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Atmospheric Chemistry and Physics Discussions

Interactive comment on "On the impacts of phytoplankton-derived organic matter on the properties of the primary marine aerosol – Part 2: Composition, hygroscopicity and cloud condensation activity" *by* E. Fuentes et al.

Anonymous Referee #2

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The discussion paper has changed quite significantly since the very first submission as requested by other reviewer(s) and I have to admit it reads better without burying the main findings under those many details and graphs which indeed can be useful for those trying to follow-up the research, but confusing for more casual reader. The current version, therefore, appears as a more balanced effort. The paper presents a very detailed description of the experiment aimed at studying the physical effects of primary marine organic matter at the point of particle activation into CCN. It is not surprising that the effects of marine organic matter on particle activation are far from understood due

to the fact that very little is known about the exact chemical composition of that organic matter. Very little is known about either water soluble or insoluble components/species of marine organic aerosol or about the processes contributing to either WSOC/WIOC. It has become quite well established that primary processes are mainly contributing to at least WIOC, however, the presence of colloidal organic matter makes WSOC/WIOC operational definition less reliable. Last but not least problem is not only the formation of either WSOC or WIOC, but its evolution, which in case of anthropogenic/terrestrial organic matter has become better conceptually defined (Jimenez et al., 2009, Science). The paper is well structured and reads well with many details available for the interested parties. I certainly recommend it publishing in ACP, but only subject to addressing my main critical comment about general validity of author's conclusions after applying an unhelpful methodological approach of filtering primary organic matter proxies through 0.2um membrane filter. My considerations are also valid for the Part 1 paper which has been already published in ACP.

The main problem I have with the paper is that it makes general conclusions about phytoplankton-derived organic matter impacts on the marine aerosol cloud condensation activity after essentially filtering out majority of organic matter via ultra-filtration (0.2um membrane filter) if there was any significant water insoluble particulate or colloidal matter present. Therefore, the title and abstract should clearly state that the studied effects were due to mainly dissolved organic matter. If there wasn't significant insoluble material then same argument applies. I will argue that in more detail where appropriate.

Ultra-filtration through 0.2um filter is normally used to separate insoluble organic matter (particulate organic matter, colloidal organic matter, viruses, bacteria or any live material). Author's claim that they did not filter out colloidal (largely insoluble) material is unsupported by direct experimental evidence and comparative literature study does not help to defend the statement that most of the colloidal material has actually passed through the filter. Authors must provide independent measurements of filtered and unfiltered (or filtered through coarse filter) material to show similarity of OM or to present measurements of WSOC versus WIOC of their filtrate to prove that significant amount of insoluble material was indeed present after ultra-filtration. My argument can be supported by an air filtration principle where 99.99% of all particles are retained by filters of 2um pore size. That is because filtration employs three mechanisms: diffusion/interception, impaction and physical retention of particles. Same is true when filtering water with lots of material (especially colloids) intercepted/impacted when filter becomes clogged. Colloidal material is especially prone to agglomeration (colloids can largely be agglomerates of large organic molecules) which would clearly dominate filtering process though membrane filter when pores become progressively clogged and colloids move longer distance to the next available pore. Therefore, I expect that authors either provide direct evidence that significant amount of insoluble material was present in their proxies or avoid using term “colloids” or “insoluble material” throughout the paper. I strongly suggest emphasizing in the abstract and possibly the title that studied impacts were of mainly soluble OM. I have to admit to authors credit that they considered the filtering effect in their conclusions, however, more casual reader would be mislead by suggesting that the studied impacts generally apply to the whole marine organic matter pool.

Experimental methods

Little attention is given to filtration method as I already argued.

It would be appropriate to justify OM concentrations used in the experiments. How 512uM concentration compares to the real world? 512uM would convert to $\sim$6mg/l concentration which is unheard off in anthropogenicaly unperturbed environment. Considering a largely dissolved material in the filtered proxies, 512uM concentration would be even more staggering.

Results and Discussion

P26165, lines 22-27. There was little effect when monolayer method was applied.

However, one could argue that absence of the effect could be due to wrong monolayer approach. For example, monolayer is possibly forming at every air/water interface of rising bubbles, thus proving against single monolayer approach. Authors may well be right, but it should be more extensively discussed.

P26169-26170. I have a problem with Figure 5 as it is presented and discussed. This plot was already introduced in Part 1 paper, which lies on a dubious assumption that 80% of OM is present in the 0.2um filtrate (again only supported by reference and not by the measurement). Reverse the assumption that only 20% of OM is left after ultra-filtration and the plot will easily match O’Dowd/Facchini/Keene experiments.

P26170, line 13. Comparison with Sellegri 2006 and Modini 2009 is only valid when considering that in both studies OM was dominated by DOC: Sellegri used artificial fully soluble organic compound SDS while Modini et al. admitted that the OM in the seawater could have been dominated by significant river run-off (inevitably containing lots of DOC).

P26171, line 25. There was no truly hydrophobic material (at least there is no direct evidence provided), therefore, I would suggest using term “less hydrophilic”.

P26172. The whole story of this paper is conceptually built around dissolved organic carbon which is particularly evident in this chapter. The whole theoretical framework used in this paper can not accommodate particulate nor colloidal organic matter of largely insoluble material. In their Part 1 paper authors demonstrated that the main particle size which was largely enhanced by primary production using various proxies was around 40nm. This is very different not only from O’Dowd/Facchini observations as stated in this and Part 1 paper, but also those of Ellison et al. (1999, JGR) who also proposed a theoretical model for the observed insoluble/hydrophobic material. The observed particle size in Ellison paper was around 200nm, quite similar to the accumulation mode size in O’Dowd/Facchini/Keene papers. I argue that the main reason for such discrepancy are not various temperature, wind speed effects or secondary processes invoked by authors in Part 1 paper, but particulate and colloidal material which was filtered out by ultra-filtration. According to authors approach organic material is forming a film with an area of 119.54cm2 and mass of 24ug. Assuming OM density of 1.4g/cm3 that converts to a film thickness 1.5nm. According to the thermodynamic model of Oppo et al. (1999, Marine Chemistry) only particles as small as 1.5nm would be 100% organic assuming such film thickness. It seems that Oppo model suits this paper perfectly with very thin films producing particles in the size range of 40-100nm with little organics. It must be colloidal and particulate organic material which would be capable of producing larger particles highly enriched in OM which remains to be proven.

P26173, line 8. Could it be that the lower end values obtained here are again due to the filtering effect?

P26175, line 23. The statement "...are in the order of molar mass and hydroscopic growth of biopolymers present in the marine exudate" needs evidence. Where was it measured?

P26177. Is the low sensitivity to OM density and GF due to low OM content in the studied particle sizes or series of assumptions used? Low sensitivity needs better discussion of why and how that can be true.

P26177. I am quite puzzled about the dominance of the linear Raoult term over the non-linear Kelvin term. To me this is only possible in relatively small particles produced by specific DOC. For larger particles Kelvin term should dominate as demonstrated by Dusek et al. (2006, Science).

P26180, lines 1-3. I would argue that while being questionable it is not unlikely that primary marine OM are responsible for the increased cloudiness. Methodological constraint of this study using ultra-filtration does not allow such a general conclusion and, therefore, should be rewritten in a more balanced way.

P26181, lines 22-30. Was the effect small just because of little organics present in the particles?

Summary and Conclusions

I would suggest not using term "colloids" and "colloidal" in this paper as authors do not have direct evidence of that. Quite contrary, colloidal material could have been largely filtered out which remains valid until overturned by evidence.

I am confused by the circular argument of this study: the observed growth factor and activation effects are due to small amount of organic matter, which was indirectly estimated from growth factor measurements. How else can it be?

Minor comments:

P26159, line 18 (also next page line 4). The term "atmospheric seaspray" is new and possibly requires small introduction.

P26166, line 19-20. Species names should be properly spelled and in italic.

P26170, line 7. O'Dowd 2008 paper deals with primary not secondary organics. Wrong style or please explain.

P26171, line 16. "higher effect" should be replace with "stronger effect".

P26173, line 5. should be "regression coefficients above 0.87". Also please state significance level, e.g. "P<0.01" or similar. Coefficients themselves mean nothing until statistical significance is stated which depends on the number of points/observations constraining regressions.

P26174, line 12. Keene et al. 2007 measured soluble OC, not WIOC which dominated in Facchini 2008 study. Please explain if not a miss-print?

P26175, line 18. "represents and undissolved" should be "an" instead of "and".

Same page, line 21. "on study" should possibly be "studied".

P26177, line 23. "...due to dominance of the Raoult..."

P26178, line 1. I believe "organic fraction" should be "mass" otherwise doesn't make sense.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 26157, 2010.