Response to Review

Frequent Ultrafine Particle Formation and Growth in Canadian Arctic Marine and Coastal Environments

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Anonymous Referee #2:

Collins et al. (2017) is a great piece of work characterising aerosol in a difficult environment (the Arctic), on a challenging platform (an icebreaker) for two different years (2014 and 2016). I congratulate very much to the authors, and to the Canadian program NETCARE which should be an example of interdisciplinary studies to follow. I think the paper should be well accepted in ACP, following few major revisions which I am confident the author will be able to carry out.

The authors thank the referee for their thoughtful review of the manuscript and appreciate their kind words about the NETCARE program.

1) It is mentioned a number of times in the text that the Arctic marine microbial communities are likely to be responsible for the large increase of new particle formation recorded in 2016 vs 2014 (41% and 6% of the time, respectively). For example, on page 15 line 16-18 "The source strengths of gas-phase precursors and reactive species, which are generally not well understood in the marine environment, are key remaining factors for explaining differences in ultrafine particle production". Reading section 3.3, one may get the feeling that this is the main reason for the large increase observed in 2016 relative to 2014, given other meteorological and physical conditions did not change substantially. I suggest to modify the abstract (a bit too general in the current state) and report - for example - important conclusion such as line 33 pg 13 "CS may not be a factor that directly limits the formation of UPF in this region". I think is important to stress that chemical precursors (likely coming from Arctic marine communities) may play an important rule in increasing UPF, and physical conditions (different CS, for example) may not be as important as chemical precursors availability. If that is the case, it should be stressed in the abstract, in the current stage too general and not representative of the discussions and conclusions presented across the manuscript.

Given the lack of a clear delineation of the importance of biogeochemical factors versus meteorological factors leading to the formation and growth of UFP within this study, the authors feel it is not prudent to change the abstract to reflect greater certainty in the conclusion of a biogenic driver behind inter-annual differences in UFP formation. Indeed, our findings are suggestive that the differences in UFP formation

and growth *may* be tied to differences in sea ice coverage and/or the phase of biological activity in the Canadian Arctic – and this study provides an interdisciplinary analysis of key observations. However, decreased cloud fraction and increased solar radiation were also documented in 2016 compared with 2014, and may also help lead to greater UFP formation and/or growth. Ongoing study within NETCARE using computational tools may help clarify conclusions about which factors may be driving UFP formation in this region. We have added a statement in the conclusions highlighting the importance of computational tools to deriving insight on the mechanisms behind UFP formation and growth.

Page 18, lines 18-20 – sentence added: "In addition, chemical transport models and other computational tools, in conjunction with the observations reported in this study, may lend important insight into the drivers of UFP formation in the Canadian Arctic, and may be translatable to other remote locations."

2) Figure S5 should be a main part of the paper (maybe as new Figure 12) because it stresses a major difference across the two different years (differences up to 13-25% in sea ice concentrations) - therefore associating UFP events to open water, higher percentages of sea ice marginal zones, and less packed ice. On this regards, the authors should refer to a recent paper (Arctic sea ice melt leads to new particle formation, Dall'Osto et al., 2017a, Scientific Reports | 7: 3318 | DOI:10.1038/s41598-017-03328-1), where air mass trajectory analysis and atmospheric nitrogen and sulphur tracers linked frequent nucleation events to biogenic precursors released by open water and melting sea ice Arctic regions. Additionally, when discussing this (I leave to the author if prefer to discuss this in the result discussion part or in the conclusion paper) they should also discuss this potential source (polar open water and sea ice marginal Arctic sea ice regions) and put into context another recent paper from NETCARE (Croft et al, 2016, Nature Comm, another possible source of UFP related to bird colonies).

The referee's suggestion to include Figure S5 in the main text (as Figure 12) has been included in the revisions. While a short discussion addressing the ability of discontinuous ice to enable air-sea interaction was present in the initial manuscript, references to the work by Dall'Osto et al. (2017b) and Sharma et al. (2012) have now been included, and a further concluding statement at the end of the paragraph (p16, lines 2-5) has been added. The authors agree with the referee that the change in sea ice could lead to differences in air-sea exchange of volatile UFP precursors, and this has been clarified in the revised manuscript. A statement (p16, lines 18-21) connecting the discussion to coastal sources of UFP precursors has also been added, including not only bird colonies (Croft et al., 2016; Weber et al., 1998), but also intertidal zones (O'Dowd et al., 2002; Sipilä et al., 2016). In addition, a discussion of the interaction of marginal sea ice and atmospheric chemistry in polar regions has now been added to the manuscript (p17, lines 21-29).

Minor comments

- Section 3.3.2 - oceanic conditions. I congratulate to the authors for improving the paper with this interdisciplinary part, an interesting one. Whilst DOC - among other marine biological measurements - during different years were almost identical, Figure S6 shows interesting differences for nitrate (among other variables), suggesting phytoplankton production season was more advanced and well into post bloom phase during 2016 (relative to 2016). A recent paper (Dall'Osto et al., 2017, Antarctic sea ice is a source of organic nitrogen in aerosols, Scientific Report, DOI:10.1038/s41598-017-06188-x) also go in the same direction, showing sea ice marginal region with more advanced post bloom phase enhanced in UFP. It may be worth to stress that in polar regions (both Antarctic and Arctic) the biology is playing a role (and seems not Chl, but the stage of the bloom, is the key factor) and more interdisciplinary studies are needed.

As the referee describes, the manuscript discusses the importance of the bloom phase on marine biosphere-atmosphere interactions (e.g., p16 starting on line 10). The conclusion that the bloom state was different between the two summers was reached by holistically analyzing the nitrate concentration near the sea

surface, primary production rates, dimethyl sulphide concentrations in seawater, and the nuanced information content within the size-segregated chlorophyll concentrations. The importance of post-bloom phase biogeochemistry on air-sea interactions has also been noted in various previous studies (Collins et al., 2013; Lee et al., 2015; O'Dowd et al., 2015; Wang et al., 2015), which are cited within the manuscript along with foundational studies of bloom dynamics (Azam et al., 1983). Indeed, biogeochemistry in the marginal ice zone is germane to this study as CCGS *Amundsen* encountered sea ice commonly during both summers, and sea ice concentrations in the region were a major distinguishing factor between the 2014 and 2016 expeditions. A discussion of the importance of the marginal ice zone to atmospheric chemistry in polar regions is warranted and has been added to the manuscript (p17, lines 21-29). It is important to point out that the impact of specific sources of UFP formation and growth precursors were not scrutinized in this study, as air mass histories indicate the inclusion of a variety of potential source characterizations (e.g., coastal, open water, sea ice) for each UFP formation event described in the manuscript. Consequently, a more broad approach to characterize the region as a whole was undertaken.

- pg 3 line 30-25. Whilst the authors do a decent job in addressing the different chemical precursors, it may be more appropriate to cite only works carried out in Arctic regions (not Atlantic or other oceans) and not forget Sippila et al 2016 (Nature) and also to address recent new findings (Croft et al., 2016, Birds colony emissions) and marginal sea ice (Dall'Osto et al., 2017a, Scien Rep).

Since so little is known about marine emissions of UFP precursors (and as the literature on aerosol nucleation chemistry develops in parallel), the authors feel that it is important to include relevant findings from various marine regions in light of the desire for process-level understanding in the long run. Relatively few measurements have been made to connect UFP formation with specific precursors, so it is important to keep an open mind on the possible chemical drivers. While it is becoming clear that organic material leads to particle growth in the Arctic (Willis et al., 2016), and that an accurate accounting for ammonia is important for modeling UFP formation (Croft et al., 2016), the level of understanding in the marine atmosphere lags behind the terrestrial biosphere to a great degree. The key points about sources of N-containing material in secondary marine aerosol and in biogenic material retrieved from sea ice are important contributors to accounting for possible marine UFP precursors (e.g., Dall'Osto et al., 2017a; Facchini et al., 2008). As noted by the referee, UFP formation in coastal and marginal ice zones have been observed but much more information is needed to understand these processes fully. Iodine chemistry that is characteristic of intertidal emissions (Allan et al., 2015; Sipilä et al., 2016) and marginal ice emissions of sulfur- and nitrogen-containing compounds (Dall'Osto et al., 2017a; Levasseur, 2013) are of interest to the community, and are now appropriately acknowledged and cited within the Introduction. (p3, lines 30-34)

- Pg 11 line 2-5, it is possible to access the importance of coastal vs open ocean sources? As Rev 1 suggests, is this study more related to a specific environment, such as Archipelagos, and not to be extrapolated to open ocean and marginal sea ice zone Arctic areas?

As noted in a prior comment to this referee (*vide supra*), the comparative analysis of marine biological parameters and atmospheric aerosol observations are deliberately broad in nature. Since the Canadian Arctic can have influences from coastal margins, open water regions, and transport from the high Arctic, the authors felt it prudent to retain a regional scale analysis that included all of these sources in a 'synoptic' sense. At the suggestion of the referees, a more developed discussion of the impacts of marginal ice, coastal seabirds, and intertidal zones has been included in various parts of Section 3 to clarify for the reader the potential importance of such sources to UFP formation and growth in this region. More targeted study of each of these sources may be required to understand their impacts on the environment as a whole.

- pg 15 line 23 - I think it is figure S5

This figure reference has been changed to ‘Figure 12’ as Figure S5 has been moved to the main text.

-pg 15 line 22. I think the authors should improve this section and decide what is more appropriate (if include figure S5 as figure 12, and expand this section). I think maybe presenting an average map for the two different seasons (2014 and 2016) but I am not sure the 1st of August is representative, I would use a longer period, or present figure S5 in the main text.

In accordance with another of this referee’s comments, Figure S5 has been incorporated in the main text as Figure 12, which the authors feel enhances the manuscript in an important way. The spatial representation of Figure 11 remains unchanged in the revised manuscript, as it is provided as an example of the pattern of differences in sea ice concentration throughout the region, but the quantitative changes are well represented by Figure 12. In addition, the connection between differences in sea ice concentration and biological activity have been further developed in the context of UFP formation throughout Section 3.3.2, in response to the referee’s comments. Discussions of interactions between aerosol chemistry and transport over open ocean (Sharma et al., 2012), associations between sea ice concentration and UFP formation (Dall’Osto et al., 2017b), and possible influences of sea ice on marine biology in the surface ocean (Dall’Osto et al., 2017a; Levasseur, 2013) have been enhanced or added to the manuscript.

References

Allan, J. D., Williams, P. I., Najera, J., Whitehead, J. D., Flynn, M. J., Taylor, J. W., Liu, D., Darbyshire, E., Carpenter, L. J., Chance, R., Andrews, S. J., Hackenberg, S. C. and McFiggans, G.: Iodine observed in new particle formation events in the Arctic atmosphere during ACCACIA, Atmos. Chem. Phys., 15(10), 5599–5609, doi:10.5194/acp-15-5599-2015, 2015.

Azam, F., Field, J. G., Graf, J. S., Meyer-Rei, L. A. and Thingstad, F.: The Ecological Role of Water-Column Microbes in the Sea, Mar. Ecol. Prog. Ser., 10, 257–263, 1983.

Collins, D. B., Ault, A. P., Moffet, R. C., Ruppel, M. J., Cuadra-Rodriguez, L. A., Guasco, T. L., Corrigan, C. E., Pedler, B. E., Azam, F., Aluwihare, L. I., Bertram, T. H., Roberts, G. C., Grassian, V. H. and Prather, K. A.: Impact of marine biogeochemistry on the chemical mixing state and cloud forming ability of nascent sea spray aerosol, J. Geophys. Res. Atmos., 118(15), 8553–8565, doi:10.1002/jgrd.50598, 2013.

Croft, B., Wentworth, G. R., Martin, R. V., Leaitch, W. R., Murphy, J. G., Murphy, B. N., Kodros, J. K., Abbatt, J. P. D. and Pierce, J. R.: Contribution of Arctic seabird-colony ammonia to atmospheric particles and cloud-albedo radiative effect, Nat. Commun., 7, 13444, doi:10.1038/ncomms13444, 2016.

Dall’Osto, M., Ovadnevaite, J., Paglione, M., Beddows, D. C. S., Ceburnis, D., Cree, C., Cortés, P., Zamanillo, M., Nunes, S. O., Pérez, G. L., Ortega-Retuerta, E., Emelianov, M., Vaqué, D., Marrasé, C., Estrada, M., Montserrat Sala, M., Vidal, M., Fitzsimons, M. F., Beale, R., Airs, R., Rinaldi, M., Decesari, S., Facchini, M. C., Harrison, R. M., O’Dowd, C. and Simó, R.: Antarctic sea ice region as a source of biogenic organic nitrogen in aerosols, Sci. Rep., 7, 6047, doi:10.1038/s41598-017-06188-x, 2017a.

Dall’Osto, M., Beddows, D. C. S., Tunved, P., Krejci, R., Ström, J., Hansson, H.-C., Yoon, Y. J., Park, K.-T., Becagli, S., Udisti, R., Onasch, T., O´Dowd, C. D., Simó, R. and Harrison, R. M.: Arctic sea ice melt leads to atmospheric new particle formation, Sci. Rep., 7, 3318, doi:10.1038/s41598-017-03328-1, 2017b.

Facchini, M. C., Decesari, S., Rinaldi, M., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Moretti, F., Tagliavini, E., Ceburnis, D. and O’Dowd, C. D.: Important Source of Marine Secondary Organic Aerosol from Biogenic Amines, Environ. Sci. Technol., 42(24), 9116–9121, doi:10.1021/es8018385, 2008.

Lee, C., Sultana, C. M., Collins, D. B., Santander, M. V., Axson, J. L., Malfatti, F., Cornwell, G. C., Grandquist, J. R., Deane, G. B., Stokes, M. D., Azam, F., Grassian, V. H. and Prather, K. A.: Advancing Model Systems for Fundamental Laboratory Studies of Sea Spray Aerosol Using the Microbial Loop, J. Phys. Chem. A, 119(33), 8860–8870, doi:10.1021/acs.jpca.5b03488, 2015.

Levasseur, M.: Impact of Arctic meltdown on the microbial cycling of sulphur, Nat. Geosci., 6(9), 691–700, doi:10.1038/ngeo1910, 2013.

O'Dowd, C., Ceburnis, D., Ovadnevaite, J., Bialek, J., Stengel, D. B., Zacharias, M., Nitschke, U., Connan, S., Rinaldi, M., Fuzzi, S., Decesari, S., Facchini, M. C., Marullo, S., Santoleri, R., Dell'Anno, A., Corinaldesi, C., Tangherlini, M. and Danovaro, R.: Connecting marine productivity to sea-spray via nanoscale biological processes: Phytoplankton Dance or Death Disco?, Sci. Rep., 5, 14883, doi:10.1038/srep14883, 2015.

O'Dowd, C. D., Jimenez, J. L., Bahreini, R., Flagan, R. C., Seinfeld, J. H., Hämeri, K., Pirjola, L., Kulmala, M., Jennings, S. G. and Hoffmann, T.: Marine aerosol formation from biogenic iodine emissions, Nature, 417(6889), 632–636, doi:10.1038/nature00775, 2002.

Sharma, S., Chan, E., Ishizawa, M., Toom-Sauntry, D., Gong, S. L., Li, S. M., Tarasick, D. W., Leaitch, W. R., Norman, A., Quinn, P. K., Bates, T. S., Levasseur, M., Barrie, L. A. and Maenhaut, W.: Influence of transport and ocean ice extent on biogenic aerosol sulfur in the Arctic atmosphere, J. Geophys. Res. Atmos., 117(D12), D12209, doi:10.1029/2011JD017074, 2012.

Sipilä, M., Sarnela, N., Jokinen, T., Henschel, H., Junninen, H., Kontkanen, J., Richters, S., Kangasluoma, J., Franchin, A., Peräkylä, O., Rissanen, M. P., Ehn, M., Vehkamäki, H., Kurten, T., Berndt, T., Petäjä, T., Worsnop, D., Ceburnis, D., Kerminen, V.-M., Kulmala, M. and O'Dowd, C.: Molecular-scale evidence of aerosol particle formation via sequential addition of HIO3, Nature, 537, 532–534, doi:10.1038/nature19314, 2016.

Wang, X., Sultana, C. M., Trueblood, J., Hill, T. C. J., Malfatti, F., Lee, C., Laskina, O., Moore, K. A., Beall, C. M., McCluskey, C. S., Cornwell, G. C., Zhou, Y., Cox, J. L., Pendergraft, M. A., Santander, M. V., Bertram, T. H., Cappa, C. D., Azam, F., DeMott, P. J., Grassian, V. H. and Prather, K. A.: Microbial Control of Sea Spray Aerosol Composition: A Tale of Two Blooms, ACS Cent. Sci., 1(3), 124–131, doi:10.1021/acscentsci.5b00148, 2015.

Weber, R. J., McMurry, P. H., Mauldin, L., Tanner, D. J., Eisele, F. L., Brechtel, F. J., Kreidenweis, S. M., Kok, G. L., Schillawski, R. D. and Baumgardner, D.: A study of new particle formation and growth involving biogenic and trace gas species measured during ACE 1, J. Geophys. Res. Atmos., 103(D13), 16385–16396, doi:10.1029/97JD02465, 1998.

Willis, M. D., Burkart, J., Thomas, J. L., Köllner, F., Schneider, J., Bozem, H., Hoor, P. M., Aliabadi, A. A., Schulz, H., Herber, A. B., Leaitch, W. R. and Abbatt, J. P. D.: Growth of nucleation mode particles in the summertime Arctic: a case study, Atmos. Chem. Phys., 16(12), 7663–7679, doi:10.5194/acp-16-7663-2016, 2016.