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Ocean Science
Discussions

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

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We thank the reviewer for the constructive and thoughtful comments on our manuscript. We provide responses to the comments and concerns shown as below:

General comments: 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 characterization 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 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 microlayer 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 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.

Reply: We fully agree with the reviewer that a surface microlayer (SML) is not always stable and persistent and it depends greatly on the wind condition. Although temporary disruption of SML by breaking waves can occur, the SML can be rapidly reformed (i.e., within seconds) through rising air bubble plumes (Liss, 1975; Williams et al., 1986) based on both laboratory and field studies. Several studies from the open ocean have shown that surface active organics can even be consistently enriched in the SML at wind speeds up to 10 m s-1 (Wurl et al., 2011; Carlson et al., 1983; Reinthaler et al., 2008). The extent of accumulation/disruption of organics at SML also depends on the chemical composition of seawater. For example, Wurl et al. (2001) suggested that SML could be reformed more easily after disruption by wave motion when higher fraction of surfactants is present in seawater. Within the ice-covered central Arctic, wind speeds are typically low (< 6 m s-1 on average) which would have suppressed turbulence, preventing microlayer mixing and dilution with subsurface water. Similar as suggested by the reviewer, Leck et al. (2002) found that, over the Arctic open leads, both the film and jet drops have a strong exponential, wind-speed dependence. For low winds (< 5 m s-1), however, they observed an enhanced presence of film drops which contained a substantial fraction of micropolymer gels (Bigg and Leck, 2008). We agree with the reviewer that it is not conclusive whether the enrichment and dynamics of organics observed in the Arctic open lead can apply to the lower latitude oceans, where higher wind speeds are more prevalent. A short discussion on the dependency of SML properties on wind condition was already given in the manuscript (Section 3,

page 225, lines 21-29 and page 226, line 1-4). We discuss this issue further at the end of Section 5 in the revised version and clarify that the enrichment and dynamic pattern of polysaccharides (accumnation/disruption) observed at the Arctic open leads might differ from those in the open ocean at low latitude where breaking waves prevail. We also modified one sentence at the end of the abstract and stress that the proposed mechanism for the enrichment of polysaccharides applies in the high Arctic region. A similar modification was made to the last sentence of Section 6 (Conclusion).

Comment: 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.

Reply: Our bubble experiment was designed to investigate the chemical dynamics of polysaccharides in seawater in the presence of rising bubbles as well as to understand the sea-to-air transport of organic materials in the case of bubble bursting. Such bubbling experiments have been performed in previous studies with similar bubble spectra and rate using glass frits (i.e., Hoffman and Duce, 1976; Keene et al., 2007; Tseng et al., 1992; Zhou et al., 1998). We agree with the reviewer that the properties of bubble produced by bubbling experiments may differ from those using water jets or occuring in real conditions at the open lead, and the enhancement of organics at SML as well as the flux of sea-to-air of organic production might not be representative of in situ conditions. Although there is much debate on the appropriateness of different styles of bubbling apparatus (review of sea spray function by de Leeuw et al. 2010), we added details in Methods (Section 2.3) and the Section of Results and discussion.

Comment: 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.

Reply: We address these issues in the course of the rewritten introduction as: “Fresh aggregates of microcolloids could act as CCN directly because of the gel’s strong surface-active properties. Despite being predominately hydrophobic in nature (with growth factors slightly above 1), the marine gels have effectively a higher CCN activation efficiency than more soluble, but inorganic aerosol (Ovadnevaite et al., 2011). When surface tension counteracts water activity, the net effect is an enhancement of particle CCN activity. This is in agreement with a model study by Lohmann and Leck (2005) that found it necessary to invoke a highly surface-active, Aitken mode of aerosols, assumed to be polymer gels, externally mixed with a sulfur-containing aerosol population in order to explain the observed CCN over the pack ice.”

Comment: 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.

Reply: The fractions of DOC and POC were obtained by filtration based on their different size, rather than by solubility. This is now clarified at the end of Section 2.5. We further point out the DOM pool actually comprises both colloidal matter and truly dissolved organic matter. We used TFA in this work as a reagent for acidic hydrolysis to release monomers from “newly” produced extracellular organic material. It was already mentioned in Section 2.6 (Page 223, lines 7-9).

Comment: Table 2. POC should be presented in uM 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%?

Reply: Done as suggested. The percentage of POC in TOC is, on average, 9 %, which is now indicated in the table as well.

Comment: 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.

Reply: We removed Table 3 entirely from the modified manuscript and describe the correlation in the text instead since only 4 data points had significant correlation (those with asterisk in previous version of manuscript)

Minor corrections:

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

Reply: Done.

Comment: 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.

Reply: we replaced “particle” with “water droplets”

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

Reply: Done

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

Reply: Skoog et al. (2008) was added now as a reference.

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

Reply: Done.

References:

Bigg, E. K. and Leck, C.: The composition of fragments of bubble bursting at the ocean surface, J. Geophys. Res, 113, D11209, doi:10.1029/2007JD009078, 2008. Carlson, D.J. 1983. Dissolved organic materials in surface microlayers: Temporal and spatial variability and relation to sea state. Limnology and Oceanography 28, 415-431. Hühnerfuss, H., Walter, W., Kruspe, G., 1977. On the variability of surface tension with mean wind speed. Journal of Physical Oceanography (7), 567–571. Lang, C., 2002. Mass transfer in bubbly flows: influence of physicochemical and hydrodynamic conditions. In: Donelan, M., Drennan, W., Saltzman, E., Wanninkhof, R. (Eds.), Gas transfer at water surfaces. Geophysical Monograph. American Geophysical Union, Washington, D.C., pp. 363–370. Leck, C., Norman, M., Bigg, E. K., and Hillamo, R.: Chemical composition and sources of the high Arctic aerosol relevant for fog and cloud formation, J. Geophys. Res., 107, D12, doi:10.1029/2001JD001463, 2002. Liss, P.S., 1975. Chemistry of the sea surface microlayer. In: Riley, J.P., Skirrow, G. (Eds.), Chemical Oceanography, Vol. 2. Academic Press, London, U.K., pp. 193–244. Reinthaler, T., Sintes, E., Herndl, G., 2008. Dissolved organic matter and bacterial production and respiration in the seasurface microlayer of the open Atlantic and the western Mediterranean Sea. Limnology and Oceanography 53, 122–131. Williams, P.M., Carlucci, A.F., Henrichs, S.M., Van Fleet, E.S., Horrigan, S.G., Reid, F.M.H., Robertson, K.J.1986. Chemical and microbiological studies of sea-surface films in the Southern Gulf of California and off the West Coast of Baja California. Marine Chemistry 19, 17–98. Wurl, O., Wurl, E., Miller, L., Johnson, K., Vagle, S., 2011. Formation and global distribution of sea surface microlayers. Biogeosciences 8, 121–135.

Interactive comment on Ocean Sci. Discuss., 9, 215, 2012.