Responses to the Reviewers

We would like to thank all three reviewers for their thorough comments on this manuscript, which helped to improve the paper. Our responses to general and specific comments are below.

The comments of the reviewers are printed in bold. All line numbers in bold refer to the original manuscript, all others to the revised version.

Reviewer 2

Reviewer general comments: This paper investigates ultrafine particle (UFP) concentrations in the Canadian Arctic through aircraft measurements. The topic is of interest and important given the rapid changes expected for this region. Overall, I think an attempt at a more quantitative analysis, a more in-depth discussion of the limitations of the approach used in this work, (given that this has been grappled with and addressed in the past literature) and a more complete citation of the existing publications on this topic is needed.

A stated goal is to understand new particle formation (NPF) events (ie, the source of UFP) and how they evolve (grow) to affect radiative forcing through acting as CCN.

The paper really mainly focuses on the NPF events. A number or instruments were deployed, most important for addressing this question are measurements of all particle number concentrations larger than 5nm and number size distributions of particles larger than 20 nm. By difference, the authors determine the number between 5 and 20 nm to assess NPF. There is a substantial body of published literature on the the subject of investigating NFP using difference measurements, ie, typically this was done by subtracting data from a UFCPC (eg, TSI 3025) and CPC (eg, TSI 3010 or similar), to obtain concentrations of particle in the 3 to 10 nm range, and the limitations with this type of difference approach. In this study, these limitations are more severe as UFPs are defined over a larger size range, 5 to 20 nm, and smallest size is higher, 5 nm, further away from the size of the newly nucleated particle (1 to 1.5 nm). Furthermore, there are no measurements of possible nucleation gas-phase precursors, such as sulfuric acid, (or SO2 and estimated OH could work, but not as well), ammonia and possible low volatile VOCs. Since new stable particles have sizes near 1 or so nm, and in pristine environments particle growth rates can be slow, it can take considerable time for the NPF event to be observable with the the deployed instrumentation. This make interpretation of this data very challenging for investigating nucleation conditions. Thus, essentially, the authors instrumentation is not ideal for addressing the scientific aim of defining NPF conditions in the Arctic.

First, it is recommended that the authors present a thorough assessment of the limitations with their method. This should include: 1) An analysis of the LOD of the difference method used to determine N(5-20) is needed. This will likely show that only significant concentrations of N(5-20) particles can be detected with certainty, potentially leading to a view biased by focusing only on larger nucleation events, which should be discussed. (This should likely include uncertainty in counting statistics, integrated size distributions to get total N of the measured distribution, N20, both instrument flow uncertainties, errors associated with subtracting two large numbers of small difference, etc. 2) The uncertainty in conditions that actually existed at time of the NPF event versus what

existed at the time of the measurement due to expected times between the two (ie, if possible, estimate the delay from nucleation to detection based on estimated or assumed growth rates of nanoparticles).

Without measurements of possible new particle precursor gases and lack of particle concentrations near the critical nucleation diameter it is very difficult to discuss conditions leading to NPF with certainty. For example, it is noted that often an inverse relation is seen between N(5-20) and larger particle concentrations. This could be due to formation of these smaller particles in cleaner air (ie, nucleation precursor vapors can build up due to lack of vapor condensational sink), or the new particles in the cleaner region just have a longer life span compared to particles that may have been formed in the other regions that had higher concentrations of pre-existing particles, which depleted the N(5-20) particles faster. Thus, how can one conclude that the only particle formation events are in the clean regions (possible confirmation bias). I think the authors have provided evidence that UF particles are generated in the Arctic BL and it can occur under clean conditions, but what happens in more polluted air masses is not really known. Specifically, how (by what process), under what conditions (where), is not definitively known. More analysis, involving calculations (estimations) of lifetimes, more discussion of possible differences in measured total particle surface areas between regions, may allow more definitive conclusions. Some data is clearly not available to make more quantitative assessments, but maybe typical values reported in clean similar environments can set a bound.

Finally, it is not clear what is special about the clouds that leads to NPF in their vicinity. Since this is one major finding of this paper, more details are warranted, including a more comprehensive analysis of the literature, eg; [Clarke et al., 1999a; Clarke et al., 1999b; Hegg, 1991; Hegg et al., 1990; Hoppel et al., 1994; Mauldin et al., 1997; Perry and Hobbs, 1994; Radke and Hobbs, 1991; Raes, 1995; Weber et al., 2001; Wiedensohler et al., 1997]

Responses – We thank the reviewer for their comments, which help to improve the paper. The following are a few responses to the reviewer's more general comments:

1) As discussed below, we have included some of the additional references the reviewer suggests.

2) We agree with the reviewer that growth rates may be slower in pristine environments. However, in this study we were apparently very close to a source of particle precursors (biologically productive sea and sea-ice interface). In other words, we were not necessarily pristine from the point of view of potential precursors, even though we were pristine by comparison with anthropogenic environments. The work of Willis et al. (2016) illustrates rapid aerosol growth in this environment.

The main point of the paper is to demonstrate that ultrafine particles are associated with the ocean surface during the Arctic summer when particle mass concentrations are extremely low. Airborne measurements of NPF associated with open water in the Arctic are surprisingly few: Leaitch et al. (1983 and 1994). This work offers a unique perspective on the issue. With respect to growth of the particles to reach 5 nm and beyond 20 nm, we note that in the absence of significant coagulation (the effect of which will be reduced due to the relatively low

concentrations of particles smaller than 20 nm) it requires more than 100 times more condensable precursor for particles to grow from 20 nm to 50 nm compared with particles growing from 1 nm to 10nm. Willis et al. (2016) showed that for this environment particles were able to grow to 50 nm low over the open water over approximately one hour, which means that the growth from 1 nm to 10 nm can occur over one minute or less, justifying our use of instruments that are sensitive to 5 nm particles and larger. Of course, we would have very much have liked to have instruments operating sensitive to 1 nm particles but they were not available to us for this study. It is our belief that doing the first systematic altitude-resolved study of particle size distributions in the summertime Arctic marine environment with a standard set of instrumentation makes this work noteworthy.

Also, please note that we may have misled readers (and the reviewer) of the ACPD version of the paper by averaging all data in our vertical profiles, which led to a bias by overweighting single flights at some altitude intervals. We apologize for this. The new averaging method used in the revised manuscript equally weights data from all flights at all altitudes intervals. We added a brief description to the paper (line 244-249): "An average profile for a single flight was obtained by binning all data from the respective flight into altitude intervals of 100m starting at the lowest flight altitude. In addition to data obtained during vertical profile flights, data acquired while flying at a constant level were also included. Average profiles containing data of more than one flight were calculated by averaging the respective single flight profiles. " We revised all figures showing average profiles (Figure 5-8).

Figure 5 and Figure 8 originally showed that the maximum in the UFP concentration over open water was above the lowest sampling level. To the new version of Figure 8, we have added N_{tot}, which was sampled every second and shows the increase in particles over open water is also associated with the lowest sampling level. That observation is consistent with the results of Willis et al. (2016) as well as past observations related to polynyas (Leaitch et al. 1983 and 1994).

As for the limit of detection, Leaitch et al. (2013) found an average CPC-SMPS of 47/cc for points during dark periods at Alert, Nunavut (1861 one hour averages) with a standard deviation of 73/cc and a 95^{th} percentile of 144/cc, indicating that values of CPC-SMPS in excess of 200/cc are reasonable indicators for NPF. Our discussion on lines 338-345 of the original manuscript (363-370 of revised paper) already addresses this concern.

3) With respect to the reviewer's comments concerning the conditions under which we observe NPF, we now indicate in the Abstract that high levels of UFPs are observed when the condensation sink is smallest, i.e. lowest numbers of larger particles. We feel that this is an accurate short summary, based on the observations made in the study. The reviewer suggests that the "precursor vapors can build up due to the lack of a condensation sink" but it is not clear what sort of 'build up' is needed. The formation of 1000 particles/cc, each of which is 10 nm in diameter, requires very little precursor. Over a biologically productive sea, it is very likely that sufficient precursor will be available for NPF if the condensation sink is low enough, as in the early part of this study.

The reviewer suggests that "the new particles in the cleaner region just have a longer life span compared to particles that may have been formed in the other regions that had higher concentrations of pre-existing particles, which depleted the N(5-20) particles faster." If that were the case, then we would have seen the NPF occur at other locations and not principally associated with the ocean surface.

Finally, the reviewer argues that "what happens in more polluted air masses is not really known". This may be true but we find less evidence for NPF associated with less pristine conditions. It is clear that in this relatively clean background environment, a low condensation sink is a necessary condition. The paper does not address more polluted conditions.

4) As in our response to the reviewer's comment concerning lines 573-575, we have added a sentence to elaborate on the potential role of clouds in this instance (lines 608-611 of the revised manuscript). We use two of the references suggested by the reviewer (one reference the reviewer suggested was already present): Clarke et al. (1999) and Mauldin et al. (1997). These are on lines 601-602 of the revised manuscript. Of course it is not unique that NPF is associated with clouds. We also added two more references suggested by the reviewer that illustrate a connection of new particles with clouds (Radke and Hobbs 1991, Wiedensohler et al. 1997). What is important here is that relative to the cloud-free observations over ice and water, the UFP over cloud were common and the associated concentrations are higher (Figure 8).

References added:

- Clarke, A. D., Kapustin, V. N., Eisele, F. L., Weber, R. J. , and McMurry, P. H.: Particle production near marine clouds: sulfuric acid and predictions from classical binary nucleation, Geophys. Res. Lett., 26, 2425-2428, doi: 10.1029/1999GL900438, 1999.
- Mauldin, R. L., Madronich, S., Flocke, S. J. , Eisele, F. L. , Frost, G. J. and Prevot, A. S. H. : New insights on OH: Measurements around and in clouds, Geophys. Res. Lett., 24(No 23), 3033-3036, doi:10.1029/97GL02983, 1997.
- Radke, F. L. and Hobbs, P. V.: Humidity and particle fields around some small cumulus clouds, Journal of atmospheric sciences, 48(9), 1190-1193, doi: http://dx.doi.org/10.1175/1520-0469(1991)048<1190:HAPFAS>2.0.CO;2, 1991.
- Wiedensohler, A. H.-C. Hansson, D. Orsini, M. Wendisch, F. Wagner, K.N. Bower, T.W. Chourlarton, M. Wells, M. Parkin, K. Acker, W. Wieprecht, M.C. Facchini, J.A. Lind, S. Fuzzi, B.G. Arends, M. Kulmalao: Night-time formation and occurrence of new particles associated with orographic clouds, Atmos. Env., 31(16), 2445-2559, doi: http://dx.doi.org/10.1016/S1352-2310(96)00299-3, 1997.

Specifics:

Reviewer - Lines 73 to 76. These statements are unsupported and possibly not accurate. It all depends on the conditions (thus the statement must be qualified) and also depends on what is defined as ultrafine particles.

Response – We feel these statements are supported by the observations, as discussed above.

Reviewer - Should explicitly calculate estimated losses associated with sampling 5 nm particles (ie, this is the worst case scenario).

Response – In response to Reviewer 1 and this comment, we have added on lines 159-165 of the revised paper: "Although the transfer of the aerosol from outside to the instruments is relatively fast (5 seconds and less), volatilization of some components of the particles may have occurred. However, it has been demonstrated that the growth of smaller particles by organic condensation occurs primarily by low volatility organic components (e.g. Riipinen et al., 2011; Pierce et al., 2012). Thus, the integrity of the smaller particles that are the focus of the discussion here is more likely to have been maintained. We do expect increasing line losses of particles with sizes decreasing from 10 nm. Therefore our observations will underestimate $N_{5\text{-}20}$."

Reviewer - For given AMS LODs, what was the AMS sampling rate.

Response – The sampling rate was 30 seconds. This has now been added to the paper (line 222).

Reviewer - Was N(tot) every defined? Ie, what is the smallest size.

Response – Yes, it was defined on line 179 of the ACPD manuscript as the UCPC measurement, which on line 176 refers to particles larger than 5 nm. In addition, we have added on lines 194-196: ", noting as above that diffusional losses of particles smaller than 10 nm make the Ntot observations lower limits."

Reviewer - Line 339, what exactly does a burst of N(5-20) mean, was it a burst because the aircraft flow through a small region of high concentrations, or is it being implied that there was a burst in NPF? If the latter, how is that known? In fact, the use of "burst" throughout the paper is confusing since what it really means is isolated regions of high UF particles were encountered, not the typical meaning of a large nucleation event occurring over a short period of time (which I believe is what is implied). It is not clear that the latter can be determined from this sampling approach.

Response – Bursts here refers to sudden increases in N5-20. We have clarified that on line 359-361 of the revised manuscript by the addition of "Here we refer to "bursts" of particles as a sudden and relatively large increase in $N_{5\text{-}20}$. This may reflect inhomogeneities in the NPF process or may reflect the aircraft flying in and out of a NPF event."

Reviewer - Lines 350: on possible reasons for high fractions of UF particles; this could also include, very slow growth rates, biased aircraft sampling (ie, you went looking for them).

Response – As above, the results in Willis et al. (ACP, 2016) do not suggest very slow growth rates, and we do not include that as a possibility. We agree that there could be some bias associated with our sampling, and accordingly we have added the following sentence to lines 379-381 of the revised manuscript: "Also, since observations of UFP were one focus of this study, the fractional occurrence of the UFP mode may be slightly biased due to longer sampling times associated with UFP occurrence."

Reviewer - Lines 462-465. This sentence seems to exactly confirm the limitations with the analysis used in the paper; the presence of UFP may have mostly to do with residence time in the BL and not mechanism that formed them.

Response – If these particles were resident for a long time in the BL, then we should have observed them everywhere. But this was not consistent with the observations.

Reviewer - Line 497-498; This conclusion is not the only possible one, it is also possible that they just are not scavenged and so have a longer life time (as noted already). Without measuring the nucleation precursor species, it is hard to tell. Calculations of life times of particles of 5 to 20nm due to coagulation, based on given size distributions may be insightful. Growth out of the 5 to 20 nm size range due to condensation is likely more important. Maybe if some assumptions are made on typical concentrations of H2SO4 or low volatile VOCS one could also estimate this, or use reported growth rates in other clean regions?

Response – Our response is the same as to the comment immediately above as well as our above responses to the reviewer's general comments.

Reviewer - Lines 573-575 and 594-595. Not clear what the all the ideal conditions for NPF were, is it just high OA levels? More details would be good, see references (eg, precipitating clouds scavenge accumulation mode aerosols, reducing surface area, but nucleation precursor gases can pass through (eg, SO2) forming H2SO4 in the high OH (high actinic flux and RH) in the cloud outflow, plus high RH leads to NPF…

Response – Thank you. We have added the following on lines 608-611 of the revised manuscript: " In other words, precipitating clouds scavenge aerosol particles, reducing the surface area for condensation, but some fraction of nucleation precursor gases with lower Henry's Law constants can pass through (e.g. SO_2) leaving the potential for H_2SO_4 in the higher OH in the cloud outflow (a discussion of the processes can be found in Seinfeld and Pandis, 1998)."

Reviewer - Lines 647-648: I think this sentence should be clarified. It cannot be said that the open water is the source of the observed particles, it may be true, but it could also be that stable new particles of sub 5 nm size were formed elsewhere and just grew to your detectable size due to ocean emissions.

Response – See response to above comment concerning lines 462-465 and our above responses to your general comments.

References

Leaitch, W.R., Hoff, R.M., Melnichuk, S., and Hogan, W.: Some chemical and physical properties of the Arctic winter aerosol in northeastern Canada. J. Climate Appl. Meteorol., 23, 916-928, http://dx.doi.org/10.1175/1520-0450(1984)023<0916:SPACPO>2.0.CO;2, 1984.

Leaitch, W.R., Barrie, L.A., Bottenheim, J.W., Li, S.-M., Shepson, P. and Yokouchi, Y.: Airborne observations related ozone depletion at polar sunrise. J. Geophys. Res., 99, 25499-25517, 10.1029/94JD02750, 1994.

Leaitch, W. R., Sharma, S., Huang, L., Toom-Sauntry, D., Chivulescu, A., Macdonald, A. M., von Salzen, K., Pierce, J. R., Bertram, A. K., Schroder, J. C., Shantz, N. C., Chang, R. Y. W. and Norman, A.-L.: Dimethyl sulfide control of the clean summertime Arctic aerosol and cloud, Elem. Sci. Anth., 1(1), 17, doi:10.12952/journal.elementa.000017, 2013.

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., 7663–7679, doi:10.5194/acp-16-7663-2016, 2016.