

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 comments on our manuscript. All of the comments and concerns will be addressed accordingly in the revised manuscript. We provide point-by-point replies to the comments as following:

General comment: This paper describes experiments on the organic composition of seawater and SSML samples collected from Arctic open ice leads, in connection with the organic composition of the aerosol generated by artificially bubbling air through the collected seawater samples. Results show that the SSML was systematically more enriched in organics than the bulk seawater, with polysaccharides accounting for a significant fraction of the organic composition of the collected samples. Significant findings in this study are that the aerosol generated was more enriched in organic matter than

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the source seawater (eg. factor between 22-70 for polysaccharides) and that large colloidal aggregates were formed by aggregation of low molecular weight gels during the bubbling process. My major concern about this work is that the bubbling experiments, as described, do not seem to be representative of the bubbling rate expected to occur in ice leads, which could affect the results and conclusions of this study. While the authors provide only vague information on how their bubbling experiments would match bubble production in ice leads, their description on the experimental operation of this system leads to think that a bubbling rate inducing a significant formation of foam (221, lines 3-9; 236 lines 8-10) was applied. The formation of a foam layer in these experiments implies that bubble production was much higher than the gentle bubble generation expected in open ice leads. If bubbles are responsible for the transport of organic matter from the bulk to the surface, these laboratory experiments would have led to an enhanced transport of organic matter to the SSML with respect to the real process in open ice leads; thus leading to an overestimation of the organic enrichment of the organic aerosol with respect to real bubble/aerosol production and to an enhanced aggregation of organic colloids. Although I consider that these experiments are useful to understand the underlying processes, their quantitative estimations may not be valid for extrapolation to real conditions; hence, unless the authors can prove otherwise, they should clearly state and discuss the caveats implicit in their experimental approach. Besides this aspect, I consider that this study and its results are interesting and of value for further discussion on the role of biogenic organics on cloud formation and climate regulation in Arctic regions. Hence, I recommend its publication in ACP after the above issues and specific comments indicated below have been addressed.

Reply: We fully agree with the reviewer that the properties of the bubble produced by our bubbling experiments might differ from those occurring in real conditions at the open lead, with regards to the spectra of bubble size, concentration, lifetime and so on. However, it was not our intent to reproduce the natural system; rather, our bubble experiment was designed to investigate the chemical dynamics and transformation of polysaccharides in seawater in the presence of rising bubbles as well as to understand

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the sea-to-air transport of organic material in the case of bubble bursting. As a result, the magnitude of the organic matter transport to the surface microlayer as well as the flux of sea-to-air of organics is enhanced. This is now indicated in at the end of Section 5.2 in the revised version. We pointed out in the manuscript (Page 239, lines 17-26) that the bubbles generated mechanically in the glass column have both higher rising velocity and larger bubble sizes compared to the in situ naturally occurring bubbles, as described in Norris et al. (2011). Water temperature was warmer and path length was constant, which may also be different from the real conditions at open leads; this was also indicated in the original manuscript (Page 239, line 22) and now also in the Section of Methods. Even with these dissimilarities, the dynamic behavior of bubble coagulation of surface active materials and the underlying processes are the same, i.e., enrichment of polysaccharides in surface water as well as in the nascent aerosols. The influence of bubble production on sea-to-air flux has been demonstrated by previous studies (e.g. Hoffman and Duce, 1976; Keene et al., 2007; Tseng et al., 1992) based on similar laboratory experiments with temperate or tropical waters. Their studies showed that sea-to-air flux is proportional to the rate at which the organics are transferred to the surface by rising bubbles. The flux of sea-to-air of organics also increases with the increasing path length of rising bubbles and with decreasing bubble size. We point out in Section 5 that the visible foam layer and rising bubbles in the experiment were never noticeable or noticed in the dynamic open leads during field work.

Specific comments: Comment: Abstract. The standard classification of organic fractions used by the authors (i.e. POC and DOM) could be misleading, since these organic fractions are separated as a function of size and not solubility (see discussion in Fuentes et al. (2011)). For example, the DOM fraction, although defined as "Dissolved" Organic Matter comprises a fraction of insoluble colloidal organic matter. Although the authors include a description of the size ranges for the different organic fractions in the methods section, it would be helpful that they specify the size range for these organic pools in the abstract as well. I also recommend the authors to clarify in the abstract that the aerosol was artificially produced by performing bubbling experiments and not

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sampled over ice leads.

Reply: Size range is now specified in the abstract (particulate organic matter, $>0.22 \mu\text{m}$, and dissolved organic matter, $<0.22 \mu\text{m}$, obtained after filtration). It is also indicated in Section 2.5 (Ultrafiltration) that the separation of particulate and dissolved phase was accomplished by filtration rather than obtained by solubility. We also indicate in the abstract that the aerosol particles were generated artificially by bubbling experiments.

Comment: Page 217, Lines 11-15: This statement seems a bit speculative. Orellana et al. (2011) identified a significant amount of biogenic gel material in aerosol, fog and cloud water samples collected in the Arctic pristine region. This is certainly important for consideration on the effect of this organic matter on particles CCN behavior in Arctic regions; however, it does not demonstrate that the aerosol particles are purely composed of biogenic gels, i.e., that these particles are externally mixed and that these gels can effectively act as CCN. Furthermore, a recent study by Martin et al. (2011) on the CCN behavior of particles sampled over ice leads shows that marine biogenic organics, rather than promoting the formation of CCN, suppress the CCN activity of aerosols, in agreement with previous findings by Leck et al. (2002) and laboratory simulation by Fuentes et al. (2011). I believe the authors should not neglect these findings. I recommend the authors to revise this text and briefly mention findings from the studies cited above.

Reply: The results of Martin et al. (2011) suggested by the reviewer are quite interesting and connected to our background introduction. The reference is now cited.

Comment: Page 220, Lines 25-27. The authors should explain which techniques they employed to ensure that their bubble experiments were representative of the very gentle bubble production occurring in ice leads. It is mentioned that bubbles of 300 microns were produced for the experiments; however no information is given regarding the bubble concentration, which must be also relevant for the bubble scavenging process. It

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would be helpful if the authors provided a comparison between the bubble spectrum from their experiments and measurements by Norris et al. (2011). If the bubble production in their simulation experiments is higher than in real ice leads, then the rate of transport of organic material from the bulk to the water surface and the particle aggregation process may be overestimated with respect to real production. As indicated above, the authors should discuss this issue and reveal any relevant caveats in their experimental work.

Reply: The chosen pore size of the glass frit at the controlled air flow enabled the generation of air bubbles of around 300 μm diameter. Previous studies, such as Keene et al. (2007), Tseng et al. (1992) and Hoffman and Duce (1976), employed a similar bubbling experimental design (bubble spectra and rate) for the study of sea-to-air flux of aerosol particles and their dependency on bubble production; these studies provided the inspiration for ours, now conducted in a polar environment with very different environmental conditions. As indicated above, our experiment was not intended to match in situ condition at the open lead. This is now included in Section 2.3. We also added a comment on the relationship between the experimental bubble size and the in situ bubble spectra measured by Norris et al. (2011). The experimental bubbles were within the size range observed (30–560 μm) but were larger than the dominant bubble population (30–100 μm diameter); according to Norris et al., number concentrations of 200–560 μm are roughly comparable with open ocean measurements done elsewhere under winds of about 5 ms^{-1} . Unfortunately, neither Norris et al (2011) or ourselves measured effective bubble rising speeds; their system quantified the bubble number population in 1 m^3 during multiple 2 min sampling periods, then extrapolated to a daily average that, over the field work period, approximates <1 bubble/ml/min. Our experimental air flow rate was 150 ml/min through a 20 μm pore size frit; these rates have different units and are thus not comparable

Comment: 221-222, 1-2: “We simulated the accumulation of SML materials by rising bubbles.” This statement seems a bit premature, before the results on the concentration

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of organic groups are explicitly discussed.

Reply: Sentence is removed and replaced by “aiming to investigate the chemical dynamics of polysaccharides in seawater in the presence of rising bubbles”.

References

Hoffman, E.J. and Duce, R.A.: Factors influencing the organic carbon content of marine aerosols: a laboratory study, *J. Geophys. Res.*, 81, 3667–3670, 1976. Keene, W.C. et al.: Chemical and physical characteristics of nascent aerosols produced by bursting bubbles at a model air-sea interface, *J. Geophys. Res.*, 112, D21202, doi: 10.1029/2007JD008464, 2007. Tseng, R.-S., Viechnicki, J.T., Skop, R. A., and Brown, J. W.: Sea-to-air transfer of surface-active organic compounds by bursting bubbles, *J. Geophys. Res.*, 97, 5201–5206, 1992.

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