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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A physically-based framework for modelling the organic fractionation of sea spray aerosol from bubble film Langmuir equilibria" *by* S. M. Burrows et al.

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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 phytoplankton 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.

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