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

C. Leck et al.

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Anonymous Referee #2

General Comments:

This paper is an interesting study of the monosaccharide composition of Arctic aerosol particles. The authors compare measurements of ambient particles and particles generated in open leads to confirm the source of monosaccharides in the Arctic. It will be a good contribution to the understanding of the composition and sources of organic Arctic aerosol particles. The focus of this study, based on the title and abstract, appears to be on polysaccharides in Arctic aerosol. The actual measurements that were made were of monosaccharides. More explanation needs to be given as to why the measured

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monosaccharides are assumed to be in their combined form as polysaccharides. This is not clearly stated and is necessary, based on the title. This is especially important because the dissolved organic mass in the ocean could include monosaccharides, as well as polysaccharides. The paper goes back and forth between discussing monosaccharides and polysaccharides, which is not ideal. While this paper has some very interesting points, it would benefit from some restructuring to better highlight those points. It would be helpful if the authors included some context on why these findings are important. The conclusions need to emphasize the main points and why they are relevant and interesting. Additionally, this paper provides a lot of background information, which distracts from the main point of the paper. A lot of the discussion of meteorological conditions (temperatures, backtrajectories, etc.) could be shortened or moved to the Supplementary Material, especially the parts that have been previously published. There is a lot of information that is introduced in the beginning that is not tied back in during the concluding paragraphs (for example: Arctic low level clouds). Also, the authors should check the grammar and writing style, as well as check for typos. There are some instances where poor sentence structure makes it difficult to understand the main point. The comparison between the ambient particle and the generated particle composition is interesting. The bubbling experiment provides support for assigning the source of monosaccharides in the Arctic. This section should be expanded and should clearly state the results and implications. Also, the authors should discuss other potential sources of organic mass in the Arctic, such as frost flowers. REPLY: We thank rev. 2 for a positive and 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.

Specific Comments:

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Title: The word “airborne” could be better replaced with “atmospheric”. REPLY: Done throughout the text.

P. 9802, L. 23: Be clearer about how the particles were created in the leads. What does “experimentally” mean? By bubbling air in the leads? REPLY: The text in section 2.3 was revised to give a better explanation of the in situ generation of nascent aerosol by artificial bubble bursting.

P. 9802, L. 23-25: Where does the air come from that creates the bubbles in the leads? Also, can leads be considered “sea” in the air-sea interface? Did you look at different sizes of leads? REPLY: Clarified, see revised text in section 1, background: Norris et al. (2011) have presented the first measurements of bubble size spectra within the surface waters of open leads within sea ice in the central Arctic Ocean. Substantial numbers of bubbles were found with diameters between 30 and 400 μm . The concentrations are comparable with those observed in the open ocean under modest wind speeds (order of 10 ms^{-1}) $D < 100 \mu\text{m}$, but decrease more rapidly with increasing size than for open ocean spectra; no bubbles larger than 560 μm were observed. The total bubble number concentration showed two distinct dependencies on the local environmental conditions: concentrations were highest when the sampled ocean flow has a significant fraction of surface water open to the atmosphere. Concentrations were about an order of magnitude lower when the surface was completely frozen or when the flow was from under the large ice floe, thus isolated from open air for a period of order 10 h or more. With an open water surface, exposed to the atmosphere, the total number concentrations of bubbles also increased with increasing heat flux from the surface to the atmosphere. The observation of significant numbers of bubbles confirms the existence of a plausible mechanism to inject biogenic material from the water surface into the atmospheric surface layer, even in the absence of wind-driven wave breaking. However, still the actual process forming the bubbles is unknown. Open leads are ever changing open water/sea channels (extending 10-30% of the ice pack ice area), ranging from a few meters up to 2000 m in width. For the month of August we drifted

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with an ice flow, thus the experimental site of the lead represented an ever-changing water body of variable size during the course of the drift.

P. 9803, L. 6: Expand on what is meant by “most of the time”. Or change to “Arctic low-level clouds mainly warm the surface”. Does the warming depend on season? REPLY: Section removed.

P. 9804, L. 5-8: Include the size range of aerosol particles produced from these production mechanisms (film and jet drops) for reference. Line 10 mentions that the particles produced are “in CCN sizes”. Is that true for both the film and the jet drops? REPLY: Clarified, see insert of new text in section 1.

P. 9804, L. 10: Be more specific as what is meant by “debris”. REPLY: Revised see new text in section 1.

P. 9804, L. 13: It has been determined that submicron marine aerosol particles, which are produced by bubble bursting film drops, are not composed of only sea salt but also have organic fractions too. This sentence needs to be re-written to emphasize that it is an old, disproven assumption, a simplified assumption used in some models, or that sea salt is a fraction of marine aerosol in general. Blanchard and Woodcock (1957) suggested that marine aerosol particles produced from bubble bursting also contain surface-active OM. REPLY: Revised see new text in section 1.

P. 9804, L. 15: It would be helpful to add a reference for the wind speed needed for breaking waves, in addition to the typical size (length and width) of leads in the Arctic. REPLY: Revised see new text in section 1.

P. 9804, L. 20: How likely is it that the surface heat flux is the source of bubbles? Does it produce the same number and size of bubbles as air entrained from wave breaking? REPLY: See above.

P. 9805, L. 7: Does the size of jet drops influence their ability to act as CCN? REPLY: Revised see new text in section 1.

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P. 9806, L. 3: What is the immunological technique? REPLY: Revised see new text in section 1.

P. 9808, L. 6: Was the mast facing upwind “to maximize sampling time” or to prevent the inlet from sampling particles from the ship exhaust? Was the ship always pointing in to the wind, or could the inlet be rotated in to the wind? REPLY: Revised see new text in section 2.2. The inlet could not be rotated in to the wind.

P. 9809, L. 17-20: How was the depth of the frits chosen? How do you think the bubbles and resulting aerosol would change with a different bubble production depth? How was the flow rate of the bubble chosen? Did the bubbles persist at the surface and form rafts, dissipate, or burst immediately? REPLY: Clarified, see revised text in section 2.3. To find a configuration for the in situ generation of nascent aerosol by artificial bubble bursting that produced a large number of bubbles with a diameter of about 400 μm or less, the depth of the frits and the flow rate were varied in laboratory experiments. With a flow rate of 200 ml min⁻¹ we found that frits in a depth of 10 – 20 cm below the water surface produce the required bubble sizes. For these laboratory measurements, we used seawater from the Baltic Sea in Sweden. We were aware of the fact that the different composition and temperature of the seawater in the Arctic likely would affect the bubble production process. Therefore, in the Arctic we adjusted the frits of the bubblers to a depth of 12 cm below the water surface, and placed the filter holders at 13 cm above the water surface. Under these conditions, the bubbles burst immediately at the air-sea interface.

P. 9809, L. 22: What do you think is the influence of ambient gases and aerosols during this collection process? How much of the aerosol that was produced was collected? REPLY: Due to the close proximity of the filter holders to the water surface, and due to the extremely clean conditions in the high Arctic, we consider the influence of ambient gases and aerosol particles to be minor. 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.

P. 9810, L. 7-9: How were these 7 monosaccharides chosen? What is their significance? REPLY: Clarified in text, section 1. The targeted 7 monosaccharides constitute the backbone of polysaccharides for algae and their exudates, verified by Gao et al., 2012. Fructose is an example on one another common monosaccharide but is considered to be relevant for plants on land.

P. 9810, L 25: Because glucose and mannose were quantified together as a sum of the sugars, they cannot be reported separately. REPLY: Their quantitative determinations are not reported separately.

P. 9811, L. 12: This is discussing polysaccharides, but earlier only monosaccharides were listed. REPLY: Sorry for the unclearness. Now hopefully clarified in text, see section 1. The analyses were performed with the novel use of liquid chromatography coupled with highly selective and sensitive tandem mass spectrometry (LC/MS/MS) with a triple-quadrupole mass spectrometer. However, there can be thousands or more different type of polysaccharide in the phytoplankton -and sea ice algae secretions. The building block monomers of the polysaccharides can also be joined together in various orders or with different functional groups. Even more, the polysaccharides can be linear or branched. The linear polysaccharides differ from each other by the degree of polymerization (the number of repeated unit of monosaccharides) and will thus have differences in molar masses. This variety in molar masses allows for multiple mass-to-charge (m/z) ratios, which makes their mass spectroscopic analysis extremely difficult. Furthermore, searching for polysaccharides with specific values of m/z leads to a drastic drop in signal and increase in detection of limit. Finally, a triple triple-quadrupole mass spectrometer, which was used in this study, has a molar mass range limitation. To overcome the above limitations, the particulate polymer polysaccharide molecules collected were split into their monosaccharide units by hydrolyze prior to

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determination.

P. 9811, L. 25: Is 100 m³ an example of an actual sampled volume? It is better to use a relevant range than an assumed volume. REPLY: We normalize our detection limit to a sampling volume of 100 m³ to provide a reference number for subsequent users and at the same time to give an estimate how this affected the required length of sampling in this study.

P. 9812, L. 22: Based on these uncertainties in backtrajectories, how certain is the calculated DOI? How precise are the origins of the backtrajectories? Why was an arrival height of 100m chosen? Were heights other than 100m considered and compared? REPLY: 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. Backward trajectories were calculated for three different arrival heights (100 m, 500 m, 2000 m), every 6 hours for four arrival times (0 UTC, 6 UTC, 12 UTC, 18 UTC) at the position of the ship. To use the ship's position as a starting point gives a starting point that is very precisely measured with GPS. The summer Arctic boundary layer is typically a well-mixed shallow layer at the surface (with depths usually below 200 m), capped by a temperature inversion. The inversion may at times be strong, such as when there is substantial advection of warmer air from lower latitudes, while the free troposphere is stably stratified. The calculated trajectories (not used in this study) at 500 m and 2000 m were chosen heights for representing the inversion (approximately) and the lower free troposphere. The height of 100 m is a compromise to ensure that at least the receptor point is fairly close to the surface where we have our measurements (25 m above sea level), and at least in the well-mixed layer but also that trajectory, due to rounding errors and interpolation, do not run too great a risk to "hit the surface" in the backward calculations. Section 4.2 on the vertical structure of the high Arctic atmosphere is merged into section 3.2 where we also have clarified our choice of 100 m as the arrival height.

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P. 9813, L. 10-21: This description could be shortened, since it is described by Tjernstrom et al. (2012), as stated. There seems to be a lot of description of meteorology, which needs to be shortened or better tied in to the main point of the paper. REPLY: We would like to maintain the rather short met discussion, which we feel to be essential for the interpretation of our results.

P. 9813, L. 8: What method was used to split these backtrajectories in to clusters? Was the shape of the trajectory and the time spent over other regions considered or only the origin? REPLY: The back-trajectories shown in Fig. 3 b-e, were for the PI-drift subjectively classified in four clusters depending on their geographical origin, that is only taken their origin into account.

P. 9813, L. 16-18: How is a “subsiding pathway from the free troposphere” shown in Figure 3d? The heights of the backtrajectories are not shown in the figure. How was this determined? Overall, this sentence is unclear and/or this statement needs more explanation. REPLY: Instead of complicating Fig 3 with also the vertical component of the back-trajectories we prefer to only discuss this in the text. Now clarified in text.

P. 9817, L. 9: Expand on how much pack ice remains left to melt August. How much of the nutrients are available to be released from winter storage? Were some of the nutrients released in the spring season? REPLY: We have no information to answer these three questions; the experiment was not conducted during springtime.

P. 9817, L. 26 to P. 9818, L. 10: This group of sentences seems like a discussion of Gao et al. (2012). It needs to be clear here what was determined by Gao et al. (2012) and what are new ideas based on the previous work. REPLY: Clarified, see new text

P. 9819, L. 16-29: The main point needs to be better emphasized so that it stands out. This may be included later, but why is this interesting or important? REPLY: To characterize the temporal distribution of the aerosol modal appearance will give insight on sources, sinks and transformation processes in the atmosphere.

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P. 9820, L. 28: Instead of using “stage”, it would be more helpful to the reader to include the size range related to that stage. REPLY: The size range covered by the stage has been added.

P. 9821, L. 19: Is this the basis for the polysaccharide measurements? All of the measurements discussed have been monosaccharides, so some explanation is required before it can be inferred that the measured monosaccharides make up polysaccharides. REPLY: For the connection polysaccharides and monosaccharides, see text below. A clarification is made, see new text in section 1.

P. 9822, L. 3: Same comment as before – how do you know that the monosaccharides that were measured are polysaccharides or “monosaccharides in combined form”? REPLY: This study is concerned with the characterization of atmospheric particles associated with the polymer gel aggregates found in the open lead surface microlayer. These aggregates are polysaccharide molecules (monosaccharides in combined form) spontaneously forming three-dimensional networks inter bridged with divalent ions ($\text{Ca}^{2+}/\text{Mg}^{2+}$). In this study the aerosol particles collected including the particulate polymer polysaccharide molecules were split into their monosaccharide units by hydrolyses prior to determination. To make sure that our results were not biased with naturally free monosaccharide’s SML samples were compared for all the 7 targeted monosaccharides. The resulting molar ratios between free monosaccharides and hydrolyzed monosaccharides were zero for all monosaccharides but for glucose that gave a ratio of 2%. See new text in section 2.4.

P. 9822, L. 9-11: This comparison to amino acids should be excluded. Or it should be rephrased. Multiple assumptions must be made to go from relative levels of amino acids and carbohydrates in DOM in the ocean to those in marine aerosol particles. This is not fully explained here. It will take more effort to explain why they can be compared than is worth the comparison. REPLY: Removed.

P. 9823, L. 13: It would be helpful to state the ratio of Cl to Na in seawater here and

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why a ratio of 1 shows that there is little Cl depletion and thus a recent emission. Also, why are the salt particles produced specifically from jet drops in this case? And with the time spent over the ice, is it possible that the organics are coming from frost flowers or that the ratio of Cl to Na would be different in sea ice melt than in bulk seawater? 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 quite 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; Gershay R.M., Characterization of seawater organic matter carried by bubble-generated aerosols. 1983. Limnol. Oceanog., 28, 309-319).

P. 9825, L. 1-6: Explain why a larger fraction of glucose + mannose would imply that the particles were from combustion sources. Glucose can be found both in seawater and in plant material, also. 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 Glucose+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.

P. 9827, L. 17-18: Were polysaccharides actually measured? Or were measurements of monosaccharides combined to imply polysaccharides? If the monosaccharides were measured, how was it determined that they were in the form of polysaccharides? REPLY: Clarified, see above

P. 9828, L. 1-3: This is an interesting result that should be explained more clearly. The lowest concentrations of monosaccharides were found in the air masses that spent more than 5 days over the pack ice. This implies that the open ocean produces more monosaccharides than sources over pack ice. Is this just because open leads make up a small fraction of pack ice compared to the same area of open ocean? Is there less

bubble-bursting in open leads? Is the concentration of aerosol the same and just the fraction of monosaccharides lower?

REPLY: Section 6.1 gives the following suggested explanation for the clear decrease in THNS concentrations observed, 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. Also as referred to above 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.” Yes, the open leads make up a small fraction of pack ice compared to the same area of open-ocean, which is seen in the flux estimates. 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.

P. 9828, L. 7-11: Explain why this is an interesting and relevant result. REPLY: Clarified, see new text.

Figure 1: The caption does not discuss the dark blue dashed line. REPLY: Sorry for the mistake, which is now corrected. An updated version of Fig. 1 was inserted in the submitted version.

Figure 3: Why was Cluster 4 split in to two sub-clusters? REPLY: To be able to view the distribution in the measured polysaccharide data between R3 and R4 (different meteorological conditions encountered) we divided the samples collected within the 4th trajectory cluster into two sub-clusters, Fig. 3f (DOY 240-243) and Fig. 3g (DOY 244 -246), respectively. This was pointed out in section 6.1 but is now also clarified in section 4.1.

Figure 4: The way the lines connect the points in the figure is distracting. The curvature

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of the lines make it look like a single line was fit through all of the points, instead of just connecting the lines between the points. Because the emphasis is not on the connection between the values, a bar graph could also be used. REPLY: Agree, Figure 4 has been altered and clarified.

Figure 5: This figure could be compressed to contain less panels and more easily portray information, depending on the focus. To emphasize the differences between the monosaccharides for one sampling location, all of the PI-Drifts, etc. could be merged. If the emphasis is instead to show the difference in sampling location on a monosaccharide distribution, then the plots with the same monosaccharides could be combined. As the figure is, there is a lot of empty space and repeated information that could be removed. REPLY: We are sorry to see that the reviewer did not like the graphs of Fig. 5. However this is the standard way for presenting chemical size distribution, which we would like to keep.

Figure 8: Include the relevance of DOY 242. Where was this taken? REPLY: Clarified, see new text.

Table 2: Some of this information would be better presented as a figure. The monosaccharide composition could easily be made in to a bar graph since the values are all percentages of the total monosaccharide concentration. REPLY: We prefer to maintain the results as presented in the form of Table 2 because this format keeps the maximum resolution of the result for subsequent users.

Technical Corrections:

P. 9802, L. 2: Replace “determination” with “identification” REPLY: Do not agree, we would like to stay with “determination” as that is the proper analytical wording to be used. To clarify we have replaced “determination” with “quantitative determination”.

P. 9802, L. 7: Replace “sizes” with “particle sizes” REPLY: Done.

P. 9803, L. 9: Change to: “controlled by the fraction of aerosol particles capable” RE-

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PLY: Done.

P. 9803, L. 13: Is this “open-water” referring to “leads”? REPLY: Clarified, see new text.

P. 9803, L. 13: Change “low-lewel” to “low-level”. REPLY: Done.

P. 9803, L. 14-17: This sentence is unclear. Try removing “apparently thus” and replacing “To be able to” with “The ability”. REPLY: Done.

P. 9803, L. 18: Does this refer to any water or seawater or open leads specifically? REPLY: Clarified.

P. 9804, L. 7: Remove the space in “upward- moving”. REPLY: Done.

P. 9804, L. 6: Replace “thrown” with “emitted” or “injected”. REPLY: Done.

P. 9805, L. 1-6: Rephrase these two sentences for clarity. REPLY: Done.

P. 9806, L. 5: Change “To further strengthen” to “Strengthening”. REPLY: Done.

P. 9806, L. 22: Change “Determinations” to “Identification” or “Measurements”. REPLY: See above.

P. 9808, L. 17: Replace “determination” with “analysis” or “measurement”. REPLY: See above.

P. 9809, L. 16: “frit” should be “frits” REPLY: Done.

P. 9810, L. 24: “baselined” REPLY: Done.

P. 9812, L. 2-5: Rephrase to be similar to: “To our knowledge, using LC/MS/MS to measure natural occurring monosaccharides...”. REPLY: Done.

P. 9815, L. 1: Change “would allow” to “allows” REPLY: Done.

P. 9815, L. 4: Need a (“ before “2)”. REPLY: Not clear on what the requested change is.

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P. 9816, L. 19-21: Rephrase this sentence to read similar to: “In order to fully understand the characteristics of the gel-particles derived from bubbles bursting at the seawater surface, the biological activity of the SML and its connection to the presence of the gel-particles needs to be understood.” REPLY: Done.

P. 9819, L. 27: “pentose” REPLY: Done.

P. 9821, L. 15: “relative” is used twice. REPLY: Rephrased.

P. 9823, L. 4: Replace “is” with “are”. REPLY: Done.

P. 9823, L. 4-28: This paragraph makes multiple points and would be easier to read if it was further split in to multiple paragraphs. REPLY: Clarified, see new text.

P. 9823, L. 14: Why is “ca.” used here? REPLY: It’s appropriate in this context.

P. 9824, L. 26-27: Change “is distinguishable in terms of” to “can be distinguished by”. REPLY: Done.

P. 9824, L. 28: Insert a period after “Fig. 8c”. REPLY: Done.

P. 9825, L. 20-21: This line states “three categories”, but the list either includes four or the commas should be redistributed. REPLY: Clarified.

P. 9825, L. 26: “increase” REPLY: Done.

P. 9826, L. 25: Remove “the” REPLY: Done.

P. 9827, L. 13-14: This sentence should be rewritten. REPLY: Done, see new text.

P. 9827, L. 15: Remove “for determination”. REPLY: Done.

P. 9828, L. 1: Rephrase: “It is hoped that”. REPLY: Done.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 9801, 2013.

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