

## ***Interactive comment on “On the chemical dynamics of extracellular polysaccharides in the high Arctic surface microlayer” by Q. Gao et al.***

**Anonymous Referee #2**

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The paper is a valuable and detailed study about chemical composition and dynamic changes of organic matter in the surface water layers of the ocean. Organic matter in both water and aerosol phases once characterised in detail has many significant climatic implications. This is yet another valuable extension in terms of characterisation of organic matter sources and composition of the established biogenic organic matter source region which is the Arctic Ocean. Similar studies are badly lacking in other productive regions, especially high latitude North Pacific and Southern Ocean in general. The manuscript is clearly suitable for publication, but I would like authors to better consider some of the important caveats when interpreting and extrapolating their results.

A surface micro layer is a well established concept and it clearly exist under certain

C66

conditions, however, the implications are often overstated. Surface micro layer is a thin interface between bulk water and the atmosphere which is neither stable nor persistent. Even at a moderate wind speed of 8–10 m/s the wave height and the entrained air cavities create enough turbulence and mixing to disrupt such a layer. However, it is the moderate and high wind speed at which sea spray source function really kicks in due to power law dependence on the wind speed. While at low wind speed organic matter enrichment in sea spray can be significantly higher than at high wind speed (Gantt et al. 2011), the aerosol production and absolute amount of released organic matter follows the opposite pattern. Clearly, surface micro layer plays very significant role at the onset of whitecap (circa 4–5 m/s), but becomes insignificant at higher wind speeds which is typical of Southern Ocean (Roaring Forties and Fifties), North Pacific or North Atlantic. I argue that in terms of significant organic matter production and significant CCN effects organic matter enrichment at the air-sea water interface of rising bubbles plays the most important role. While authors are right stating that rising bubbles concentrate surface active compounds into surface micro layer that is largely true in laboratory conditions (especially when using frits as in this study), but same micro layer does not form in stormy seas. However, the transport of organic material towards the surface by rising bubbles is enough to cause significant enrichment when bubbles burst. That was the concept used by Long et al. (2011) to obtain a new conceptual sea spray source function based on air entrainment. I argue that surface microlayer can be very useful natural laboratory studying chemical dynamics, but has limited value when extrapolating to natural sea spray production. However, if similar extracellular polysaccharide enrichment is confirmed in aerosol phase over other oceanic regions, it would constitute a significant breakthrough.

I think this study goes a bit too far when moderate organic matter enrichment found in the Open Lead is extrapolated to considering significant regional effects. The authors would agree that sea spray production at low wind speed observed during most of their study (and especially during conditions of ice (re)formation) would be limited. A big question is whether the enrichment and dynamical changes observed in this study

C67

apply to the open ocean. In the end Open Leads do not exactly represent open ocean (except icy fringes of the Arctic) mainly due to low wind speeds which both facilitate enrichment through the effective formation of surface micro layer and limit primary sea spray production.

Authors should be aware that the use of frits is not recommended as they create static conditions as opposed to using water jets and, therefore, not applicable to the real world where wave breaking creates a lot of motion and turbulence. Moreover, bubble and aerosol particle spectrum has been found to represent real world better when using jets rather than frits as extensively documented by e.g. Sellegri et al. (2006 JGR), Fuentes et al. (2010 Aerosol Measurement Techniques) or Kim Prather (personal communication). In conclusion, while the experimental design used in the study is valid in elucidating dynamics of chemical compounds, extrapolation of the results to the real world should be cautious and discussed accordingly.

Considering the effects of organics produced by bursting bubbles the recent study by Ovadnevaite et al. (2011 GRL) fits the picture very well in terms of CCN activation and potential reasons behind it. I see the above paper as a perfect companion to Orellana et al. (2011) paper. Marine microgels found by Orellana et al. (2011) are the ones postulated in Ovadnevaite et al. (2011 GRL) to explain peculiar marine CCN activation. It could well be that the above considerations are mostly valid over eutrophic regions (higher latitude North Atlantic, Arctic, North Pacific, Southern Oceans), but that is enough to emphasize its significance due to high productivity (biological and physical (high winds)) of the above regions.

Authors should give a better discussion of what they consider as DOC and POC with respect to literature consensus which is based on operational definition of solubility in water. As authors used TFA to dissolve carbohydrates this could have many implications when compared to water soluble organic carbon. For example, study of Facchini et al. (2008) documented both water and TFA extracted organic carbon chemical composition.

C68

Table 2. POC should be presented in  $\mu\text{M C}$  to have a better view of how much TOC has been resolved which can be included in the Table as percentage. I estimate this was about 20%?

Table 3 should be reorganised. A mirror image of correlations above the diagonal should be removed. Non-significant correlation should also be removed as they are meaningless. Only correlations which are significant (those with asterisk) should be presented.

Minor corrections:

Page 218, line 10. I believe it should be “free organic molecules” not “organic free molecules”.

Page 221, line 10. It is misleading to state that aerosol particles were collected by the glass plate just 10cm above the liquid. At this height those are still film and jet drops, not particles yet.

Page 221, line 27. It should be “derivatization”.

Page 223, line 19. Reference should be given to support multiplication factors.

Page 227, line 7. Should be “significantly correlated”

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C69

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Sellegri K.; O'Dowd C. D.; Yoon Y. J., Jennings S. G., de Leeuw G. (2006) Surfactants and submicron sea spray generation. *J. Geophys. Res.*, 111(D22), doi: 10.1029/2005JD006658.

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