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Discussions

Interactive comment on "Size resolved airborne particulate polysaccharides in summer high Arctic" *by* C. Leck et al.

C. Leck et al.

lina@misu.su.se

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Anonymous Referee #1

The paper presents the important information of previously unquantified particulate polysaccaharides in marine environment with size resolved information being an important asset. The paper comes from a productive group specializing in Arctic environment and producing series of papers on different aspects of particulate organic matter in the Arctic. In this paper, however, the authors include too much of the secondary information which often does not help to clarify the processes, but instead defocuses and confuses the whole story. Overall, the paper is very detailed and would be suitable for publication in ACP after removing the most speculative statements, restructuring the

paper and addressing other important issues. The English of the manuscript needs a particular attention as at the moment the paper contains too many bad style sentences. There are many instances suggesting that large sections were written by an inexperienced researcher and was not carefully read by the lead author before submission. REPLY: We thank rev. 1 for a constructive evaluation of our manuscript. To meet the criticism of both reviewers the general structure and use of English and punctuation have been improved. A final language check from the ACP editorial office is very much appreciated. Also a clarification to why the measured monosaccharides are assumed to be in there combined form as polysaccharides is given. The remaining of the above general comments will be covered by our replies to the specific and technical comments made below.

The major comments are the following:

1. Abstract should be restructured as at the moment it is loosely connected with size resolved information interspersed by the bulk chemical composition. I am not convinced that the relative abundance of submicrometer polysaccharides is closely related to length of time that the air mass spent over ice (see comments below). It is not a speculation that any significant chemical species could potentially alter CCN activation, but that is a more general claim. REPLY: We are sorry that the reviewer is not convinced of the obvious co-variation of the relative abundance and length of time the air mass spends over ice (DOI) but this is what our results show.

2. The introduction of the paper looks rather comprehensive, but I wonder if the authors missed the paper of Ovadevaite et al. (2011) who presented highly relevant phenomenon of dual behaviour of sea spray OM in sub and supersaturated conditions. In my view, evidence of Orellana et al. (2011) about the existence of exopolymer gels in cloud droplets is very consistent with the ground measurements of Ovadnevaite et al. in the North Atlantic. While not directly relevant in the context of the paper it would add contextual clarity to the implicated effects of marine organics to the cloud processes. REPLY: Added, see insert of new text in section 1.

3. I am very surprised at the reasoning of the turbulent flow in the inlet. The laminar flow conditions not only ensure lossless (or as close as possible) sampling, but also favour isokinetic split sampling of different instruments. Lossless sampling is crucial while turbulent flow enhances losses. The authors claim that turbulent flow helps mixing of air in the inlet, but there is nothing to mix when surface friction and turbulent eddies have already done that job. There is no gain with turbulent flow – only the loss. REPLY: Sorry for our mistake. Rephrased, see insert of new text in section 2.2.

4. The entire section 4 is assembled out of context, it's like putting cart in front of the horse. A lot of the information presented in this section is indeed important, but would only become relevant during the discussion. At the moment the reader is forced to believe upfront that all the presented information will have to be somehow related to the author's cause – which is against a scientific method proving everything point by point. Moreover, while the authors present all possible conditions potentially influencing the characteristics of aerosol samples, only selected conditions reiterated further in the discussion. Hence, major restructuring is required distributing portions of section 4 where appropriate. REPLY: The section is restructured and shortened.

5. The phenomenon of Days Over Ice (DOI) is inflated out of proportion. It is natural to expect that the supermicron particles will be present in decreasing numbers further from the primary source (open water) due to dry and wet deposition, thereby enhancing relative contribution of submicron ones which are typically removed only by wet deposition or in-cloud scavenging. Figure 2 can be easily replaced by a single sentence, stating the average time the air mass spent over the ice. The section 6.2 is quite misleading as well. Aren't the results broadly demonstrating the effect of deposition, especially considering accuracy and analytical uncertainties which make some of the claims hardly statistically significant? To me the Figure 9 suggests just that. REPLY: Figure 2 is removed. Section 6.1 gives the following suggested explanation for the clear decrease in concentration observed of the sum of the 7-monosaccharides determined, with increasing length of time spent over the pack ice since last contact

with open sea: "This is consistent with previous result from samples collected over the central Arctic Ocean by Heintzenberg et al. (2006) and during ASCOS (Heintzenberg and Leck, 2012) based on modal statistics of aerosol concentration by number." Leck and Persson (1996) also report on accumulation – and coarse mode particles with increasing length of time spent over the pack ice, in general being a factor of 10 lower in mass concentration over the inner parts of the pack ice relative to the ice edge and the waters south thereof. We agree, one possible cause of the most effected mass fraction is the efficient wet deposition through drizzle commonly caused by fogs, thought to be dominating in the marginal ice zone, as relatively warm moist air is advected in over the pack ice, while being saturated by cooling from the surface as suggested by (Heintzenberg et al., 2006; 2012; Nilsson and Leck, 2002). Also stated in section 6.1 the stronger aerosol flux reported over the open sea compared with those from the open leads (Nilsson et al., 2001; Held et al., 2011a) could serve as an explanation of our measurements. However, there is no general conclusion that the modal mass ratio between accumulation – and coarse modal should increase, that is that the coarse particles will be present in decreasing numbers with time since last contact with the marginal ice zone (cf. Table 2). Figure 9 (discussed in section 6.2) does show the relative contribution of Aitken+ Accumulation (stage 1 and 2) mode to Total mass (stahe 1-5). The result of Fig. 9 shows an obvious co-variation in the modal apportion of submicron (Aitken and accumulation mode) to total mass (%), of THNS, deoxysugars and the sum of pentose and hexose as a function of travel time over ice. The method of calculating the DOI times is based on Nilsson (1996), who states that large marine sources of atmospheric constituents could well resolve five days or more backward in time. In the text we refer to Nilsson (1996) for the questions concerning the uncertainties. We would like to maintain use the concept if DOI, which we feel to be essential for the interpretation of our results: a method proven very useful in more that handful publications concerned with the high Arctic over the last two decades.

6. The authors present highly speculative idea of primary particles produced through the ice pores. There is no physical quantitative evidence presented in the paper or

elsewhere in support of the above process leading to significant primary production. The differences in the polysaccharide content can equally be well explained by the air masses of different region/location, laden with varying amounts of primary polysaccharides. Different regions/locations of open water not only can experience different wind speeds, but more importantly different biological activity (trophic levels). REPLY: We are sorry about the misunderstanding of ice pores emitting EPS directly into the air. Nowhere in this MS we are speculating about such a process. If the reviewer feels that the differences in polysaccharides can “equally well” be explained by air masses of different region/location (within the pack ice) we would like to see this equally substantiated by the reviewer.

7. Another highly speculative idea not supported quantitatively is the production of particles by the breakup of fog droplets. While the idea was presented back in 1999, no quantitative support was provided to strengthen the idea since then. Can the authors present a physical/mechanistic explanation of the process, never mind the chemical one? Possibly some production may occur via the proposed pathway (especially considering nanosized particles - 5nm as in the referenced paper), but authors should at least consider conservation of mass in the context of this paper. Making more particles out of the bigger fog or cloud droplets does not yield mass, only number. The only gain in mass, which is needed to match primary fluxes with the measurements of polysaccharides, can come from oxidation or secondary production. The oxidation process can only contribute limited mass (doubling the primary OM at best), while invoking secondary production process invalidates the authors claim of primary origin of particulate polysaccharides. Actually, secondary production sounds very plausible considering VOCs emanating through the ice pores if production over ice is indeed proven in a more robust fashion. REPLY: We will not carry out a more detailed discussion on the above matter in the MS as we regard this to be irrelevant to the observations. However, we can recommend the reviewer to read the very recent paper by Karl et al, which will clarify the raised questions above. Karl, M., Leck, C., Coz, E., and Heintzenberg, J.; Marine nanogels as a source of atmospheric nanoparticles in the high Arctic. Geophys.

Res. Lett., 40, 3738-3743, doi:10.1002/grl.50661, 2013.

8. The use of the term “mass” is very loose throughout the text. The authors should make it crystal clear what was the percentage of polysaccharides contributing to the total sea spray mass if primary or total particulate mass if secondary processes are involved. That can be done by calculating enrichment factor (EF=THNS/(THNS+SS)) or just referring to the total mass. At the moment the reader is confused about the significance of THNS contribution as there are numerous references to “the full mass median size distribution” or “total mass of polysaccharides determined”. The author perhaps could instead use the word “combined mass of polysaccharides” since “total” has the meaning of ALL mass including all chemical species. REPLY: We are sorry about the caused misunderstanding of the meaning of THNS. The concept of THNS has now been clarified in length in section 1. Given the low aerosol masses available over the pristine pack ice area it is presently not possible from a technical point of view to determine total sea spray mass divided into primary or total particulate mass if secondary processes are involved.

9. The authors implicate wind speed explaining the differences in polysaccharide content between submicron and supermicron particles. However, all the existing sea spray source functions (Monahan, Gong, Martensson, Fuentes) include wind speed only as an overarching parameter. Even if there was some evidence that wind speed affects production of different size particles in a slightly different way it is far premature trying to corroborate the observed changes in chemical composition when existing primary organic matter source functions consider sea spray OM in bulk (typically submicron mode only). As it stands in the paper, it is another speculative idea. REPLY: For more details on how wind speed affects production of different size particles over the Arctic pack ice area see Leck et al., 2002.

10. Comparison with bubble bursting experiment is valuable, but authors should consider not only similarity in chemical composition, but also the enrichment. REPLY: Clarified, see insert of new text in section 1. It is difficult assessing quantitatively how

much of the produced aerosol was actually collected. However, the artificial production of bubbles amplified the natural bubble bursting process dramatically. Therefore, even with collection times of 30 min, an aerosol sample sufficiently large for subsequent analysis was collected. The corresponding sampling time for the atmospheric samples had to be 40 to 80 times longer to achieve detection.

11. Conclusions are not concise. Some of the quantitative information is missing, namely percentage contribution of THNS to total sea spray mass, while speculative comments should remain in the discussion only, not conclusions. REPLY: See above, the manuscript is not concerned with determining the total sea spray mass. This is unfortunately not possible over the pristine summer pack ice due to the extremely low aerosol masses.

Minor comments:

1. How RH was of the impactor flow was controlled at 50%? REPLY: Clarified, see insert of new text in section 1.

2. What was it meant for “1um nylon filters” used for sampling artificially produced sea spray? Was it filter pore size? Was there any size cut applied or there were total suspended particulates sampled? If TSP, what would be the implication for the comparison with impactor samples? REPLY: Clarified, see insert of new text in section 1.

3. Impactor concentrations refer to standard temperature and pressure. What was the range of actual temperatures and pressures? REPLY: For details of the temperature and pressure encountered during the length of the expedition we refer to Tjernström et al., 2013. A brief description of the temporal changes in temperature is given in section 4.1. Corresponding numbers of pressure for the samples are max: 1010.1 hPa: min 10001.2 hPa: average 1005.7 hPa.

4. Why the accuracy of LC/MS/MS was so poor as presented in Table 1 (close to and

above 100%? REPLY: The accuracy was not poor at all. The unit of the given numbers is now more user friendly expressed, see an updated Table 1. Sorry for being unclear.

5. Section 4.2 is unclear. The use of the term “recoupling” is confusing. If back trajectories suggested that air in the upper boundary layer had come from different region than in the lowest 100m that would suggest de-coupling, wouldn’t it? REPLY: Clarified, see insert of new text in section 1. For details we refer to Shupe et al., 2013.

6. P9821, line 2. “jet drop sized aerosol particles” must be rephrased. Same applies to “similarly active film drop mode” on P9823, line 17. REPLY: Clarified, see insert of new text in section 1.

7. I disagree with the statement that film drops would produce chemically different particles than fresh jet drops. Please rephrase or explain clearly. P9823, line 14. REPLY: Consider the well-known substantial differences between the BW and SML chemical differences between the chemical characteristics of film and jet drops would be expected to be quit different (please see Liss, P. S. and Duce, R. A.: The Sea surface and global change, Cambridge University Press, 1997; Bigg and Leck, 2008; Leck et al., 2002; Gershey R.M., Characterization of seawater organic matter carried by bubble-generated aerosols. 1983. Limnol. Oceanog., 28, 309-319).

8. Figure 6. Y axis is THNS concentration, where “2/3 of the mass within Aitken mode” come from. Possibly confusion over the “mass” term as previously noted. REPLY: Most sorry for the mistake, it should read Figure 5. Corrected in text.

9. How hexose implicated anthropogenic pollution affects the overall results? REPLY: Cellulose is the macro-polymer of glucose, which at temperature above 300°C, when cellulose is polymerized, will form glucose. Glucose is therefore used as a tracer among others for influences of combustion sources. Also the shift in peak concentration of Glycose+Mannose towards smaller sizes in the sample collected during DOY 242, a period likely influenced by continental combustion sources, is consistent with the larger fraction of glucose + mannose determined. Added to text in section 6.1.

10. Figure 3. The ice drift period is not denoted by DOY. REPLY: Clarified, see insert in Figure legend.

11. Figure 5. The caption needs clarity with presented 6 graphs. Use “top”, “middle”, “bottom” graphs or name a,b,c,d,e,f,g. REPLY: Clarified, see legend in Figure 5.

12. Figure 8. What is the reason of presenting and comparing different size fractions: Aitken, Acc+Aitken and TSP. How the reader should interpret them? REPLY: Now clarified in legend text.

Few examples of bad English: P9812, lines 20-21. REPLY: Done.

P9813, lines 3-4. REPLY: Done.

P9815, lines 18-21. REPLY: Done.

P9820, lines 9-11. REPLY: Done.

P9823, lines 14-16 REPLY: Done.

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