

## ***Interactive comment on “Wind speed dependent size-resolved parameterization for the organic enrichment of sea spray” by B. Gantt et al.***

**Anonymous Referee #2**

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Overall: This paper describes the water insoluble organic mass fraction of sea spray (OMss) as a function of chlorophyll concentration, wind speed, and aerosol diameter. The goal is to be useful in global models containing the organic flux from ocean emissions. The paper is well written and clear, and while the authors acknowledge many of the uncertainties associated with the analysis more work needs to be done on certain points. We applaud the effort to define the OMss as a function of multiple parameters because it is clearly a multivariate system. Using just one parameter may result in overlooking the real cause of the change in OMss fraction. That being said, I believe there is a basic flaw in the logic of using SS particle size to predict SS composition — since these variables are dependent: i.e. isn't this using one particle characteristic to predict another rather than using an atmospheric or oceanic variable to predict particle production? Also, future work should really focus on moving past using only chlorophyll

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concentration as the overall proxy for all biological activity in the ocean as it is unlikely to be representative of microlayer organic fraction.

On the positive side the authors have made a first attempt to combine both meteorological and oceanic data to predict the organic fraction of sea spray aerosols (denoted as OMss). This is an important step because the complex processes controlling OMss are likely occurring in both the ocean and the atmosphere. However, there are sizeable uncertainties in all of the concepts and data that the authors base their parameterization on. In addition, I believe that there are some large mistakes in the method used to derive the parameterization, which I detail below. Consequently, the authors' conclusion that they have identified the three “most important” controlling factors is not merited.

Major Points The conceptual picture presented in Fig. 1 is not as certain as the authors would have us believe. Wurl et al., (2010) (referenced in the paper) contains a sizeable dataset that suggests that for surfactants at least SML enrichment does not depend on wind speed up to 10 m/s (plus numerous references that support this statement). Wurl et al. argue that at moderate wind speeds SML enrichment may actually be increased by an increase in the number of bubbles that effectively pump organic material to the ocean surface where it may quickly form films. This is just a hypothesis, but the point is that our understanding of SML enrichment is much more immature than the conceptual picture introduced by the authors would have the audience of atmospheric scientists believe. Note the manuscript doesn't mention other factors that affect SML enrichment such as trophic level and the specific composition of seawater organics. In addition, the discussion of SML enrichment is hampered by the fact that actual enrichment factors are never reported. In Fig. 1 enrichment is falsely represented as OC/Na ratios in the SML. These are not enrichment factors; They must be divided by the corresponding ratios in subsurface water to obtain enrichment factors. Properly reporting the range of SML enrichment factors generally observed (from less than 1 (i.e. depletion) to ~5) would give atmospheric scientists a much better physical understanding of the

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processes occurring here.

The inverse relationship between OMss and U10 displayed in Fig. 2a does not support Fig. 1 due to the following reasons. OMss is calculated from ambient OA measurements. It is highly probable that both continental OA and secondary marine OA are contributing to these ambient samples. This source of uncertainty is raised (though not quantified) by the authors in their caveats and uncertainties section (4), but it is not quantified. In addition and perhaps more importantly, local wind speed data is used to generate this plot. Most of the OA measured at the 2 coastal locations, if it is indeed from primary marine and not secondary sources, must have been generated well upwind of the 2 sites, in some cases probably a few days upwind if there were no rain to wash it out. Therefore it is incorrect to use wind speed data at the point of sampling rather than the point(s) of OMss generation. Again section 4 raises this possibility but only a weak analysis is presented (for only 1 of the 2 sites!) to suggest that this is not a significant source of error. {Note – that the existence of a correlation may occur in isolated cases when the source and receptor regions are linked by a synoptic system; generalizing this to a global model is not appropriate.} Given these issues I don't believe Fig. 2a supports the Fig. 1 conceptual picture at all. To my mind a more likely explanation for the observed inverse trend is that there are relatively constant sources of OA that are 'diluted' by increases in local (e.g. surf zone) sea spray production as winds increase (recall OMss is defined as the ratio of WIOM to WIOM + sea salt). Since the authors consider the PM1 and PM2.5 size fractions a large proportion of the added sea spray mass will come from large particles that are known to be predominantly sea salt.

I don't understand why equation 3 doesn't have a site-specific maximum OMss factor. In Eq. 1 OMss(max) was site-specific and very different for Point Reyes (0.24) and Mace Head (0.78). I don't understand how both sites, and indeed all sites across the world, can then have the same OMss(max) value of 1 in Eq. 3. Doesn't this mean if Eq. 3 was applied to Point Reyes then it would greatly over-predict the measured OA

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concentrations? The authors could check this by modeling a typical size distribution of sea spray particles being sampled at Point Reyes and then calculating the bulk PM2.5 organic fraction to compare to the measurements. This problem is part of a more fundamental problem of this study, which is that a parameterization is derived from data collected at only 2 coastal sites and then applied world-wide without any validation.

Secondly, it is far from clear that small sea spray particles (< ~250 nm) are always dominated by organics. Only two studies have found such particles to have high organic fractions (~80%). Both studies are quoted in the current manuscript (Facchini et al., 2008; Keene et al., 2007). However, there are also considerable hygroscopicity measurements that suggest small sea spray particles frequently have only moderate to minor OMss values (< ~40%) (Sellegrì et al., 2008; Modini et al., 2010, Fuentes et al., 2010, 2011; only one of these studies is quoted in the manuscript). Given this I don't believe it's reasonable to assume that the maximum organic fraction of sea spray particles is 1. Again the authors raise this point briefly in the caveats and uncertainties section 4, but I'm still wondering how different the estimated emission rates would be if, say, the maximum OMss value allowed was only 50%, or even 10%?

Finally, I have an issue with the absence of an artificial cut-off for OMss at low wind speeds. It is true that such a cut-off may not be required since OMss will presumably be combined with sea spray source functions that will predict no sea spray production during calm conditions (WS<3-4 m/s) (although this point is never explicitly made in the manuscript). Nevertheless, not enough is made of the simple fact that OMss will not be produced during calm conditions. This is potentially very misleading.

Specific comments:

P10527, L 11: The OA concentration reported is a peak that has only been observed once. Average concentrations are far lower and should be reported (for Mace Head and other sites) to give the reader a more realistic picture of marine OA levels.

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P 10528, L 28: Provide references for thickness of microlayer films. Also, it should be pointed out that depletion of organics in the SML is also a possibility.

P 10528, L 29: Organic enrichment at the air-sea interface is not represented in Fig. 1 because it contains OC/Na ratios in the SML, not enrichment factors. See general comment above.

P 10529, L 23: Should read ‘...an additional...’, not ‘...the mechanism for sea spray generation...’ Why would bubble bursting stop at wind speeds greater than 11 m/s?

P 10530, L24: Studies that have found lower organic fractions for submicron sea spray particles should also be discussed here. See general comment above.

P 10531, L 8: More precise details on the location of the Point Reyes station should be provided since it is not directly on the coast. Are there any non-marine sources (e.g. roads) that could potentially be influencing the results even during on-shore flow?

P 10531, L 22: Why does this avoid potential Na problems? Please explain.

P 10532, L 14: The number of OMss measurements used for each of the 2 sites should be explicitly stated somewhere in this section.

P 10533, L 22: I think it is incorrect to use non-weighted ocean chemistry data in this analysis. If high surface Chl a and DOC regions occurred concurrently with low wind speeds (<4 m/s), which is probable in the North Atlantic during summer for example, then these regions would not add primary organic material to the atmosphere because bubble formation and therefore sea spray generation would not be occurring. Only ocean chemistry data in regions where the wind speed is high enough to cause sea spray generation should be used in this analysis.

P 10535, L 6: Needs to be pointed out that these are weak correlations.

P 10535, L 26: Should this be less than 1.5 m/s?

P 10536, L 4: I don't think it can be claimed that an inverse relationship holds for the

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low Chl a case, which has a correlation coefficient of only 0.08.

P 10536, L 8: Using a single, anomalously high OA concentration measurement to validate Eq.1 does absolutely nothing to increase confidence in it. I'm sure long term AMS data exists for Mace Head; why not validate the equation against these measurements?

P 10536, L 22: What size range is this Eq. 2 valid over?

P 10537, L 16: Eq. 1 was site-specific through the factor OMss(max). Where has this site-specificity gone now Eq. 1 is combined with Eq. 2 to produce Eq. 3? I believe this is a large mistake and will likely introduce significant errors into the OMss values predicted by Eq. 3 for some sites. However, I don't know this for sure because no effort has been made to validate Eq. 3 against measurements. Even though size-resolved measurements of marine OA are rare this might be done by assuming typical size distributions and calculating bulk OA concentrations.

P 10539, L 19: Two is not a few

P 10539, L 24: What were the actual organic fractions observed by Modini et al. (2010) and Fuentes et al. (2011) for that matter? Give the reader a feel for how large this assumption is.

P 10539, L 27: What are the ranges of WIOC/OC ratios that have been observed? Again, the reader needs to get a feel for how large this assumption is. Is this even important? What parameters is the parameterization most sensitive to?

P 10540, L 7: The 2 stated references are not enough to support the bold assertion that “...aerosol chemical composition and flux parameterizations derived from coastal measurements can provide a suitable proxy for open ocean conditions and therefore can be successfully used for global emissions assessments.” The Rinaldi reference is specific to Mace Head, so that's ok for the Mace Head data but not the Point Reyes data. The Clarke et al. study is fundamentally different because it scaled coastal

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measurements to the open ocean using whitecap coverage. It cannot be quoted in this context. Thus the authors have provided no justification for why they consider the Point Reyes data to be unaffected by coastal processes such as surf.

P 10540, L 16: What about Point Reyes? Also Fig. S3 only contains QuikSCAT data for a single 1x1 degree grid box 24 hrs upwind of Mace Head. Sea spray production should be occurring continuously along the air mass back trajectory if wind speeds are high enough and there are no sinks. Therefore, figure S3 is too simplistic to claim that the use of local wind speed data doesn't introduce large uncertainties into the approach.

P 10541, L 19: The last 2 sentences completely disregard the fact that sea spray organics are only produced at wind speeds greater than 3-4 m/s when bubble formation begins. They should be removed.

References (not already quoted in the manuscript):

Sellegri, K., Villani, P., Picard, D., Dupuy, R., O'Dowd, C., and Laj, P.: Role of the volatile fraction of submicron marine aerosol on its hygroscopic properties, *Atmospheric Research*, 90(2-4), 272-277, 10.1016/j.atmosres.2008.04.004, 2008.

Fuentes, E., Coe, H., Green, D., De Leeuw, G., and McFiggans, G.: Laboratory-generated primary marine aerosol via bubble-bursting and atomization, *Atmospheric Measurement Techniques*, 3, 141-162, 2010.

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, doi:10.5194/acp-11-2585-2011, 2011.

Minor Corrections: Abstract: Page 10526, Line 14: insert "with" "This relationship, combined with the published. . ."

Introduction: Page 10529, Line 2: Citation needed for the review of previous works.

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Data and Methods: Page 10531, Line 15: Analyzed using what technique? Page 10531, Line 20: be more specific about the "problems" with the Na measurements Page 10531, Line 23: Does Point Reyes also have a "clean sector" requirement? Mention that it is discussed in a later section, since the Mace Head clean sector is described here.

Page 10532, Line 3: Make a comment on how accurate it is to assume that 70% of the OC from Point Reyes is WIOC based on measurements at Mace Head. Are there studies at locations other than Mace Head or Amsterdam Island that would support this separation? I see now that this is discussed later, but it might be helpful to mention it here. Page 10532, Line 10: Is there any evidence of Chlorine depletion?

Results and Discussion: Page 10534, Line 22: Interesting. Showing the interdependence of chlorophyll and wind speed on determining the OMss is useful since chlorophyll and wind speed each go through a range of values.

Page 10536, Lines 21-22: The measurements by Facchini et al. (2008) were taken from the R/V Celtic Explorer and not necessarily at Mace Head. Explain why these measurements were used (matches best with the time period, technique, etc.). This seems like a large part of the parameterization, so it may require further explanation.

Page 10538, Line 9: take out "parts of the" "...fluxes in different oceans..." Page 10538, Line 21: the OMss calculated was from WIOM. How much would including the WSOM affect the growth factor and resulting conclusions? Page 10538, Line 23: Start a new paragraph at "Figure 6". Even though it is related, this paragraph is long and can be split up. The discussion of the figure seems to be a good splitting point. Page 10538, Lines 26-28: Explain this sentence more. Is it related to the figure? Or just a generalized statement based on other work?

Page 10539, Lines 4-5: "global magnitude" – do you mean global mean? Or magnitude in terms of change? Page 10539, Line 13: Check the parentheses.

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Caveats and uncertainty: Page 10539, Line 18: Good that it is acknowledged. Page 10539, Lines 24-26: I see that the WIOC/OC ratio for Point Reyes is discussed here. It may be useful to mention earlier that there is this discussion later.

Conclusion: Is there a cutoff point (minimum or maximum) for chlorophyll concentration where the parameterization of OMss no longer holds true?

Figures: Figure 2 – The font in the plots (equations) seems very small. It would help the reader if the font was larger. If this does not fit in the figure, try including the equations in the caption, instead, or even in a table. Also, the 4 points that were excluded, it may be interesting to include them in the figure, just colored differently. Do those anomalously high points say anything about the bounds to which the parameterization must stay within?

Figure 6 – Even though it is in the caption, it may be helpful to have description on the color bar. Also, what years is the annual average taken over?

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 10525, 2011.