueous solutions with oppositely charged surfactants, Journal of colloid and interface science, 225, 505–510, 2000.

Baeza, R., Carrera Sanchez, C., Pilosof, A. M., and Rodríguez Patino, J. M.: Interactions of polysaccharides with β-lactoglobulin adsorbed films at the air–water interface, Food Hydrocolloids, 19, 239–248, 2005.

Barger, W. R. and Means, J. C.: Clues to the structure of marine organic material from the study of physical properties of surface films, Marine and Estuarine Geochemistry, Lewis Publishers, Chelsea Michigan. 1985. p 47-67, 6 fig, 6 tab, 25 ref., 1985.

Bates, T. S., Quinn, P. K., Frossard, A. A., Russell, L. M., Hakala, J., Petäjä, T., Kulmala, M., Covert, D. S., Cappa, C. D., Li, S.-M., Hayden, K. L., Nuaaman, I., McLaren, R., Massoli, P., Canagaratna, M. R., Onasch, T. B., Sueper, D., Worsnop, D. R., and Keene, W. C.: Measurements of ocean derived aerosol off the coast of California, J. Geophys. Res., 117, D00V15, doi:10.1029/2012JD017588, 2012.

Benner, R.: Biogeochemistry of Dissolved Organic Matter, chap. Chemical composition and reactivity, pp. 59 – 90, Academic Press, New York, edited by D. Hansell and C. Carlson, 2002.

Blanchard, D. C.: Bubble Scavenging and the Water-to-Air Transfer of Organic Material in the Sea, in: Applied chemistry at protein interfaces, edited by Baier, R. E., pp. 360–387, American Chemical Society, Washington, D.C., 1975.

Blanchard, D. C.: The ejection of drops from the sea and their enrichment with bacteria and other materials: A review, Estuaries, 12, 127–137, doi:10.2307/1351816, 1989.

Blanchard, D. C. and Syzdek, L. D.: Water-to-air transfer and enrichment of bacteria in drops from bursting bubbles, Appl. Environ. Microb., 43, 1001–1005, http://aem.asm.org/cgi/content/abstract/43/5/1001, 1982.

Blanchard, D. C. and Syzdek, L. D.: Film drop production as a function of bubble size, Journal of Geophysical Research: Oceans (1978–2012), 93, 3649–3654, 1988.

Brzozowska, A. M., Duits, M. H. G., and Mugele, F.: Stability of stearic acid monolayers on Artificial Sea Water, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 407, 38–48, 2012.

Buonassissi, C. and Dierssen, H.: A regional comparison of particle size distributions and the power law approximation in oceanic and estuarine surface waters, J. Geophys. Res., 115, C10 028, doi:10.1029/2010JC006256, 2010.

Burrows, S. M., Hoose, C., Pöschl, U., and Lawrence, M. G.: Ice nuclei in marine air: biogenic particles or dust?, Atmospheric Chemistry and Physics, 13, 245–267, doi:10.5194/acp-13-245-2013, http://www.atmos-chem-phys.net/13/245/2013/, 2013.

Buseck, P. R. and Posfai, M.: Airborne minerals and related aerosol particles: Effects on climate and the environment, Proceedings of the National Academy of Sciences, 96, 3372–3379, 1999.

Carlson, C.: Biogeochemistry of Dissolved Organic Matter, chap. Production and removal processes, pp. 91 – 139, Academic Press, New York, edited by D. Hansell and C. Carlson, 2002.

Carlson, C. A., Hansell, D. A., Peltzer, E. T., and Smith Jr, W. O.: Stocks and dynamics of dissolved and particulate organic matter in the southern Ross Sea, Antarctica, Deep Sea Research Part II: Topical Studies in Oceanography, 47, 3201–3225, 2000.

Carslaw, K. S., Boucher, O., Spracklen, D. V., Mann, G. W., Rae, J. G. L., Woodward, S., and Kulmala, M.: A review of natural aerosol interactions and feedbacks within the Earth system, Atmos. Chem. Phys., 10, 1701–1737, 2010.

Christian, J. and Anderson, T.: Biogeochemistry of Dissolved Organic Matter, chap. Modeling DOM biogeochemistry, pp. 717 – 756, Academic Press, New York, edited by D. Hansell and C. Carlson, 2002.

Christodoulou, A. P. and Rosano, H. L.: Effect of pH and nature of monovalent cations on surface isotherms of saturated C_{16} to C_{22} soap monolayers, Adv. Chem. Ser, 84, 210–34, 1968.

Collins, D. B., Ault, A. P., Moffet, R. C., Ruppel, M. J., Cuadra-Rodriguez, L. A., Guasco, T. L., Corrigan, C. E., Pedler, B. E., Azam, F., Aluwihare, L. I., Bertram, T. H., Roberts, G. C., Grassian, V. H., and Prather, K. A.: Impact of marine biogeochemistry on the chemical mixing state and cloud forming ability of nascent sea spray aerosol, J. Geophys. Res.-Atmos., 118, 8553–8565, doi:10.1002/jgrd.50598, 2013.

Cook, M. A. and Talbot, E. L.: Surface Hydrolysis in Sodium Lauryl Sulfate Solutions and its Effect on Surface Tension and on Adsorption at the SolidAqueous Solution Interface, The Journal of Physical Chemistry, 56, 412–416, 1952.

Croot, P., Passow, U., Assmy, P., Jansen, S., and Strass, V.: Surface active substances in the upper water column during a Southern Ocean Iron Fertilization Experiment (EIFEX), Geophysical research letters, 34, 2007.

Cunliffe, M., Engel, A., Frka, S., Gašparović, B., Guitart, C., Murrell, J. C., Salter, M., Stolle, C., Upstill-Goddard, R., and Wurl, O.: Sea surface microlayers: a unified physicochemical and biological perspective of the air-ocean interface, Progress in Oceanography, 109, 104–116, doi:10.1016/j.pocean.2012.08.004, 2012.

Dai, Z., Dukhin, S., Fornasiero, D., and Ralston, J.: The inertial hydrodynamic interaction of particles and rising bubbles with mobile surfaces, Journal of colloid and interface science, 197, 275–292, 1998.

Dai, Z., Fornasiero, D., and Ralston, J.: Particle–bubble collision models – a review, Advances in Colloid and Interface Science, 85, 231–256, 2000.

Damodaran, S. and Razumovsky, L.: Competitive adsorption and thermodynamic incompatibility of mixing of β-casein and gum arabic at the air–water interface, Food hydrocolloids, 17, 355–363, 2003.

Deane, G. and Stokes, M.: Scale dependence of bubble creation mechanisms in breaking waves, Nature, 418, 839–844, 2002.

Dinar, E., Taraniuk, I., Graber, E. R., Katsman, S., Moise, T., Anttila, T., Mentel, T. F., and Rudich, Y.: Cloud condensation nuclei properties of model and atmospheric HULIS, Atmos. Chem. Phys., 6, 2465–2482, 2006.

Dittmar, T. and Kattner, G.: Recalcitrant dissolved organic matter in the ocean: major contribution of small amphiphilics, Marine chemistry, 82, 115–123, 2003.

Doney, S. C., Lima, I., Moore, J. K., Lindsay, K., Behrenfeld, M. J., Westberry, T. K., Mahowald, N., Glover, D. M., and Takahashi, T.: Skill metrics for confronting global upper ocean ecosystem-biogeochemistry models against field and remote sensing data, Journal of Marine Systems, 76, 95–112, 2009.

Ebben, C. J., Ault, A. P., Ruppel, M. J., Ryder, O. S., Bertram, T. H., Grassian, V. H., Prather, K. A., and Geiger, F. M.: Size-Resolved Sea Spray Aerosol Particles Studied by Vibrational Sum Frequency Generation, The Journal of Physical Chemistry A, 117, 6589–6601, 2013.

Elliott, S.: Dependence of DMS global sea-air flux distribution on transfer velocity and concentration field type, J. Geophys. Res., 114, G02 001, doi:10.1029/2008JG000710, 2009.

Elliott, S., Maltrud, M., Reagan, M., Moridis, G., and Cameron-Smith, P.: Marine methane cycle simulations for the period of early global warming, J. Geophys. Res., 116, G01 010, doi:10.1029/2010JG001300, 2011.

Elliott, S., Burrows, S., Deal, C., Liu, X., Long, M., Oluwaseun, O., Russell, L., and Wingenter, O.: Prospects for the Simulation of Macromolecular Surfactant Chemistry in the Ocean-Atmosphere, submitted, 2013.

Facchini, M. C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E. D., de Leeuw, G., Martino, M., Woeltjen, J., and O'Dowd, C. D.: Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates, Geophys. Res. Lett., 35, L17 814, doi:10.1029/2008GL034210, http://www.agu.org/journals/gl/gl0817/2008GL034210/, 2008.

Fraga, F.: Phytoplanktonic biomass synthesis: application to deviations from Redfield stoichiometry, Scientia Marina, 65, 153–169, 2001.

Frew, N. M.: The Sea Surface and Global Change, chap. The role of organic films in air-sea gas exchange, pp. 121–171, Cambridge University Press, Cambridge, U.K., eds. Liss, P. S. and Duce, R. A., 1997.

Frew, N. M., Goldman, J. C., Dennett, M. R., and Johnson, A. S.: Impact of phytoplankton-generated surfactants on air-sea gas exchange, Journal of Geophysical Research: Oceans (1978–2012), 95, 3337–3352, 1990.

Frossard, A. A., Russell, L. M., Massoli, P., Bates, T. S., and Quinn, P. K.: Side-by-Side Comparison of Four Techniques Explains the Apparent Differences in the Organic Composition of Generated and Ambient Marine Aerosol Particles, Aerosol Science and Technology, 48, v–x, 2014.

Fuentes, E., Coe, H., Green, D., de Leeuw, G., and McFiggans, G.: Laboratory-generated primary marine aerosol via bubble-bursting and atomization, Atmos. Meas. Tech., 3, 141–162, doi:10.5194/amt-3-141-2010, http://www.atmos-meas-tech.net/3/141/2010/, 2010a.

Fuentes, E., Coe, H., Green, D., de Leeuw, G., and McFiggans, G.: On the impacts of phytoplankton-derived organic matter on the properties of the primary marine aerosol–Part 1: Source fluxes, Atmos. Chem. Phys., 10, 9295–9317, 2010b.

Fuentes, E., Coe, H., Green, D., and McFiggans, G.: On the impacts of phytoplankton-derived organic matter on the properties of the primary marine aerosol–Part 2: Composition, hygroscopicity and cloud condensation activity, Atmos. Chem. Phys., 11, 2585–2602, 2011.

Gantt, B. and Meskhidze, N.: The physical and chemical characteristics of marine primary organic aerosol: a review, Atmos. Chem. Phys., 13, 3979–3996, 2013.

Gantt, B., Meskhidze, N., Facchini, M. C., Rinaldi, M., Ceburnis, D., and O'Dowd, C. D.: Wind speed dependent size-resolved parameterization for the organic mass fraction of sea spray aerosol, Atmos. Chem. Phys., 11, 8777–8790, doi:10.5194/acp-11-8777-2011, http://www.atmos-chem-phys.net/11/8777/2011/, 2011.

Gaonkar, A. G.: Surface and interfacial activities and emulsion characteristics of some food hydrocolloids, Food Hydrocolloids, 5, 329–337, 1991.

Gardner, W., Mishonov, A., and Richardson, M.: Global POC concentrations from in-situ and satellite data, Deep Sea Research Part II: Topical Studies in Oceanography, 53, 718–740, 2006.

Garrett, W. D.: Stabilization of air bubbles at the air-sea interface by surface-active material, Deep Sea Research and Oceanographic Abstracts, 14, 661–672, doi:10.1016/S0011-7471(67)80004-4, http://www.sciencedirect.com/science/article/pii/S0011747167800044, 1967.

Garrett, W. D.: The influence of monomolecular surface films on the production of condensation nuclei from bubbled sea water, Journal of Geophysical Research, 73, 5145–5150, 1968.

Garrett, W. D.: Organic chemistry of natural sea surface films, in: Organic Matter in Natural Waters, edited by Hood, D., pp. 469–477, Inst. Mar. Sci. Occas. Publ. 1, Univ. Alaska, Fairbanks, 1970.

Gašparović, B. and Ćosović, B.: Surface-active properties of organic matter in the North Adriatic Sea, Estuarine, Coastal and Shelf Science, 58, 555–566, 2003.

Gašparović, B., Kozarac, Z., Saliot, A., Ćosović, B., and Möbius, D.: Physicochemical Characterization of Natural and *ex-Situ* Reconstructed Sea-Surface Microlayers, Journal of colloid and interface science, 208, 191–202, 1998.

Gašparović, B. and Ćosović, B.: Distribution of surface-active substances in the northern Adriatic Sea, Marine chemistry, 75, 301–313, 2001.

Giribabu, K. and Ghosh, P.: Adsorption of nonionic surfactants at fluid–fluid interfaces: Importance in the coalescence of bubbles and drops, Chemical engineering science, 62, 3057–3067, 2007.

Graham, D. E. and Phillips, M. C.: Proteins at liquid interfaces: I. Kinetics of adsorption and surface denaturation, Journal of Colloid and Interface Science, 70, 403–414, 1979a.

Graham, D. E. and Phillips, M. C.: Proteins at liquid interfaces: II. Adsorption isotherms, Journal of Colloid and Interface Science, 70, 415–426, 1979b.

Graham, D. E. and Phillips, M. C.: Proteins at liquid interfaces: III. Molecular structures of adsorbed films, Journal of Colloid and Interface Science, 70, 427–439, 1979c.

Gregg, W. W., Ginoux, P., Schopf, P. S., and Casey, N. W.: Phytoplankton and iron: validation of a global three-dimensional ocean biogeochemical model, Deep Sea Research Part II: Topical Studies in Oceanography, 50, 3143–3169, 2003.

Hansell, D. A.: Recalcitrant dissolved organic carbon fractions, Annual Review of Marine Science, 5, 421–445, 2013.

Hansell, D. A., Carlson, C. A., and Schlitzer, R.: Net removal of major marine dissolved organic carbon fractions in the subsurface ocean, Global Biogeochemical Cycles, 26, GB1016, doi:10.1029/2011GB004069, 2012.

Harper, K. L. and Allen, H. C.: Competition between DPPC and SDS at the Air-Aqueous Interface, Langmuir, 23, 8925–8931, 2007.

Hawkins, L. and Russell, L.: Polysaccharides, proteins, and phytoplankton fragments: four chemically distinct types of marine primary organic aerosol classified by single particle spectromicroscopy, Adv. Meteorol, 2010, 612 132, doi:10.1155/2010/612132, 2010.

Hawkins, L. N., Russell, L. M., Covert, D. S., Quinn, P. K., and Bates, T. S.: Carboxylic acids, sulfates, and organosulfates in processed continental organic aerosol over the southeast Pacific Ocean during VOCALS-REx 2008, J. Geophys. Res., 115, D13 201, doi:10.1029/2009JD013276, 2010.

Hedges, J. I., Baldock, J. A., Gelinas, Y., Lee, C., Peterson, M., and Wakeham, S. G.: Evidence for non-selective preservation of organic matter in sinking marine particles, Nature, 409, 801–804, 2001.

Heikkila, R. E., Deamer, D. W., and Cornwell, D. G.: Solution of fatty acids from monolayers spread at the air-water interface: identification of phase transformations and the estimation of surface charge, Journal of Lipid Research, 11, 195–200, 1970.

Hubberten, U., Lara, R. J., and Kattner, G.: Amino acid composition of seawater and dissolved humic substances in the Greenland Sea, Marine chemistry, 45, 121–128, 1994.

Hultin, K., Krejci, R., Pinhassi, J., Gomez-Consarnau, L., Mårtensson, E., Hagström, Å., and Nilsson, E.: Aerosol and bacterial emissions from Baltic Seawater, Atmospheric research, 99, 1–14, 2011.

Hultin, K. A., Nilsson, E. D., Krejci, R., Mårtensson, E. M., Ehn, M., Hagström, Å., and de Leeuw, G.: In situ laboratory sea spray production during the Marine Aerosol Production 2006 cruise on the northeastern Atlantic Ocean, J. Geophys. Res., 115, D06 201, 2010.

Hurrell, J. W., Holland, M., Gent, P. R., Ghan, S., Kay, J. E., Kushner, P. J., Lamarque, J.-F., Large, W., Lawrence, D., Lindsay, K., Lipscomb, W. H., Long, M. C., Mahowald, N., R., M. D., Neale, R. B., Rasch, P. J., Vavrus, S., Vertenstein, M., Bader, D., Collins, W., Hack, J., Kiehl, J., and Marshall, S.: The Community Earth System Model: A Framework for Collaborative Research, Bulletin of the American Meteorological Society, 94, 1339–1360, doi:10.1175/BAMS-D-12-00121.1, http://journals.ametsoc.org/doi/abs/10.1175/BAMS-D-12-00121.1, 2013.

Ittekkot, V.: Variations of dissolved organic matter during a plankton bloom: qualitative aspects, based on sugar and amino acid analyses, Marine Chemistry, 11, 143–158, 1982.

Jachimska, B., Warszynski, P., and Malysa, K.: Influence of adsorption kinetics and bubble motion on stability of the foam films formed at¡ i¿ n¡/i¿-octanol,¡ i¿ n¡/i¿-hexanol and¡ i¿ n¡/i¿-butanol solution surface, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 192, 177–193, 2001.

Jarvis, N. L., Garrett, W. D., Scheiman, M. A., and Timmons, C. O.: Surface chemical characterization of surface active material in seawater, Limnol. Oceanogr., 12, 88–97, 1967.

Johnson, B. D. and Wangersky, P. J.: Microbubbles: Stabilization by monolayers of adsorbed particles, Journal of Geophysical Research: Oceans (1978–2012), 92, 14 641–14 647, 1987.

Kaiser, K. and Benner, R.: Biochemical composition and size distribution of organic matter at the Pacific and Atlantic time-series stations, Marine Chemistry, 113, 63–77, 2009.

Karydis, V. A., Capps, S. L., Russell, A. G., and Nenes, A.: Adjoint sensitivity of global cloud droplet number to aerosol and dynamical parameters, Atmos. Chem. Phys., 12, 9041–9055, doi:10.5194/acp-12-9041-2012, http://www.atmos-chem-phys.net/12/9041/2012/, 2012.

Keene, W. C., Sander, R., Pszenny, A. A., Vogt, R., Crutzen, P. J., and Galloway, J. N.: Aerosol pH in the marine boundary layer: A review and model evaluation, Journal of Aerosol Science, 29, 339–356, 1998.

Keene, W. C., Maring, H., Maben, J. R., Kieber, D. J., Pszenny, A. A. P., Dahl, E. E., Izaguirre, M. A., Davis, A. J., Long, M. S., Zhou, X., Smoydzin, L., and Sander, R.: Chemical and physical characteristics of nascent aerosols produced by bursting bubbles at a model air-sea interface, J. Geophys. Res.-Atmos., 112, D21 202, doi:10.1029/2007JD008464, http://www.agu.org/journals/jd/jd0721/2007JD008464/, 16 pp., 2007.

Krzan, M., Zawala, J., and Malysa, K.: Development of steady state adsorption distribution over interface of a bubble rising in solutions of n-alkanols (C5, C8) and n-alkyltrimethylammonium bromides (C8, C12, C16), Colloids and Surfaces A: Physicochemical and Engineering Aspects, 298, 42–51, 2007.

Kujawinski, E. B., Farrington, J. W., and Moffett, J. W.: Evidence for grazing-mediated production of dissolved surface-active material by marine protists, Marine chemistry, 77, 133–142, 2002.

Kuznetsova, M. and Lee, C.: Dissolved free and combined amino acids in nearshore seawater, sea surface microlayers and foams: Influence of extracellular hydrolysis, Aquatic sciences, 64, 252–268, 2002.

Kuznetsova, M., Lee, C., Aller, J., and Frew, N.: Enrichment of amino acids in the sea surface microlayer at coastal and open ocean sites in the North Atlantic Ocean, Limnol. Oceanogr., 49, 1605–1619, doi:10.4319/lo.2004.49.5.1605, 2004.

Kuznetsova, M., Lee, C., and Aller, J.: Characterization of the proteinaceous matter in marine aerosols, Mar. Chem., 96, 359–377, doi:10.1016/j.marchem.2005.03.007, http://dx.doi.org/10.1016/j.marchem.2005.03.007, 2005.

Lan, Q., Bassi, A. S., Zhu, J.-X. J., and Margaritis, A.: A modified Langmuir model for the prediction of the effects of ionic strength on the equilibrium characteristics of protein adsorption onto ion exchange/affinity adsorbents, Chemical Engineering Journal, 81, 179–186, 2001.

Langmuir, I.: The adsorption of gases on plane surfaces of glass, mica and platinum., Journal of the American Chemical society, 40, 1361–1403, 1918.

Large, W. G., McWilliams, J. C., and Doney, S. C.: Oceanic vertical mixing: A review and a model with a nonlocal boundary layer parameterization, Reviews of Geophysics, 32, 363–403, 1994.

Laß, K., Bange, H. W., and Friedrichs, G.: Seasonal signatures in SFG vibrational spectra of the sea surface nanolayer at Boknis Eck Time Series Station (SW Baltic Sea), Biogeosciences, 10, 5325–5334, 2013.

Lehninger, A. L.: Biochemistry: The molecular basis of cell structure and function, Worth Publishers, Inc., second edition edn., 1975.

Lewis, R. and Schwartz, E.: Sea salt aerosol production: mechanisms, methods, measurements and models — a critical review, vol. 152, American Geophysical Union, Washington, D.C., 2004.

Li, Z., Williams, A. L., and Rood, M. J.: Influence of soluble surfactant properties on the activation of aerosol particles containing inorganic solute, Journal of the atmospheric sciences, 55, 1859–1866, 1998.

Lindsley, W., Skop, R., and Brown, J.: Surface pressure and wave-damping effects of surface-active organic compounds on seawater, Ocean engineering, 18, 593–601, 1991.

Lomas, M. W., Glibert, P. M., Clougherty, D. A., Huber, D. R., Jones, J., Alexander, J., and Haramoto, E.: Elevated organic nutrient ratios associated with brown tide algal blooms of *Aureococcus anophagefferens* (*Pelagophyceae*), Journal of Plankton Research, 23, 1339–1344, 2001.

Long, M., Keene, W., Kieber, D., Erickson, D., and Maring, H.: A sea-state based source function for size-and compositionresolved marine aerosol production, Atmos. Chem. Phys, 11, 1203–1216, 2011.

Longhurst, A.: Ecological Biogeography of the Sea, 1998.

Macintyre, F.: Geochemical fractionation during mass transfer from sea to air by breaking bubbles, Tellus, 22, 451–462, 1970.

Malcolm, R. L.: The uniqueness of humic substances in each of soil, stream and marine environments, Analytica Chimica Acta, 232, 19–30, 1990.

Maltrud, M. E., Smith, R. D., Semtner, A. J., and Malone, R. C.: Global eddy-resolving ocean simulations driven by 1985–1995 atmospheric winds, Journal of Geophysical Research: Oceans (1978–2012), 103, 30 825–30 853, 1998.

Marty, J., Ẑutić, V., Precali, R., Saliot, A., Ćosović, B., Smodlaka, N., and Cauwet, G.: Organic matter characterization in the Northern Adriatic Sea with special reference to the sea surface microlayer, Marine Chemistry, 25, 243–263, 1988.

McGregor, M. A. and Barnes, G.: Equilibrium penetration of monolayers VI: Cholesterol-cetrimonium bromide system, Journal of pharmaceutical sciences, 67, 1054–1056, 1978.

Melville, W.: The role of surface-wave breaking in air-sea interaction, Annual review of fluid mechanics, 28, 279–321, 1996.

Meskhidze, N. and Nenes, A.: Phytoplankton and cloudiness in the Southern Ocean, Science, 314, 1419–1423, 2006.

Modini, R. L., Russell, L. M., Deane, G. B., and Stokes, M. D.: Effect of soluble surfactant on bubble persistence and bubble-produced aerosol particles, Journal of Geophysical Research: Atmospheres, pp. 1388–1400, doi:10.1002/jgrd.50186, 2013.

Moore, J. K., Doney, S. C., Kleypas, J. A., Glover, D. M., and Fung, I. Y.: An intermediate complexity marine ecosystem model for the global domain, Deep Sea Research Part II: Topical Studies in Oceanography, 49, 403–462, 2001.

Moore, J. K., Doney, S. C., and Lindsay, K.: Upper ocean ecosystem dynamics and iron cycling in a global three-dimensional model, Global Biogeochemical Cycles, 18, GB4028, doi:10.1029/2004GB002220, 2004.

Moore, R. H., Ingall, E. D., Sorooshian, A., and Nenes, A.: Molar mass, surface tension, and droplet growth kinetics of marine organics from measurements of CCN activity, Geophys. Res. Lett., 35, L07 801, doi:10.1029/2008GL033350, 2008.

Moore, R. H., Karydis, V. A., Capps, S. L., Lathem, T. L., and Nenes, A.: Droplet number uncertainties associated with CCN: an assessment using observations and a global model adjoint, Atmos. Chem. Phys., 13, 4235–4251, doi:10.5194/acp-13-4235-2013, http://www.atmos-chem-phys.net/13/4235/2013/, 2013.

Mulqueen, M., Datwani, S. S., Stebe, K. J., and Blankschtein, D.: Dynamic surface tensions of aqueous surfactant mixtures: Experimental investigation, Langmuir, 17, 7494–7500, 2001a.

Mulqueen, M., Stebe, K. J., and Blankschtein, D.: Dynamic interfacial adsorption in aqueous surfactant mixtures: Theoretical study, Langmuir, 17, 5196–5207, 2001b.

Nagata, T.: Microbial Ecology of the Oceans, chap. Bacterial production and biomass in the oceans, pp. 207–241, Wiley Series in Ecological and Applied Microbiology, Wiley-Blackwell, New York, ed.: Kirchman, D.. 2nd edn., 2008.

Nilsson, L. and Bergenståhl, B.: Adsorption of hydrophobically modified starch at oil/water interfaces during emulsification, Langmuir, 22, 8770–8776, 2006.

O'Dowd, C., Langmann, B., Varghese, S., Scannell, C., Ceburnis, D., and Facchini, M.: A combined organic-inorganic sea-spray source function, Geophys. Res. Lett., 35, L01 801, doi:10.1029/2007GL030331, 2008.

O'Dowd, C. D. and de Leeuw, G.: Marine aerosol production: a review of the current knowledge, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 365, 1753–1774, 2007.

O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y. J., and Putaud, J.: Biogenically driven organic contribution to marine aerosol, Nature, 431, 676–680, doi:10.1038/nature02959, http://www.nature.com/nature/journal/v431/n7009/abs/nature02959.html, 2004.

Oliver, M. J. and Irwin, A. J.: Objective global ocean biogeographic provinces, Geophys. Res. Lett., 35, L15 601, doi:10.1029/2008GL034238, 2008.

Oppo, C., Bellandi, S., Degli Innocenti, N., Stortini, A., Loglio, G., Schiavuta, E., and Cini, R.: Surfactant components of marine organic matter as agents for biogeochemical fractionation and pollutant transport via marine aerosols, Marine chemistry, 63, 235–253, 1999.

Parra-Barraza, H., Burboa, M. G., Sánchez-Vázquez, M., Juárez, J., Goycoolea, F. M., and Valdez, M. A.: Chitosan-cholesterol and chitosan-stearic acid interactions at the air-water interface, Biomacromolecules, 6, 2416–2426, 2005.

Parrish, C. C.: Dissolved and particulate marine lipid classes: a review, Marine Chemistry, 23, 17–40, 1988.

Parrish, C. C., Bodennec, G., Macpherson, E. J., and Ackman, R. G.: Seawater fatty acids and lipid classes in an urban and a rural Nova Scotia inlet, Lipids, 27, 651–655, 1992.

Parsons, T. R., Takahashi, M., and Hargrave, B.: Biological oceanographic processes, Elsevier Science and Technology, Amsterdam, 1983.

Patro, R., Leifer, I., and Bowyer, P.: Better bubble process modeling: Improved bubble hydrodynamics parameterization, Gas Transfer at Water Surfaces, pp. 315–320, 2002.

Perez, A. A., Sánchez, C. C., Rodríguez Patino, J. M., Rubiolo, A. C., and Santiago, L. G.: Surface adsorption behaviour of milk whey protein and pectin mixtures under conditions of air–water interface saturation, Colloids and Surfaces B: Biointerfaces, 85, 306–315, 2011.

Prather, K. A., Bertram, T. H., Grassian, V. H., Deane, G. B., Stokes, M. D., DeMott, P. J., Aluwihare, L. I., Palenik, B. P., Azam, F., Seinfeld, J. H., Moffet, R. C., Molina, M. J., Cappa, C. D., Geiger, F. M., Roberts, G. C., Russell, L. M., Ault, A. P., Baltrusaitisc, J., Collins, D. B., Corrigan, C. E., Cuadra-Rodriguez, L. A., Ebben, C. J., Forestieri, S. D., Guasco, T. L., Hersey, S. P., Kim, M. J., Lambert, W. F., Modini, R. L., Mui, W., Pedler, B. E., Ruppel, M. J., Ryder, O. S., Schoepp, N. G., Sullivan, R. C., and Zhao, D.: Bringing the ocean into the laboratory to probe the chemical complexity of sea spray aerosol, Proceedings of the National Academy of Sciences, 110, 7550–7555, doi:10.1073/pnas.1300262110, 2013.

Pszenny, A., Keene, W., Jacob, D., Fan, S., Maben, J., Zetwo, M., Springer-Young, M., and Galloway, J.: Evidence of inorganic chlorine gases other than hydrogen chloride in marine surface air, Geophysical Research Letters, 20, 699–702, 1993.

Quinn, P. K., Bates, T. S., Schulz, K. S., Coffman, D., Frossard, A. A., Russell, L. M., Keene, W. C., and Kieber, D. J.: Contribution of sea surface carbon pool to organic matter enrichment in sea spray aerosol, Nature Geosci., 7, 228–232, 2014.

Resch, F. and Afeti, G.: Submicron film drop production by bubbles in seawater, Journal of Geophysical Research: Oceans (1978–2012), 97, 3679–3683, 1992.

Rinaldi, M., Fuzzi, S., Decesari, S., Marullo, S., Santoleri, R., Provenzale, A., Hardenberg, J., Ceburnis, D., Vaishya, A., O'Dowd, C. D., and Facchini, M. C.: Is chlorophyll-a the best surrogate for organic matter enrichment in submicron primary marine aerosol?, J. Geophys. Res.-Atmos., 118, 4964–4973, doi:10.1002/jgrd.50417, 2013.

Rosilio, V. and Baszkin, A.: Polysaccharides at Interfaces, in: Physical Chemistry of Biological Interfaces, edited by Baszkin, A. and Norde, W., pp. 155–169, Marcel Dekker, New York, 2000.

Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K., and Bates, T. S.: Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting, P. Natl. Acad. Sci. USA, 107, 6652–6657, doi:10.1073/pnas.0908905107, http://www.pnas.org/content/107/15/6652.abstract, 2010.

Russell, L. M., Sorooshian, A., Seinfeld, J. H., Albrecht, B. A., Nenes, A., Ahlm, L., Chen, Y.-C., Coggon, M., Craven, J. S., Flagan, R. C., Frossard, A. A., Jonsson, H., Jung, E., Lin, J. J., Metcalf, A. R., Modini, R., Mülmenstädt, J., Roberts, G. C., Shingler, T., Song, S., Wang, Z., and Wonaschütz, A.: Eastern Pacific Emitted Aerosol Cloud Experiment, Bull. Am. Met. Soc., 94, 709–729, 2013.

Sallee, V. L. and Dietschy, J. M.: Determinants of intestinal mucosal uptake of short- and medium-chain fatty acids and alcohols, Journal of lipid research, 14, 475–484, 1973.

Sarmiento, J. L. and Gruber, N.: Ocean biogeochemical dynamics, Princeton University Press, Princeton, 2006.

Schmitt-Kopplin, P., Liger-Belair, G., Koch, B. P., Flerus, R., Kattner, G., Harir, M., Kanawati, B., Lucio, M., Tziotis, D., Hertkorn, N., and Gebefügi, I.: Dissolved organic matter in sea spray: a transfer study from marine surface water to aerosols, Biogeosciences, 9, 1571–1582, doi:10.5194/bg-9-1571-2012, http://www.biogeosciences.net/9/1571/2012/, 2012.

Sciare, J., Favez, O., Sarda-Esteve, R., Oikonomou, K., Cachier, H., and Kazan, V.: Long-term observations of carbonaceous aerosols in the Austral Ocean atmosphere: Evidence of a biogenic marine organic source, J. Geophys. Res., 114, D15 302, doi:10.1029/2009JD011998, 2009.

Sebba, F. and Briscoe, H. V. A.: The variation of the solubility of unimolecular films with surface pressure, and its effect on the measurement of true surface pressure, Journal of the Chemical Society, 1940, 114–118, doi:10.1039/JR9400000114, 1940.

Sekelsky, A. M. and Shreve, G. S.: Kinetic model of biosurfactant-enhanced hexadecane biodegradation by *Pseudomonas aeruginosa*, Biotechnology and bioengineering, 63, 401–409, 1999.

Shiraiwa, M., Zuend, A., Bertram, A., and Seinfeld, J. H.: Gas-particle partitioning of atmospheric aerosols: Interplay of physical state, non-ideal mixing and morphology, PCCP Phys. Chem. Ch. Ph., 15, 11 441–11 453, doi:10.1039/C3CP51595H, 2013.

Shogren, R. and Biresaw, G.: Surface properties of water soluble maltodextrin, starch acetates and starch acetates/alkenylsuccinates, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 298, 170–176, 2007.

Skop, R., Viechnicki, J., and Brown, J.: A model for microbubble scavenging of surface-active lipid molecules from seawater, Journal of geophysical research, 99, 16 395–16, 1994.

Spiel, D.: More on the births of jet drops from bubbles bursting on seawater surfaces, J. Geophys. Res.-Oceans, 102, 5815–5821, 1997.

Spiel, D. E.: The number and size of jet drops produced by air bubbles bursting on a fresh water surface, J. Geophys. Res.-Oceans, 99, 10 289–10 296, doi:10.1029/94JC00382, 1994.

Spiel, D. E.: On the births of film drops from bubbles bursting on seawater surfaces, J. Geophys. Res.-Oceans, 103, 24 907–24 918, doi:10.1029/94JC03055, 1998.

Stephen, A., ed.: Food polysaccharides and their application., Marcel Dekker, Inc., New York, 1995.

Sutherland, K.: Physical chemistry of flotation. XI. Kinetics of the flotation process, J. Phys. Chem.-US, 52, 394–425, 1948.

Svenningsson, B., Rissler, J., Swietlicki, E., Mircea, M., Bilde, M., Facchini, M., Decesari, S., Fuzzi, S., Zhou, J., Mønster, J., et al.: Hygroscopic growth and critical supersaturations for mixed aerosol particles of inorganic and organic compounds of atmospheric relevance, Atmos. Chem. Phys., 6, 1937–1952, 2006.

Tajima, K., Muramatsu, M., and Sasaki, T.: Radiotracer studies on adsorption of surface active substance at aqueous surface. I. Accurate measurement of adsorption of tritiated sodium dodecylsulfate, Bulletin of the Chemical Society of Japan, 43, 1991–1998, 1970.

Takahama, S., Liu, S., and Russell, L.: Coatings and clusters of carboxylic acids in carbon-containing atmospheric particles from spectromicroscopy and their implications for cloud-nucleating and optical properties, J. Geophys. Res., 115, D01 202, doi:10.1029/2009JD012622, 2010.

Tanoue, E.: Occurrence and characterization of particulate proteins in the Pacific Ocean, Deep Sea Research Part A. Oceanographic Research Papers, 39, 743–761, 1992.

Ter Minassian-Saraga, L.: Recent work on spread monolayers, adsorption and desorption, Journal of Colloid And Interface Science, 11, 398–418, 1956.

Tranvik, L. and Kokalj, S.: Decreased biodegradability of algal DOC due to interactive effects of UV radiation and humic matter, Aquatic Microbial Ecology, 14, 301–307, 1998.

Tsai, W.-t. and Liu, K.-K.: An assessment of the effect of sea surface surfactant on global atmosphere-ocean CO2 flux, Journal of geophysical research, 108, 3127, doi:10.1029/2000JC000740, 2003.

Tseng, R., Viechnicki, J., Skop, R., and Brown, J.: Sea-to-air transfer of surface-active organic compounds by bursting bubbles, Journal of Geophysical Research, 97, 5201–5206, 1992.

Tuckermann, R.: Surface tension of aqueous solutions of water-soluble organic and inorganic compounds, Atmos. Environ., 41, 6265–6275, 2007.

Tuckermann, R. and Cammenga, H. K.: The surface tension of aqueous solutions of some atmospheric water-soluble organic compounds, Atmospheric Environment, 38, 6135–6138, 2004.

Turpin, B. J. and Lim, H.-J.: Species contributions to PM2. 5 mass concentrations: Revisiting common assumptions for estimating organic mass, Aerosol Science & Technology, 35, 602–610, 2001.

Van Vleet, E. S. and Williams, P. M.: Surface potential and film pressure measurements in seawater systems, Limnol. Oceanogr., 28, 401–414, 1983.

Verity, P. G., Williams, S. C., and Hong, Y.: Formation, degradation, and mass: volume ratios of detritus derived from decaying phytoplankton, Marine ecology. Progress series, 207, 53–68, 2000.

Vignati, E., Facchini, M. C., Rinaldi, M., Scannell, C., Ceburnis, D., Sciare, J., Kanakidou, M., Myriokefalitakis, S., Dentener, F., and O'Dowd, C. D.: Global scale emission and distribution of sea-spray aerosol: sea-salt and organic enrichment, Atmos. Environ., 44, 670–677, doi:10.1016/j.atmosenv.2009.11.013, http://dx.doi.org/10.1016/j.atmosenv.2009.11.013, 2010.

Vojvodić, V. and Ćosović, B.: Fractionation of surface active substances on the XAD-8 resin: Adriatic Sea samples and phytoplankton culture media, Marine chemistry, 54, 119–133, 1996.

Vorum, H., Brodersen, R., Kragh-Hansen, U., and Pedersen, A. O.: Solubility of long-chain fatty acids in phosphate buffer at pH 7.4, Biochimica et Biophysica Acta (BBA)-Lipids and Lipid Metabolism, 1126, 135–142, 1992.

Wakeham, S. G., Lee, C., Hedges, J. I., Hernes, P. J., and Peterson, M. J.: Molecular indicators of diagenetic status in marine organic matter, Geochimica et Cosmochimica Acta, 61, 5363–5369, 1997.

Wanninkhof, R., Asher, W. E., Ho, D. T., Sweeney, C., and McGillis, W. R.: Advances in quantifying air-sea gas exchange and environmental forcing, Annu. Rev. Marine Sci., 1, 213–244, doi:10.1146/annurev.marine.010908.163742, 2009.

Weber, M. E., Blanchard, D. C., and Syzdek, L. D.: The mechanism of scavenging of waterborne bacteria by a rising bubble, Limnol. Oceanogr., 28, 101–105, 1983.

Weisiger, R. A. and Zucker, S. D.: Transfer of fatty acids between intracellular membranes: roles of soluble binding proteins, distance, and time, American Journal of Physiology-Gastrointestinal and Liver Physiology, 282, G105–G115, 2002.

Westervelt, D., Moore, R., Nenes, A., and Adams, P.: Effect of primary organic sea spray emissions on cloud condensation nuclei concentrations, Atmos. Chem. Phys, 12, 89–101, 2012.

Wilke, C. R. and Chang, P.: Correlation of diffusion coefficients in dilute solutions, A. I. Ch. E. Journal, 1, 264–270, 1955.

Wurl, O. and Holmes, M.: The gelatinous nature of the sea-surface microlayer, Marine Chemistry, 110, 89–97, 2008.

Wurl, O., Wurl, E., Miller, L., Johnson, K., and Vagle, S.: Formation and global distribution of sea-surface microlayers, Biogeosciences, 8, 121–135, doi:10.5194/bg-8-121-2011, http://www.biogeosciences.net/8/121/2011/, 2011.

Žutić, V., Ćosović, B., Marčenko, E., Bihari, N., and Kršinić, F.: Surfactant production by marine phytoplankton, Marine Chemistry, 10, 505–520, 1981.

Supplementary materials to:
A physically-based framework for modelling the organic fractionation of sea spray aerosol from bubble film Langmuir equilibria

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October 14, 2014

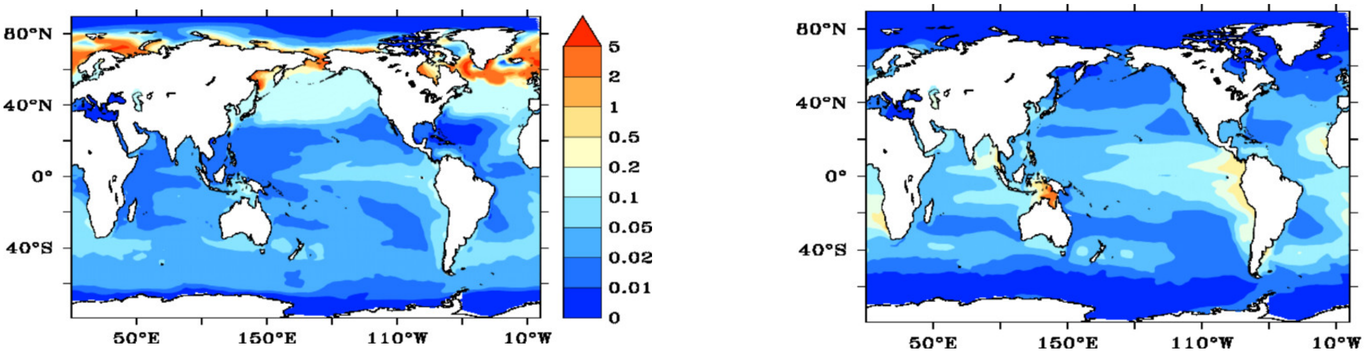
1 Mapping of macromolecules to marine biogeochemical variables: additional figures for May and August

Mapping of macromolecules to marine biogeochemical variables: additional figures for May and August.

2 Sensitivity cases

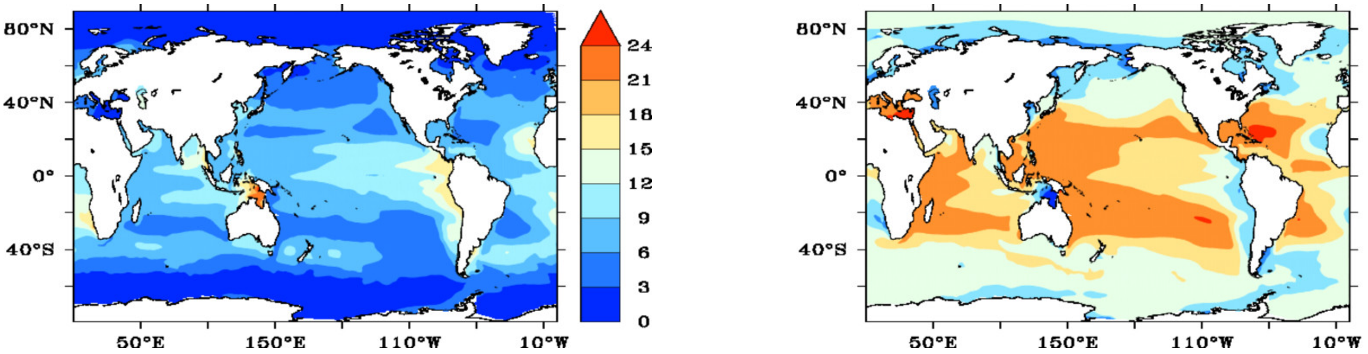
References

Fuentes, E., H. Coe, D. Green, and G. McFiggans, On the impacts of phytoplankton-derived organic matter on the properties of the primary marine aerosol–Part 2: Composition, hygroscopicity and cloud condensation activity, *Atmos. Chem. Phys.*, *11*(6), 2585–2602, 2011.



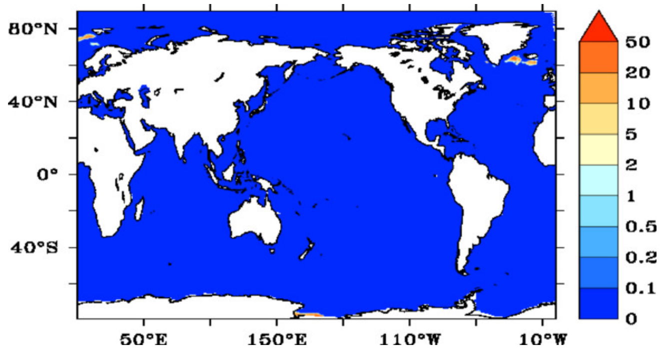
(a) Lipid-like mixture

(b) Polysaccharide-like mixture



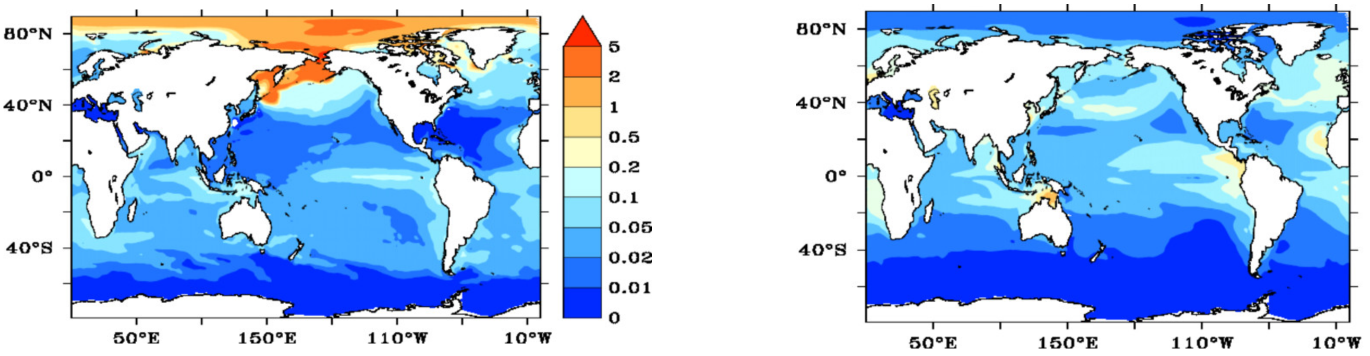
(c) Protein-like mixture

(d) Processed mixture



(e) Deep abyssal humic-like mixture

Figure 1: Ocean concentration of each compound class [μmol L^{-1}], May.


(a) Lipid-like mixture

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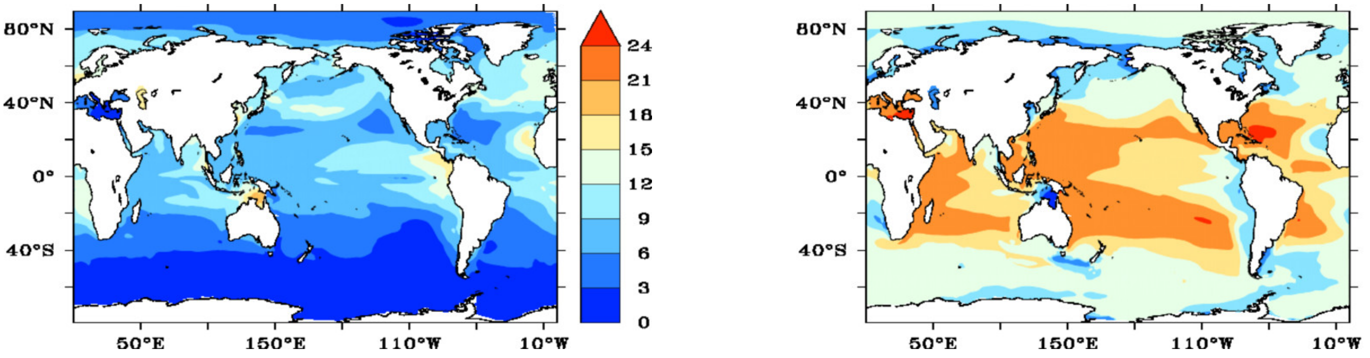

(c) Protein-like mixture

(d) Processed mixture

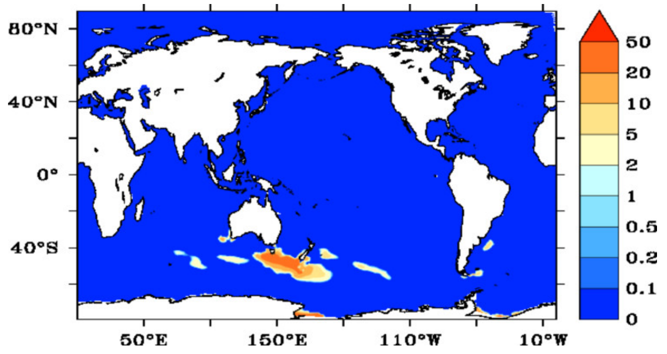
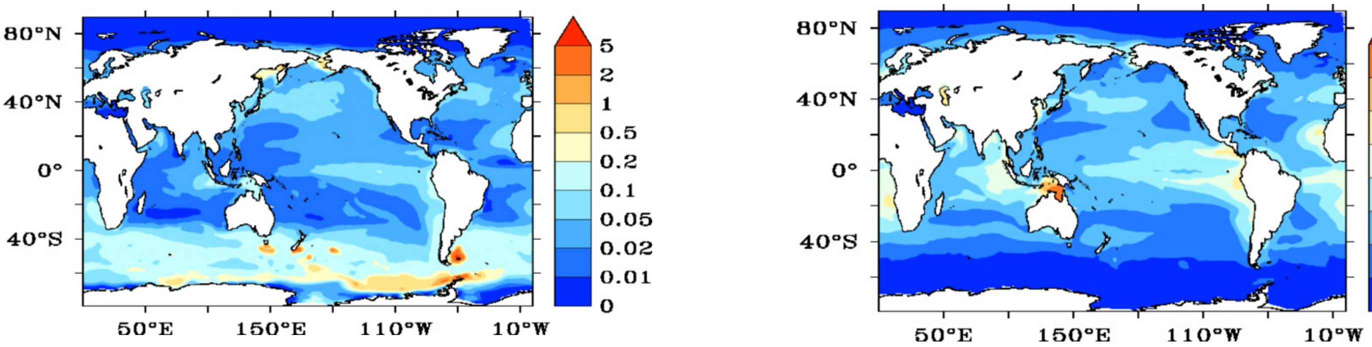
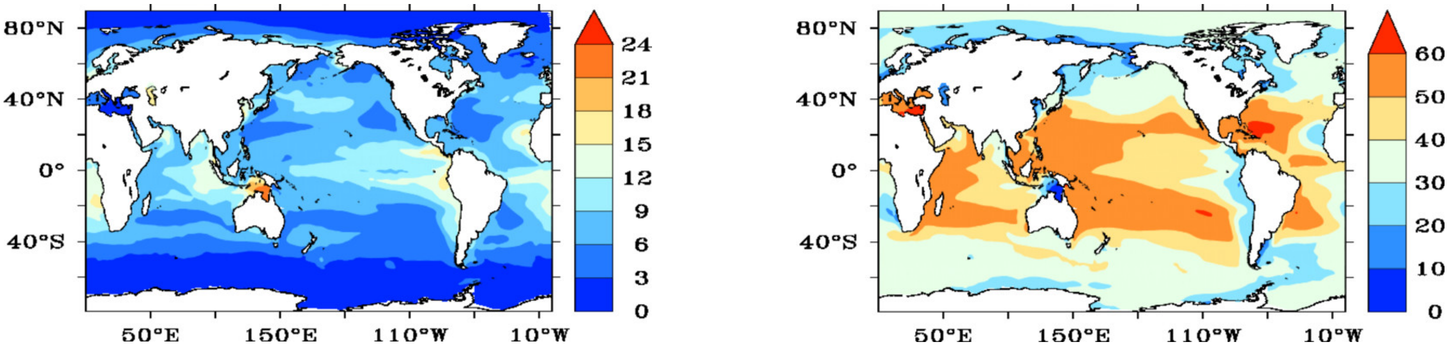

(e) Deep abyssal humic-like mixture

Figure 2: Ocean concentration of each compound class [μmol L^{-1}], August.



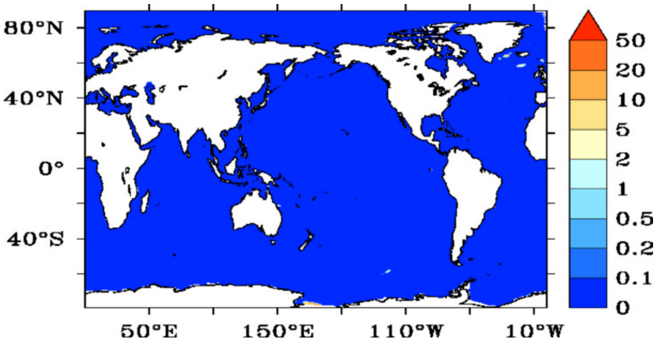
(a) Lipid-like mixture

(b) Polysaccharide-like mixture



(c) Protein-like mixture

(d) Processed mixture



(e) Deep abyssal humic-like mixture

Figure 3: Ocean concentration of each compound class [μmol L^{-1}], November.

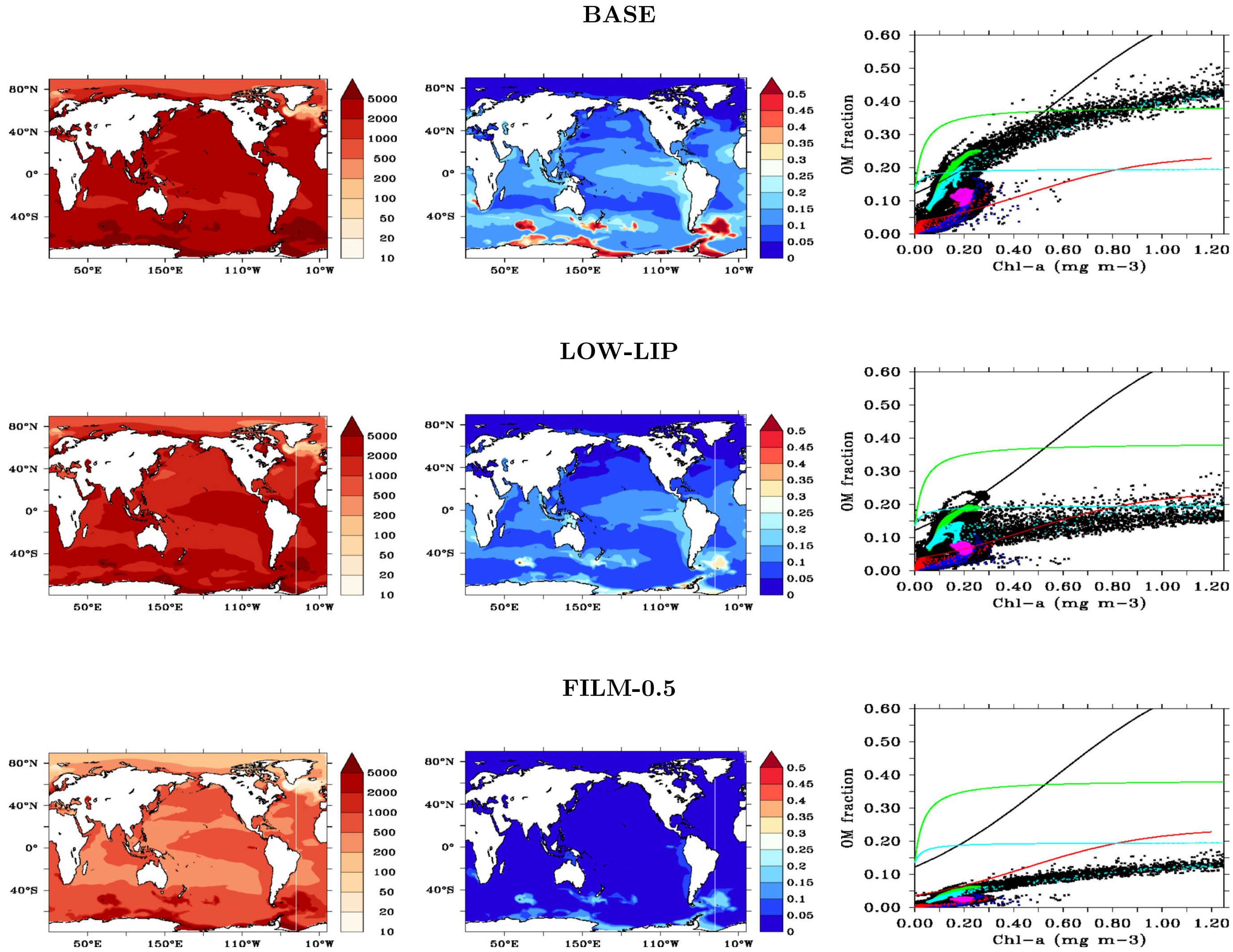
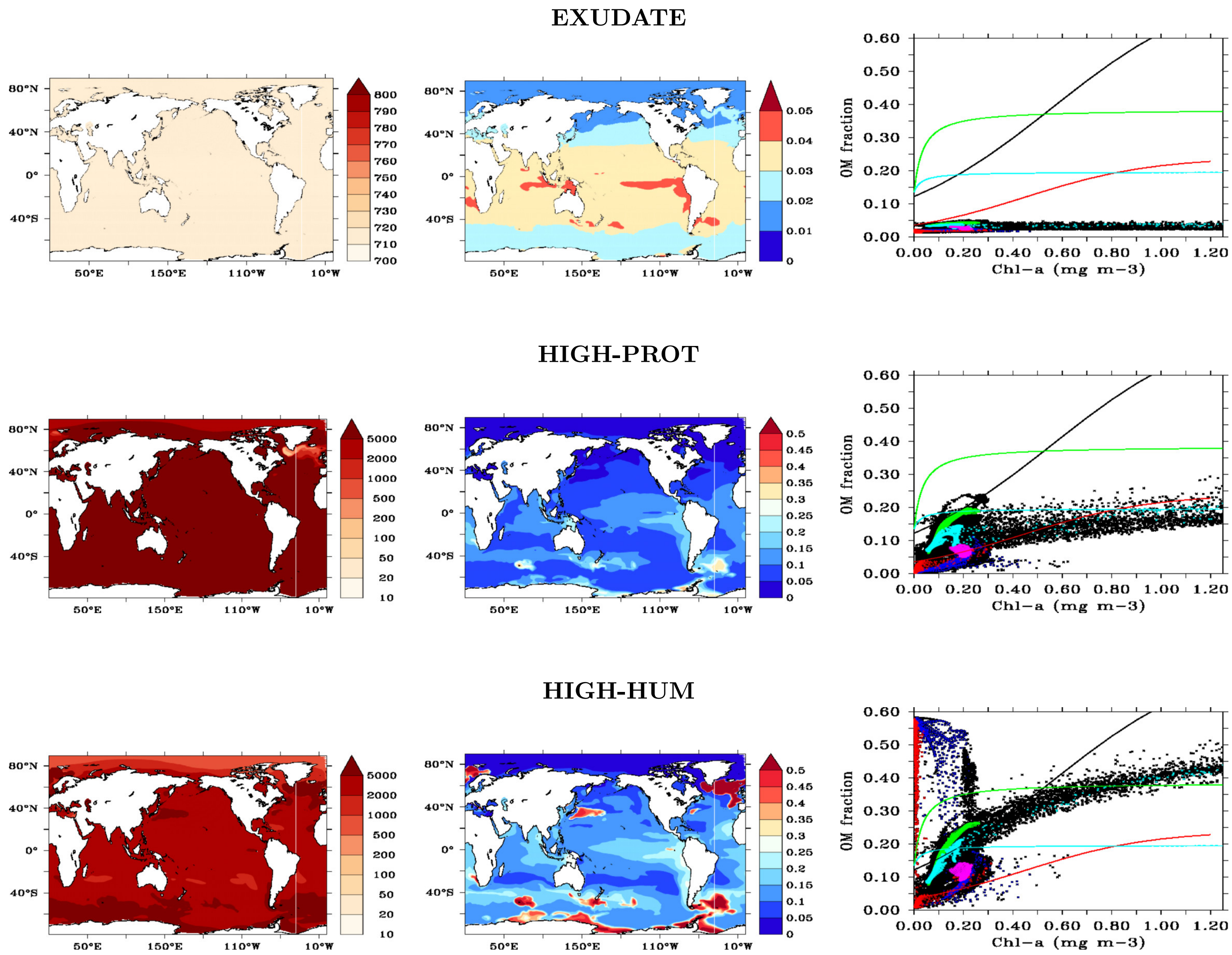


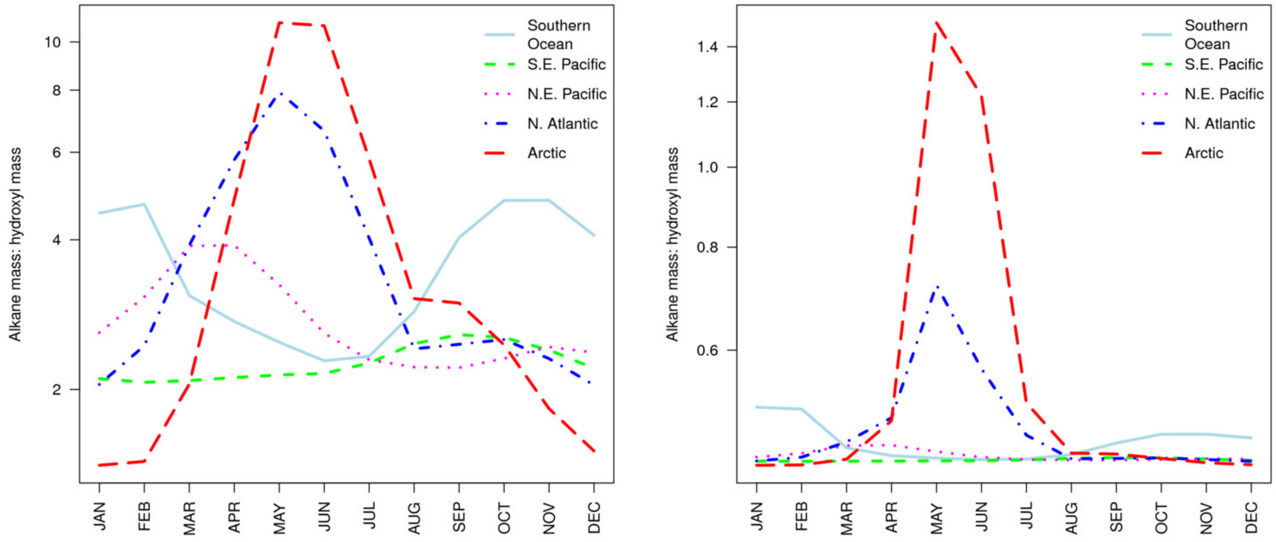
Figure 4: Global estimates of effective enrichment, organic mass fractions, and chl-vs-OM fraction relationship, February. Top: BASE case: using model compounds as described in Table 1 of main paper. Middle: Case LOW-LIP: using model compounds as described in Table 1 of main paper, but with α_{lip} decreased by a factor of ten. Bottom: Case FILM-0.5: using model compounds as described in Table 1 of main paper, but with $l_{\text{bub}} = 0.5\,\mu$m.


EXUDATE

HIGH-PROT

HIGH-HUM

Figure 5: Global estimates of organic mass fraction in nascent film drops – sensitivity cases (February). Top: Case EXUDATE: using empirical constants derived from phytoplankton exudates [*Fuentes et al.*, 2011], with the same physical constants applied to all five compound classes.B Middle: Case HIGH-PROT: using model compounds as described in Table 1 of main paper, but with α_{prot} for casein (ten times larger value). Bottom: Case HIGH-HUM: using model compounds as described in Table 1 of main paper, but with $\alpha_{\mathrm{humic}} \times 10^4$.



(a) BASE case

(b) LOW-LIP+HIGH-POLY case

(c) BASE case

(d) LOW-LIP+HIGH-POLY case

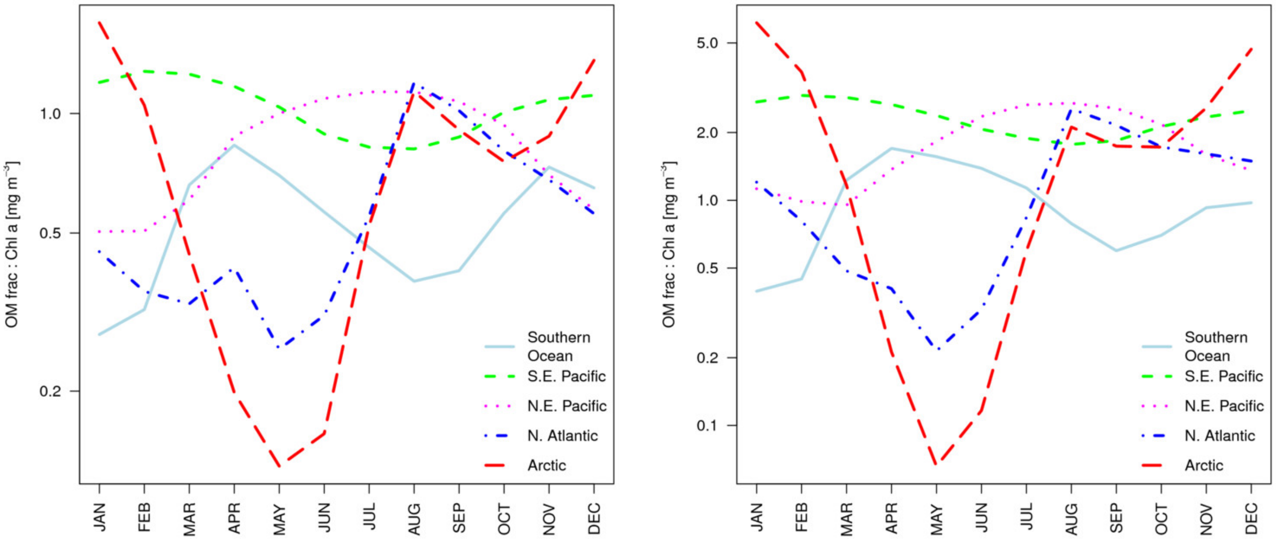


Figure 6: Seasonal cycle of the alkane-to-hydroxyl ratio as estimated from model monthly mean submicron SSA composition. Organic classes were averaged over the regions shown in Fig. 9 and converted to estimated functional group masses using the conversions indicated in Tab. 4.