Prof. Daniel Cziczo
Co-Editor of Atmospheric Chemistry and Physics

Dear Dan,

Listed below are our responses to the comments from the reviewers of our manuscript. For clarity and visual distinction, the referee comments or questions are listed here in black and are preceded by bracketed, italicized numbers (e.g. *[1]*). Authors' responses are in red below each referee statement with matching numbers (e.g. *[A1]*). We thank the reviewers for carefully reading our manuscript and for their helpful suggestions!

Sincerely,

Allan Bertram
Professor of Chemistry
University of British Columbia

Short Comment #1

[1] I really enjoyed reading this paper. It is not surprising that there were differences in the IN between years. There could even be differences within a single year. It is important to note that the production mechanism determines how much of the SSML will be transferred to SSA...and there are difs in IN activity of sea spray produced by jet vs film drops (Wang, et al., PNAS, 2017, The role of jet and film drops in controlling the mixing state of submicron sea spray aerosols). The IN efficiency of jet drops has been shown in this publication to be higher than film drops–which goes against the common assumption that there will be more bioparticles in the SSML than in bulk seawater. Further, the # of jet vs film drops can change over the course of a bloom (see Fig 1 below taken from supp info in above referenced PNAS paper). It is important to remember that physical, biological, and chemical factors all control the formation and composition of SSA and will thus affect the IN activities.

[A1] We thank Professor Kim Prather for her short comment. In the revised manuscript, we have noted that the amount of microlayer transferred to sea spray aerosol depends on the production mechanism, and we have included a reference to the work by Wang et al. (2017).

Anonymous Referee #1

The manuscript titled "Revisiting properties and concentrations of ice nucleating particles in the sea surface microlayer and bulk seawater in the Canadian Arctic during summer" by Irish et al. presents an ice nucleation study using droplets generated from bulk and surface Arctic seawater. The authors use filtration to estimate the size of the ice nucleating agent. After heating the water, freezing temperatures of droplets decreased. Finally, the authors also measure salinity, numbers of bacteria and phytoplankton cells and correlate them to the temperature at which 10% of the droplets froze, T10, in each sample. Chlorophyll satellite data was also correlated with T10. Warmer freezing temperatures correlated with decreasing salinity and decreasing bacteria concentrations. The authors also found warmer freezing temperatures in this study compared with the one conducted in 2014.

[2] Overall, I find the manuscript unsuitable for ACP in the present form as I fail to see new findings in chemistry and physics. Furthermore, the results and data analysis are essentially identical to Irish et al. (2017) with the only difference of the sampling depth due to use of a rotating drum. Granted, the data here is new because it is taken at a later year and with a well defined scientific approach. However, the results and analysis in this manuscript are essentially copies of the author's previous paper without any scientific extension. In my major comments below, I have introduced some ideas to extend their work. As it is now, I do not find any conclusions anywhere in the manuscript and the word is not even written except for the title of the section. Please understand the difference between conclusions and observational results. Overall, I will not recommend publication in ACP.

[A2] We thank the referee for pushing us to dig deeper into the data and extend our analysis beyond what was presented in Irish et al. 2017. We also thank the referee for the constructive ideas to extend our work. In response to the referee's comment, we have investigated concentrations of stable isotopes of oxygen to determine the contributions of melting sea ice and terrestrial runoff (including that from melting glaciers and permafrost) to INP concentrations. This data provides new and interesting insights into the source of the INPs and is a major focus in the revised manuscript. In addition we have modified Section 4 to clearly state conclusions from the current study. Below we respond to the individual comments from the referee.

Major Comments

[3] The authors lack ice nucleation physics. There is no nucleation theory or any application of active sites for comparison with other studies. This is because there is no surface area estimate of insoluble material in their droplets. If water and filters are still available, then total particulate mass or surface area of insoluble particles could be obtained. For example, filters can be washed, dried and weighed and water can be used to get a size distribution from the flow cytometry. Another point is that correction for freezing point depression follows a water activity approach that Koop and Zobrist (2009) used for other biogenic ice nucleators. A plot of INP vs. $\Delta a_{w,het}$ could be made which allows the authors to discusses the effect (or lack thereof) of ionic activity on ice nucleation. $\Delta a_{w,het}$ could be compared with other biogenic ice nucleators.

[A3] Thank you for the suggestion. Unfortunately, the water and filters are no longer available. To address the referee's comments we have included a new section (3.5 Predictions of INP concentrations in the Arctic marine boundary layer) where we have normalised our freezing results to the mass of sea salt. In other words, from the measured concentrations of INPs and measured salinities we have calculated the number of INPs per unit mass of sea salt. This data was then used to extrapolate our measurements to the atmospheric conditions.

[4] The authors lack cloud and atmospheric physics. The authors could use SSA production formulations measured from previous studies to calculate the number of ice forming particles per liter of air. Vertical and horizontal motion (updraft and 10 m high wind speed) provided from meteorological data, or reanalysis can then be used to give some notion of the total ice nucleating particles in air. Does the T10 data or some other percentage of droplets frozen, correspond to a mixed phase cloud base or ice water path from satellite data?

[A4] To address the referee's comments, we have included a new section (3.5 Predictions of INP concentrations in the Arctic marine boundary layer) where we have estimated the concentrations of INPs in the atmosphere from our measurements.

[5] The authors lack ocean physics. There is countless studies documenting the enrichment or lack of enrichment of material in a microlayer with respect to bulk water. These materials can be surfactants, insoluble particles, or other materials such as proteins and polysaccharides. The interesting result from both the present manuscript and Irish et al. (2017) is that the ice nucleation ability is the same for bulk and microlayer water. This could mean that the ice nucleating particles are not surface active? What compounds in the ocean are uniformly distributed through the microlayer and bulk water? Are there soluble surfactants in bulk water that are transported to the microlayer? Is there a difference in surface tension between microlayer and bulk water?

[A5] In the 2016 measurements we saw an enhancement of the concentrations of INPs in the microlayer compared to the bulk in almost 50 % of the samples. We have revised the manuscript to try and make this point clearer.

[6] p.6 l.26 - p.7 l.1-5: Clearly, freezing temperatures warmer than pure water indicate heterogeneous droplet freezing. However, the "procedural blank" resulted in freezing temperatures at -16◦ C. How is it possible that freezing was observed below this temperature? On l.4-5 the answer is given that rinsing times were different (a fact not mentioned in the experimental section), so the freezing temperatures of the "blank were due to (cross-)contamination. How can we then compare any measurements of these to the blanks? In microlayer samples, Fig. S2a shows that no data below -16◦ C can be trusted. If these were the blanks for the experiments, the freezing curves should follow exactly the procedural blank data which would be seen as a discontinuity (step in the graph) of the freezing temperature around -16◦ C. This is not the case and so I would conclude that this blank has nothing to do

with the data at all and suggest there is no blank experiment for these data using the same procedures. How is this data at all trustable? I now understand why the authors use T10 and not median freezing as reported in Koop and Zobrist (2009), because if they did there would be no difference with their freezing points of microlayer water and the blanks. I am very concerned that freezing temperatures were due to cross contamination because of the lack of reproducibility for the blanks, as the freezing temperatures of the microlayer and bulk seawater do not follow the blanks at all.

[A6] The referee is correct there is some uncertainty in the microlayer samples that froze at temperatures less than the procedural blanks. As stated in the original manuscript, the freezing temperatures of the procedural blanks should be viewed as an upper limit to the background freezing temperatures, since prior to collecting the blanks, the sampler had not been rinsed as thoroughly as before collecting the microlayer samples. To address the referee's comments, in the revised manuscript, after the difference between the procedural blanks and the samples are first reported, we have only included freezing temperatures for the microlayer that were at warmer temperatures than the procedural blanks. Note, the same conclusions are reached in the manuscript if all the microlayer data are included or if only freezing temperatures warmer than the procedural blanks are included.

[7] p.6 l.26 - p.7 l.1-5: In the same section I find that freezing temperatures of filtered water (through the sampler) are less than ultra pure water (not through the sampler) by about 5-10◦ C. I doubt the seawater was more pure than the ultrapure water, so what is wrong here? Are the authors certain of the freezing point correction with the E-AIM model? Is there an uncertainty of ±5 − 10◦ C? I cannot accept this result and it makes me seriously doubt the accuracy of these experiments. The blank should be the lowest freezing temperature.

[A7] The microlayer samples and bulk seawater samples were passed through 0.02 μm filters, whereas, the ultrapure water was only passed through 0.22 μm filters. This difference in pore size can explain the difference in freezing temperatures, as pointed out by the referee. For example, in previous experiments we observed that the freezing temperature of ultrapure water decreases when the water is passed through a 0.02 μm filter compared to a 0.22 μm filter. To address the referee's comments, this information has been added to the revised manuscript.

[8] Figure S3: The ultrapure water data here is about 5◦ C different from the ultrapure water in Fig. S2. This indicates to me that the authors experiment is reproducible to ±5 ◦ C. This is a large uncertainty which is not stated in the paper.

[A8] We apologise for this error, and thank the referee for bringing it to our attention. In the original manuscript in Fig. S2 the laboratory blanks correspond to ultrapure water from a MilliQ system in 2016. By mistake, in Fig. S3, we plotted laboratory blanks that correspond to ultrapure water from a MilliQ water system in 2014. The freezing temperatures of the

laboratory blanks in 2014 were lower than the freezing temperatures of the laboratory blanks in 2016. This difference is most likely because the UV lamp and filter on our MilliQ water system had been recently changed in 2014, but not in 2016. In the revised manuscript, only the laboratory blanks corresponding to ultrapure water from a MilliQ system in 2016 have been included.

[9] p.3 l.12: It is not possible to name your instrument as an autosampler when for the majority of the stations the authors had to manually rotate the drum.

[A9] We have changed the name from "automated sampler" to a "sampling catamaran", and "automated sampling" to "sampling" throughout the manuscript.

[10] Equation 1: How does this equation account for the possibility of multiple INP's? Does the author observe more than one nucleation event in a droplet before it crystalizes? How can they tell if the droplet has 1 or 100 INPs inside? This method of analysis is 45 years old, do the authors have an updated analysis for quantifying freezing?

[A10] In our experiments, freezing of a single droplet is due to one nucleation event, since after a nucleation event, the freezing time of a droplet is very short (< 1 second). We think the statement in the original manuscript "This equation accounts for the possibility of multiple INPs containing in a single droplet" has led to some confusion. This statement has been removed from the revised manuscript, and additional discussion on Eq. 1 has been added to improve clarity.

[11] p.8 l.23-31: The logic is flawed here. Melting sea ice decreases salinity and releases bacteria to the ocean (p.24-26). Decreasing salinity yields warmer T10 (Fig. 6 lower left). Decreasing salinity yields increasing bacteria (p.8 l.24-27). Finally, increasing bacteria yield lower T10 (Fig. 6 upper left). So why do I read in p.8 l.30-31 that bacteria are fewer in melting sea ice and that bacteria increasing ice nucleation ability? This argument is highly contradictory.

[A11] We think the referee misunderstood our argument/logic. However, in the revised manuscript we have removed this discussion.

[12] p.8 l.23-31: The most major problem I see in the manuscript is that it is a copy of the authors previous manuscript. The majority of section 4 is a repeat of Irish et al. (2017). The last paragraph of section 4 states that the only new finding is that concentrations are higher in 2016 than in 2014, but dismisses this finding due to a different sampler. This study ended in August 2016, but the Irish et al. (2017) paper (using only 2014 data) was submitted April 2017. Why wasn't the data presented in this manuscript used in Irish et al. (2017)? In any case, the authors should extend their work with new data and new discussion that includes physical and chemical understanding before I recommend publication in ACP.

[A12] Again, we thank the referee for pushing us to extend our analysis beyond what was presented in Irish et al. (2017). As mentioned above, to address the referee's comment, we have investigated stable isotopes of oxygen to determine the contribution of melting sea ice and terrestrial runoff (including that from melting glaciers and permafrost) to INP concentrations. This data has provided new and interesting insights into the source of the INPs measured. This new data is a major focus in the revised manuscript.

Minor Comments

[13] What are the "properties" of ice nucleating particles? How is that different from "freezing properties"? How is that different from "ice nucleation properties"? Properties of the microlayer? This word is used countless times but is never defined. Please include a sentence or 2 listing the actual property the author is talking about. I give one example on p.7 l.13-15. There I am told there is a positive correlation between freezing properties of microlayer and bulk water. How many properties correlate and what is actually being correlated? Please search for the word and replace it with something that is specific and measurable.

[A13] In the revised manuscript we have replaced freezing properties and ice nucleation properties with a more specific and measurable term.

[14] How can the droplet freezing technique analyse videos (p.4 l.11)? That must be automated or done by a person?

[A14] The authors have changed the wording in this sentence to the following:

"The freezing temperature of each droplet was determined visually from the videos"

[15] SYBR Green stains nucleic acids (p.5 l.25) which means it stains bacteria, phytoplankton, cyanobacteria, archaea and everything biogenic for that matter? The concentration derived from SYBR Green should be subtracted by the phytoplankton counts to get bacteria counts? In addition, there should be other things besided living organisms that stain, for example other biogenic particles such as cell fragments or gel-like particles. Are the authors counting this as well? Is there another name for these counts that should be used?

[A15] Yes, SYBR Green stains all DNA and RNA, but bacteria are easily discriminated from other organisms (or detritus or transparent exopolymeric particles) by their size (side scatter) and fluorescence intensity. In addition, autotrophs stained with SYBR Green are discriminated from heterotrophic bacteria by their chlorophyll a fluorescence. To address the referee's comments this information has been added to the revised manuscript.

[16] There is no reason for a 2 sentence long subsection (section 2.5). Please incorporate this elsewhere.

[A16] We have incorporated this sentence into section 3.1.

[17] p.6 l.22: It is not nice to the reader to be directed to the supplement for the first result. Please let me read about the main, exciting results first and then take me to those which are supplementary.

[A17] To address the referee's comments, Fig. S2 has been moved from the supplement to the main text.

[18] p.6 l.27: "In addition,...also..." is repetitive.

[A18] "In addition" has been removed in the revised manuscript.

[19] p.8 l.16-17: Why is it important to say that similar water masses were samples? The authors sampled from similar locations so why say more? Please tell me what exactly is similar about the water masses besides salinity.

[A19] To address the referee's comment, we have removed "which suggests that we sampled similar water masses in both years at those locations".

[20] p.10 l.12: The authors did not measure inter-annual variability. They did measure for a month in 2 different years.

[A20] We have removed "inter-annual" to address the referee's comment.

References

V. E. Irish, P. Elizondo, J. Chen, C. Chou, J. Charette, M. Lizotte, L. A. Ladino, T. W. Wilson, M. Gosselin, B. J. Murray, E. Polishchuk, J. P. D. Abbatt, L. A. Miller and A. K. Bertram, Atmos. Chem. Phys., 2017, 17, 10583–10595.
T. Koop and B. Zobrist, Phys. Chem. Chem. Phys., 2009, 11, 10839–10850.

Anonymous Referee #2

Irish et al. investigated the ice nucleating particles (INP) in the sea surface microlayer and bulk seawater in the Canadian Arctic during summer of 2014 and 2016. This study measured INP concentrations using the droplet freezing technique. It is also investigated the effects of heat and filtration treatments on the INP concentrations. The manuscript concluded that spatial patterns of INPs are similar between the summers of these two years, but average INP concentrations are higher in 2016 and in some cases, there is INPs enhancement in the microlayer. The manuscript provides a set of comparison (at the "same" sampling sites) for INP measurements at important geographic location (Arctic) where data are overall limited. The topic of this manuscript is within the scope of this journal. There are some issues and comments should be addressed or considered before it is recommended for the publication.

[21] For microlayer samples, the sampling devices and procedures are different when considering what is sampled (the sampling thickness of microlayer). As mentioned in P7/Line 20, how this is contributing to the difference in INP measurements in 2014 and 2016?

[21] As stated in line 20, the microlayer samples would be "diluted" by bulk sample. We have tried to make this clearer in the revised manuscript.

[22] Justification of using T10 (e.g., why not using T50) for statistical analysis is needed.

[22] T10-values were chosen since they are a convenient way to summarise the freezing data, to be consistent with our previous study, and because T_{10}-values of the samples were at warmer temperatures than the field blanks in almost all cases. Similar conclusions for bulk seawater would be reached in our manuscript if other values (e.g. T50-values were used). Initially we planned on including results of correlations of T50 values for both microlayer and bulk seawater samples. However, if we remove T50 value data from below the procedural blanks there are not enough data points for the microlayer samples. On the other hand, we have enough T50 value data for the bulk seawater. Therefore, in the revised manuscript we have included T50 values for the bulk seawater to address the referee's comments.

[23] There is a concern when the manuscript states the equation (1) accounts for the possibility of multiple INPs within a single droplet. It is better to elaborate the point that the authors try to convey.

[23] See A10 above.

[24] It is not clear how many droplets were investigated for each sample, only 15-30 droplets as stated in P4/Line7?

[24] We have clarified the number of droplets that were investigated for each sample by adding the following to section 2.2.1:

"In the freezing experiments three hydrophobic glass slides (Hampton Research, Aliso Viejo, CA, USA) were placed directly on a cold stage (Whale et al., 2015) and between 15 to 30 droplets of the sample, with volumes of 1 μL each, were deposited onto each of the glass slides using a pipette. A total of 45 to 90 droplets were analysed for each sample."

[25] Is there in situ Chl-a measurements which would be more accurate and can be used to correlated to T10?

[25] To address the referee's comment we have investigated the correlation between T10 and in situ Chl-a measurements, in addition to satellite Chl-a data.

[26] It would be benefit to the community if the manuscript can identify some possible issues when investigating the annual or seasonal variability in INPs over the ocean. This has been done in part in the manuscript, such as the last paragraph.

[26] To address the referee's comment, in the Conclusions, we have expanded on possible issues in the reported annual or seasonal variability in INPs.

Revisiting properties and concentrations of ice nucleating particles in the sea surface microlayer and bulk seawater in the Canadian Arctic during summer

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Abstract. Despite growing evidence that the ocean is an important source of ice nucleating particles (INPs) in the atmosphere, our understanding of the properties and concentrations of INPs in ocean surface waters remain insufficient. We have investigated INPs in sea surface microlayer and bulk seawater samples collected in the Canadian Arctic during the summer of 2016. Consistent with our 2014 studies, we observed that INPs were ubiquitous in the microlayer and bulk seawaters; heat and filtration treatments reduced INP activity, indicating that the INPs were likely heat-labile biological materials between 0.22 and 0.02 µm in diameter; there was a strong negative correlation between salinity and freezing temperatures; and concentrations of INPs could not be explained by chlorophyll *a* concentrations. Unique in the current study, the spatial distributions of INPs were similar in 2014 and 2016, and the concentrations of INPs were strongly correlated with meteoric water (terrestrial runoff plus precipitation). These combined results suggest that meteoric water may be a major source of INPs in the sea surface microlayer and bulk seawater in coastal regions, at least in the Arctic. In addition, based on the measured concentrations of INPs in the microlayer and bulk seawater, we estimate that the concentrations of INPs from the ocean in the Canadian Arctic marine boundary layer range from approximately 10^{-4} L^{-1} to < 10^{-6} L^{-1} at -10 °C.

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Comment [1]: Addresses [2] and [12]

1 Introduction

Ice-nucleating particles (INPs) are atmospheric particles that catalyse the formation of ice crystals in clouds at warmer temperatures and lower vapour saturations than needed for homogeneous ice nucleation, thereby influencing cloud properties and potentially impacting the Earth's radiative properties and hydrological cycle (Boucher et al., 2013; Lohmann, 2002; Lohmann and Feichter, 2005; Tan et al., 2016). Only a small subset of atmospheric particles (about 1 in 10^6) act as

INPs (DeMott et al., 2010, 2016). INPs can catalyse the formation of ice by four different mechanisms: contact freezing, condensation freezing, deposition freezing, and immersion freezing. Immersion freezing, which is the focus of this paper, occurs when an INP immersed in a supercooled water droplet initiates freezing.

One potential source of INPs to the atmosphere is the ocean. Oceans dominate the Earth's surface coverage, and sea spray generates a large fraction of the aerosol mass in the atmosphere (Lewis and Schwartz, 2004). Several pieces of evidence suggest that the ocean is an important source of INPs to the atmosphere. For example, INPs have been measured in seawater and the microlayer (Fall and Schnell, 1985; Irish et al., 2017; Rosinski et al., 1988; Schnell, 1977; Schnell and Vali, 1975, 1976; Wilson et al., 2015) and in the air above the ocean (Bigg, 1973; Rosinski et al., 1986, 1987, 1988). Marine microorganisms and their by-products can also catalyse ice formation (Burrows et al., 2013; Knopf et al., 2011; Rosinski et al., 1987; Wilson et al., 2015). In addition, modelling studies have illustrated that INP concentrations from the ocean can be important when other sources of INPs, such as mineral dust, are low (Huang et al., 2018b; Vergara-Temprado et al., 2017; Yun and Penner, 2013). Sea spray aerosol is generated at the ocean surface (Blanchard, 1964) and varies considerably in composition, depending on the production mechanism. The production mechanism determines how much of the sea surface microlayer (herein referred to as the microlayer) compared to bulk seawater will be transferred to the sea spray aerosol (Wang et al., 2017). A recent study has shown that the ice nucleating ability of sub-micrometre particles formed from jet drops is more efficient than those formed from film drops (Wang et al., 2017).

Despite growing evidence that the ocean is an important source of INPs in the atmosphere, our understanding of the properties and concentrations of INPs in the microlayer and bulk seawater remain limited. For example, information on the spatial and temporal distributions of INPs in the microlayer and bulk seawater has not been investigated in sufficient detail. Nevertheless, this type of information is needed to improve predictions of INP emissions to the atmosphere from the ocean.

Recently, we reported the properties and concentrations of INPs in microlayer and bulk seawater samples collected in the Canadian Arctic during the summer of 2014 (Irish et al., 2017). We found INPs were ubiquitous in the microlayer and bulk seawater. Heat and filtration treatment of the samples indicated that the INPs were likely heat-labile biological materials with sizes between 0.02 and 0.22 µm in diameter. In addition, we found that the freezing activity of the microlayer and bulk seawater samples was inversely correlated with salinity, implying that the INPs were associated with melting sea-ice or terrestrial runoff. We also observed that the freezing temperatures of the microlayer samples were similar to those of the bulk seawater, in almost all cases.

Building on our previous studies, we returned to the Canadian Arctic during the summer of 2016 to further investigate the properties and concentrations of INPs in Arctic Ocean waters. Locations where samples were collected during both years are indicated in Fig. 1, and the detailed sampling dates and locations in 2016 are given in Table 1. By comparing results from 2016 with those from 2014, we investigate whether the properties, concentrations and spatial profiles of the INPs vary from year-to-year at similar locations. In addition, using stable isotopes of oxygen in the water molecules, we investigated further the possible importance of melting sea-ice and meteoric water (terrestrial runoff plus precipitation) to the

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INP concentrations. Measured concentrations of INPs in microlayer and bulk seawater were also used to estimate concentrations of INPs in the Arctic marine boundary layer.

Victoria Irish 2019-1-31 1:00 PM
Comment [4]: Addresses [2] and [12]

2 Experimental

2.1 Collection methods

During July and August of 2016 samples were collected from the eastern Canadian Arctic on board the CCGS *Amundsen* as part of the NETCARE project (Fig. 1 and Table 1). Supplementary details, including notes and photographs taken at each sampling station, are provided in Table S1.

2.1.1 Sampling method

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In contrast to 2014, when we collected microlayer samples manually using a glass plate sampler (Irish et al., 2017), in 2016, microlayer samples were collected using rotating glass plates attached to a sampling catamaran (Shinki et al., 2012). At station 1, the sampling catamaran was deployed from a small inflatable, rigid-hull boat at least 500 m away from the CCGS *Amundsen*. The sampling catamaran was remotely driven at least 20 m away from the small inflatable, rigid-hull boat before the rotating glass plates were activated remotely. A rotation rate of 10 revolutions per minute was used. From station 2 onwards, the remote control of the rotating glass plates on the sampling catamaran failed. Subsequently, the sampling catamaran was kept on the upwind side of the small inflatable, rigid-hull boat with its engine turned off, at least 500 m away from the CCGS *Amundsen* to avoid contamination, and the glass plates were rotated manually between 11 to 18 revolutions per minute. The microlayer that adhered to the plates from each rotation was scrapped off with fixed Teflon wiper blades into a manifold and then pumped through Teflon tubing into high-density polyethylene (HDPE) Nalgene bottles (ranging from 250 mL to 2 L in volume). The thickness of the microlayer collected was approximately 80 µm based on the rotation rate (between 11 - 18 revolutions per minute), the average volume collected (3 L) and an average collection time (18 minutes). Bulk seawater samples were collected at the same times and locations as the microlayer samples through Teflon tubing suspended 0.2 m below the sampling catamaran. The bulk seawater was pumped, using peristaltic pumps, into HDPE Nalgene bottles (ranging from 250 mL to 2 L in volume). After collection, the Nalgene bottles containing the microlayer and bulk seawater samples were kept cool in an insulated container. Upon returning to the ship, the samples were homogenised by gently (so as to not break up cells that may be present in the samples) inverting them at least ten times and then sub-sampled into smaller bottles for subsequent analyses.

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Comment [7]: Addresses [9]

The glass plates, aluminium manifold, Teflon tubing and all Nalgene bottles were sterilised first with bleach, then cleaned with isopropanol and finally rinsed with ultrapure water. After cleaning, the sampler was further rinsed by collecting then discarding microlayer and bulk seawater for approximately 2 minutes, before samples were retained. Field blanks for the microlayer were prepared by running approximately 1 L of ultrapure water for approximately 1 minute over the glass plates, and through the manifold and tubing used to sample the microlayer. Field blanks for bulk seawater were prepared by running approximately 1 L of ultrapure water for approximately 1 minute through the tubing used to sample bulk seawater.

2.2 Ice nucleation properties of the samples

2.2.1 Droplet freezing technique and INP concentrations

INP concentrations as a function of temperature were determined using the droplet freezing technique (DFT; Koop et al., 1998; Vali, 1971; Whale et al., 2015; Wilson et al., 2015). Sub-samples of the microlayer and bulk seawater were kept in 15 mL polypropylene tubes between 1 to 4 °C for a maximum of 4 hours before INP analysis.

In the freezing experiments three hydrophobic glass slides (Hampton Research, Aliso Viejo, CA, USA) were placed directly on a cold stage (Whale et al., 2015) and between 15 to 30 droplets of the sample, with volumes of 1 µL each, were deposited onto each of the glass slides using a pipette. A total of 45 to 90 droplets were analysed for each sample. A chamber with a webcam attached to the top of it was placed over the slides to isolate them from ambient air, and a flow of ultrapure N_2 was passed through the chamber as described by Whale et al. (2015). The droplets were cooled at a constant rate of 10 °C/min from 0 °C to -35 °C and the webcam recorded videos of the droplets during cooling. The freezing temperature of each droplet was determined visually from the videos. For comparison, laboratory blanks (distilled water further purified with a Millipore system and passed through a 0.22 µm filter), as well as the field blanks, were analysed for INPs using the DFT.

The concentration of INPs per unit volume of liquid, *[INP(T)]*$_{vol,liq}$, was determined from each freezing experiment using the following equation (Vali, 1971):

$$[INP(T)]_{vol,liq} = -\ln\left(\frac{N_u(T)}{N_o}\right) N_o \cdot \frac{1}{V}, \quad (1)$$

where $N_u(T)$ is the number of unfrozen droplets at temperature T, N_o is the total number of droplets used in the experiment, and V is the volume of all droplets in a single experiment. Equation 1 represents the concentrations of INPs active at temperature, T, and has been justified using Poisson's law (Vali, 1971). The use of Eq. 1 assumes that the concentration of INPs active at temperature T is independent of the cooling rate, which is a reasonable approximation for many atmospherically relevant INPs (Murray et al., 2011; Welti et al., 2012; Wheeler et al., 2015; Wright and Petters, 2013).

2.2.2 Heating and filtration tests

The freezing temperatures of the microlayer and bulk seawater samples were also measured after they had been passed through syringe filters with three different pore sizes (Whatman 10 µm pore size PTFE membranes, Millex–HV 0.22 µm pore size PTFE membranes, and Anotop 25 0.02 µm pore size inorganic Anopore™ membranes) (Irish et al., 2017;

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Wilson et al., 2015). The sub-samples of the microlayer and bulk seawater were left for a maximum of 4 hours before filtration followed by INP analysis.

The freezing temperatures of the microlayer and bulk seawater samples were also measured after they had been heated to 100 °C (Christner et al., 2008; Irish et al., 2017; Schnell and Vali, 1975; Wilson et al., 2015). In this case, samples were stored at -80 °C for less than 6 months and analysed in the laboratory at the University of British Columbia. Before heating the stored samples, they were completely thawed and homogenised by inverting at least ten times. The freezing temperatures were determined after heating the samples at 100 °C for approximately an hour. Separate experiments show that storage of the samples at -80 °C for a maximum of six months does not affect the INP concentrations (see Fig. S1 in the Supplement).

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2.2.3 Corrections for freezing temperature depression

The measured freezing temperatures were adjusted for the depression of the freezing point by the presence of salts to generate freezing temperatures applicable to salt-free conditions (salinity = 0 g kg^{-1}), which is relevant for mixed phase clouds. In short, water activities of the samples were calculated from measured salinities using an Aerosol Thermodynamic Model (http://www.aim.env.uea.ac.uk/aim/aim.php; Friese and Ebel, 2010; Wexler and Clegg, 2002). Next, the water activity of an ice-salt solution at the median freezing temperature was calculated. The freezing temperature at salinity = 0 g kg^{-1} was then calculated from the difference in these two water activities following the procedure of Koop and Zobrist (2009).

The salinities of the microlayer and bulk seawater samples were measured within 10 minutes of sample collection using a hand-held salinity probe (SympHony; VWR, Radnor, PA, USA). The salinities (measured in practical salinity units (psu)) were corrected using a linear fit to salinometer (Guideline Autosal 8400 B) readings on parallel discrete samples. The correction for freezing point depression by the presence of salts based on the measured salinities ranged from 1.2 to 2.6 °C.

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2.3 Bacterial and phytoplankton abundance

The abundances of heterotrophic bacteria and phytoplankton < 20 µm (i.e., phycoerythrin-containing cyanobacteria, phycocyanin-containing cyanobacteria and autotrophic eukaryotes) were measured by flow cytometry. Duplicate 4 mL subsamples were fixed with glutaraldehyde (Grade I; 0.12 % final concentration; Sigma-Aldrich G5882) in the dark at room temperature for 15 min, flash-frozen in liquid nitrogen and then stored at -80 °C until analysis. Samples for heterotrophic bacteria enumeration were stained with SYBR Green I (Invitrogen) following Belzile et al. (2008) and counted with a BD Accuri C6 flow cytometer using the blue laser (488 nm). The green fluorescence of nucleic acid-bound SYBR Green I was measured at 525 nm. Archaea could not be discriminated from bacteria using this protocol; therefore, hereafter, we use the term bacteria to include both archaea and bacteria with high nucleic acid (HNA) content and low nucleic acid (LNA) content. SYBR Green I stains all DNA and RNA, but bacteria and archaea are easily discriminated from other organisms (or detritus or transparent exopolymeric particles) by their size (side scatter) and fluorescence intensity. In addition, autotrophs stained with SYBR Green I are discriminated from heterotrophic bacteria by their chlorophyll *a* fluorescence.

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Samples for < 20 µm phytoplankton abundances were analyzed using a CytoFLEX flow cytometer (Beckman Coulter) fitted with a blue (488 nm) and red laser (638 nm), using CytoExpert v2 software. Using the blue laser, forward scatter, side scatter, orange fluorescence from phycoerythrin (582/42 nm BP) and red fluorescence from chlorophyll (690/50 nm BP) were measured. The red laser was used to measure the red fluorescence of phycocyanin (660/20 nm BP). Polystyrene microspheres of 2 µm diameter (Fluoresbrite YG, Polysciences) were added to each sample as an internal standard (Marie et al., 2005; Tremblay et al., 2009).

2.4 Stable oxygen isotopes and water volume fractions

To investigate the possible importance of sea-ice melt and meteoric water (terrestrial runoff plus precipitation) to INP concentrations, we determined $\delta^{18}O$ in the samples. Measurements of $\delta^{18}O$ have been used in the past to distinguish between sea-ice melt and meteoric water in the Arctic Ocean (Alkire et al., 2015; Macdonald et al., 1995; Östlund and Hut, 1984; Tan and Strain, 1980). $\delta^{18}O$, a measure of the ratio of oxygen-18 (^{18}O) to oxygen-16 (^{16}O) in water molecules, is expressed as per mil (‰) deviations from Vienna Standard Mean Ocean Water (V-SMOW):

$$\delta^{18}O = \left(\frac{\left(\frac{^{18}O}{^{16}O} \right)_{\text{sample}}}{\left(\frac{^{18}O}{^{16}O} \right)_{\text{standard}}} - 1 \right) \times 1000 \text{‰}, \qquad (2)$$

where standard corresponds to (V-SMOW). The $\delta^{18}O$ results are expressed in per mil (‰) deviations from V-SMOW. Samples were analysed at the GEOTOP-UQAM stable isotope laboratory at the Université du Québec à Montréal using the CO_2 equilibration method (Ijiri et al., 2003), where 200 µL of sample was equilibrated with CO_2 for 7 h at 408 °C. The CO_2 was then analysed on a Micromass Isoprime™ universal triple collector mass spectrometer in dual inlet mode with an AquaPrep™ system (Isoprime Ltd., Cheadle, UK). Two internal reference water samples ($\delta^{18}O$ = -6.71 ‰ and –20.31 ‰) were used to normalise the sample data. Uncertainties in replicate measurements are ± 0.05 ‰ (1σ). $\delta^{18}O$-values were determined for all stations, except stations 1, 10, and 11.

From the measured $\delta^{18}O$ values and measured salinities of the samples, the water volume fractions of sea-ice melt (f_{SIM}), water volume fractions of meteoric water (f_{MW}), and water volume fractions of seawater (f_{sw}) were calculated using the following conservation equations (Yamamoto-Kawai et al., 2005):

$$f_{SIM} S_{SIM} + f_{MW} S_{MW} + f_{SW} S_{SW} = S_{obs} \qquad (3)$$

$$f_{SIM}\delta^{18}O_{SIM} + f_{MW}\delta^{18}O_{MW} + f_{SW}\delta^{18}O_{SW} = \delta^{18}O_{obs} \quad (4)$$

$$f_{SIM} + f_{MW} + f_{SW} = 1 \quad (5)$$

where S represent salinity and the subscripts *obs*, *SIM*, *MW*, and *SW* represent observed, sea-ice melt, meteoric water, and seawater, respectively. For S_{SIM}, S_{MW}, $\delta^{18}O_{SIM}$, and $\delta^{18}O_{MW}$ we assumed 4 g kg^{-1}, 0 g kg^{-1}, 0.5 ‰, -20 ‰, respectively, in Eqs. 3-4 (Burgers et al., 2017). The values of S_{SW} and $\delta^{18}O_{SW}$ depend on the reference seawater chosen. In our studies the samples could have been influenced by either Arctic outflow waters (S_{SW} = 33.1 g kg^{-1} and $\delta^{18}O_{SW}$ = -1.53 ‰) or west Greenland current waters (S_{SW} = 33.5 g kg^{-1} and $\delta^{18}O_{SW}$ = -1.27 ‰) (Burgers et al. (2017). When calculating f_{SIM}, f_{MW}, and f_{sw} values we used S_{SW} = 33.3 ± 0.2 g kg^{-1} and $\delta^{18}O_{SW}$ = -1.40 ± 0.13 ‰, which corresponds to average and limits for Arctic outflow waters and west Greenland current waters.

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2.5 Chlorophyll *a*

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Chlorophyll *a* concentrations for case 1 waters (waters dominated by phytoplankton) were retrieved from the GlobColour project website (http://globcolour.info, *ACRI-ST, France*). The GlobColour project provides a high resolution, long time series of global ocean colour by merging data from several satellite systems. The data used here include retrievals from either or both the Moderate Imaging Spectrometer (MODIS) on the Aqua Earth Observing System (EOS) mission and the Visible/Infrared Imager Radiometer Suite (VIIRS) aboard the Suomi National Polar-orbiting Partnership satellite. For this work we used data merged with weighted averaging, where weightings are based on the sensor and/or product. For more information regarding the weighted averaging refer to the GlobColour Product User Guide (http://www.globcolour.info/CDR_Docs/GlobCOLOUR_PUG.pdf). In this study 8-day data were used to achieve the best balance between spatial coverage (1/24°, ~4 km) and high time resolution. For the chlorophyll *a* concentration at a given sampling location, we used the grid cell corresponding to the location of that station. We determined the chlorophyll *a* concentration at all stations except station 8.

Chlorophyll *a* concentrations were also measured *in situ*. Samples for *in situ* chlorophyll *a* determination were filtered onto Whatman GF/F glass-fibre filters. Chlorophyll *a* concentrations were measured using a Turner Designs AU-10 fluorometer, after 24 h extraction in 90% acetone at 4 °C in the dark (acidification method: Parsons et al. 1984).

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3 Results and Discussion

3.1 Concentrations of INPs

The fraction frozen curves for all microlayer and bulk seawater samples measured in 2016 are shown in Fig. 2. Also shown for comparison are the fraction frozen curves of the samples after filtration through a 0.02 µm Anotop 25 syringe

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filter, the fraction frozen curves for the laboratory blanks (ultrapure water passed through a filter with a 0.22 µm pore size), and fraction frozen curves for field blanks (ultrapure water passed through the sampling catamaran). The laboratory blanks are at similar or warmer temperatures than the samples passed through a 0.02 µm Anotop 25 syringe filter. Differences are most likely due to the difference in pore sizes of the filters used: the laboratory blanks were passed through filters with a 0.22 µm pore size whereas the samples were passed through filters with a 0.02 µm pore size. Previous experiments in our laboratory have shown that ultrapure water passed through a filter with a 0.02 µm pore size can freeze at slightly colder temperatures than ultrapure water passed through a filter with a 0.22 µm pore size (Fig. S2).

For the bulk seawater, all untreated samples froze at temperatures warmer than the laboratory and field blanks. Freezing temperatures as warm as -6 °C were observed. These results indicate the presence of ice-active material in all bulk seawater samples. For the microlayer samples, all samples froze at temperatures warmer than laboratory blanks. In addition, most samples froze at temperatures warmer than the field blanks. These results also indicate that most microlayer samples contained ice-active material. For some of the samples, the freezing temperatures of the field blanks were warmer than the freezing temperatures of the samples. However, the freezing temperatures of the field blanks should be viewed as an upper limit to the background freezing temperatures, since prior to collecting the field blanks, the sampler had not been rinsed as thoroughly as before collecting the microlayer samples. For the remainder of this paper we will only show and discuss freezing data that were at warmer temperatures than the field blanks.

In Fig. 3 the concentrations of INPs, $[INP(T)]_{vol,liq}$, measured in 2016 are compared with concentrations measured in 2014 (sample locations for both years shown in Fig. 1). In both 2016 and 2014, the concentrations of INPs vary by at least 2 orders of magnitude at a given temperature, but warmer freezing temperatures were observed in 2016 compared to 2014.

Figure 4 shows the correlation between T_{10}-values (temperatures at which 10 % of the droplets froze) in the microlayer and bulk seawater samples from 2016. We focus on T_{10}-values to be consistent with our previous studies and because T_{10}-values of the samples were at warmer temperatures than the field blanks in almost all cases. Pearson correlation analysis was applied to many of the variables measured in this study to compute correlation coefficients (r). P values were also calculated to determine the significance of the correlations at the 95 % confidence level ($p < 0.05$). A strong positive correlation ($r = 0.89$ and $p < 0.001$) was observed between the T_{10}-values of the microlayer and the T_{10}-values of the bulk seawater, consistent with our previous observations (Irish et al., 2017).

In 2016, 4 out of 9 samples had warmer T_{10}-values in the microlayer compared to bulk seawater (Fig. 4). However, in the 2014 samples, only 1 out of 8 samples had warmer T_{10}-values in the microlayer compared to bulk seawater (Irish et al., 2017). The difference between 2016 and 2014 may simply be due to year-to-year variations in the properties of the microlayer relative to the bulk seawater related to variations in oceanic conditions. For example, Collins et al. (2017) documented differences in the activity of marine microbial communities between our 2016 and 2014 campaigns in the Canadian Arctic. In addition, the differences between 2016 and 2014 may be related to sampling techniques. In 2014 the glass plate technique collected a layer that was up to 220 µm thick. In contrast, in 2016 a thinner layer (approximately 80 µm thick) was collected. In the thicker layers collected in 2014, the microlayer INPs would have been diluted by bulk waters by

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roughly a factor of 2.8. Additional studies of how INP activity varies as a function of microlayer sample thickness are necessary to resolve this issue.

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3.2 Effect of heating and filtering the samples

Figure S3 shows that the fraction frozen curves were shifted to colder temperatures after the microlayer and bulk seawater samples were heated to 100 °C. These results are similar to what we observed for the 2014 samples (Irish et al., 2017). This suggests that the ice-active material we found in the microlayer and bulk seawater samples was likely heat-labile biological material (Christner et al., 2008).

Figure S4 shows that the temperature at which droplets froze in microlayer and bulk seawater samples significantly decreased after the samples were passed through a 0.02 µm filter, but not through 10 µm or 0.22 µm filters. A similar result was observed in the 2014 samples (Irish et al., 2017), suggesting that the INPs in the microlayer and bulk seawater were between 0.22 µm and 0.02 µm in size.

3.3 Spatial distributions of INPs in the Canadian Arctic

The spatial distributions of T_{10}-values for bulk seawater samples in both 2016 and 2014 are shown in Fig. 5. The spatial distributions are similar for microlayer samples (Fig. S5). In each panel the colour scales have been adjusted to easily compare the general pattern of T_{10}-values between years. For both 2014 and 2016, the T_{10}-values for samples taken from northern Baffin Bay and Nares Strait between Greenland and Canada, above 75 °N, are generally lower than the T_{10}-values elsewhere. To further investigate the similarities in spatial patterns between 2014 and 2016, we compared T_{10}-values at sampling sites in close proximity for the two years (Fig. 6a). A strong positive correlation ($r = 0.93$, $p < 0.001$) was found between the T_{10}-values measured in 2014 and T_{10}-values measured in 2016 at those proximal locations (Fig. 6b), suggesting that the general spatial distribution of T_{10}-values measured in 2014 and 2016 were similar even though warmer freezing temperatures were observed in 2016 compared to 2014 (Fig. 3).

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3.4 Correlations with biological, chemical, and physical properties of the bulk seawater

In Table 2 and Fig. 7, we present correlations between T_{10}-values for bulk seawater in 2016 and heterotrophic bacterial abundance, phytoplankton (including 0.2-20 µm photosynthetic eukaryotes and cyanobacteria) abundance, salinity, and temperature. The strongest correlation was with salinity ($r = -0.83$, $p \leq 0.001$). Similar correlations were observed for T_{50}-values (Table S2). One possible explanation for the negative correlation between T_{10}-values and salinity is a non-colligative effect of sea salt on the freezing temperature. For example, solutes can impact freezing temperature by blocking INP active sites (Kumar et al., 2018). To test this hypothesis, we varied the salinity in one of the microlayer samples (Station

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4) by adding commercial sea salt (Instant Ocean™), while keeping the concentration of ice nucleating material in the samples constant (see Supplement Section S1for more details). As the salinity of the sample was increased from 29 to 55 g kg^{-1}, the T_{10}-values for the salinity-enhanced samples (after correcting for freezing point depression) varied by less than the uncertainty in the measurements (Fig. S6 in the Supplement). These results suggest that sea salt does not have a non-colligative effect on the freezing temperature of the samples, at least not for the microlayer sample tested (Station 4). Consistent with these results, non-colligative effects have not been observed in previous studies of immersion freezing with seawater and sodium chloride solutions (Alpert et al., 2011a, 2011b; Knopf et al., 2011; Wilson et al., 2015; Zobrist et al., 2008).

As suggested in our earlier study (Irish et al., 2017), another possible explanation for the negative correlation between salinity and freezing temperature is that the INPs are associated with either sea-ice melt or terrestrial runoff (including that from melting glaciers or permafrost). Melting sea-ice and terrestrial runoff have lower salinities than seawater. In addition, sea-ice melt and terrestrial runoff often contain microorganisms and their exudates, which can be especially effective INPs (Assmy et al., 2013; Boetius et al., 2015; Christner et al., 2008; Ewert and Deming, 2013; Fernández-Méndez et al., 2014).

Figure 8 shows the T_{10}-values of bulk seawater as a function of the water volume fraction of meteoric water (f_{MW}) and water volume fraction of sea-ice melt (f_{SIM}) calculated using Eqs. 3-5. A strong positive correlation ($r = 0.91$, $p < 0.001$) was observed between T_{10} and f_{MW} in the samples. In contrast, the correlation between T_{10} and f_{SIM} in the samples was weaker and the p-value was close to 0.05 ($r = 0.63$, $p = 0.048$). These combined results suggest that meteoric water (terrestrial runoff plus precipitation) may be a major source of INPs in this area and more important than sea-ice melt. Terrestrial runoff has also been identified as a major source of INPs in temperate rivers and lakes (Knackstedt et al., 2018; Larsen et al., 2017; Moffett et al., 2018).

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3.4.1 Chlorophyll *a* correlations

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Figure 9 shows correlations between the chlorophyll data retrieved from GlobColour and the T_{10}-values for the microlayer and bulk seawater. The correlations between T_{10}-values in the microlayer or bulk seawater and chlorophyll *a* are not statistically significant. Figure S7 shows the relationship between the *in situ* chlorophyll *a* concentrations and the T_{10}-values for the microlayer and bulk seawater. Again, the correlations are not statistically significant. Our results from satellite and *in situ* chlorophyll *a* data are consistent with recent work by Wang et al. (2015), who showed that INP concentrations in sea spray aerosol emitted during a mesocosm tank experiment were not simply coupled to chlorophyll *a* concentrations.

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3.5 Predictions of INP concentrations in the Arctic marine boundary layer

In the following, we provide an initial estimate of the concentration of INPs in the Arctic marine boundary layer based on our freezing results. First, we calculated the concentration of INPs in the liquid per unit mass of sea salt, $[INP(T)]_{mass,salt}$, using the following equation:

$$[INP(T)]_{mass,salt} = -\ln\left(\frac{N_u(T)}{N_o}\right)N_o \cdot \frac{1}{V\rho S} \tag{6}$$

where ρ is the density of water and S is the salinity of the seawater. Plots of $[INP(T)]_{mass,salt}$ as a function of temperature calculated from our freezing results are shown in Fig. S8. From $[INP(T)]_{mass,salt}$, the concentration of INPs per unit volume of air in the Arctic marine boundary layer, $[INP(T)]_{vol,air}$ was estimated with following equation:

$$[INP(T)]_{vol,air} = [INP(T)]_{mass,salt} . c \tag{7}$$

where c is the concentration of sea salt in the Arctic marine boundary layer. Average concentrations of sea salt at Barrow, Alaska (71.3° N, 156.6° W), Alert, Nunavut, Canada (82.5° N, 62.5° W), and Zeppelin, Svalbard, Norway (78.9° N, 11.9° E) are 1.5, 0.1, and 0.6 µg m^{-3} in July, and 1.4, 0.1, and 0.5 µg m^{-3} in August, respectively (Huang et al., 2018a). For these exploratory calculations we used a value of 1 µg m^{-3}, which is at the upper end of the average values mentioned above. Shown in Fig. 10 are the estimated values for $[INP(T)]_{vol,air}$ based on our freezing data and a concentration of sea salt in the Arctic marine boundary layer of 1 µg m^{-3}. Based on our freezing data, the concentrations of INPs range from ~10^{-4} L^{-1} to < 10^{-6} L^{-1} at -10 °C. In addition, only the most active seawater samples resulted in INP concentrations as high as observed in direct atmospheric measurements of $[INP(T)]_{vol,air}$ in the marine boundary layer, including our 2014 campaign (Fig. 10) (DeMott et al., 2016; Irish et al., 2019). The following caveats should be kept in mind: first, we did not consider the possible enrichment of INPs in sea salt aerosols compared to the microlayer or bulk seawater samples, which can result from the bubble bursting mechanism. Second, the concentrations of sea salt used to estimate $[INP(T)]_{vol,air}$ was likely an upper limit based on the previous measurements at Barrow, Alert and Zeppelin.

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4 Summary and conclusions

The INP concentrations in microlayer and bulk seawater samples were determined at eleven stations in the Canadian Arctic during the summer of 2016 and compared to measurements made in 2014 (Irish et al., 2017). Filtration reduced the freezing temperatures of all samples, suggesting ice-active particulate material was universally present in the microlayer and bulk seawaters we studied. Some samples had freezing temperatures as high as -5 °C. Freezing temperatures also decreased after heat treatment, indicating that the ice-active material was likely heat-labile biological material, consistent with previous measurements of INPs in the microlayer (Wilson et al., 2015) and bulk seawater (Schnell, 1977; Schnell and Vali, 1975, 1976). The ice-active material we observed was between 0.22 µm and 0.02 µm in size, also consistent with previous studies of INPs in the microlayer (Wilson et al., 2015) and bulk seawater (Rosinski et al., 1986; Schnell and Vali, 1975).

We found similar spatial distribution of INPs in both years. In 2016, however, we observed generally higher concentrations of INPs nucleating ice at higher temperatures, particularly in the microlayer samples. This could, in part, be because we sampled a thinner microlayer in 2016, a hypothesis that could be tested by collecting microlayer samples using both collection methods in the same region at the same time. The observed differences could also simply be a result of variability in oceanographic conditions between the two expeditions.

We observed a strong positive correlation between T_{10}-values and the volume fraction of meteoric water in the bulk seawater samples. These results suggest that meteoric water may be a major source of INPs in Arctic coastal regions. Related, recent studies have measured high concentrations of INPs in freshwater sources such as rivers and lakes in other parts of the world (Knackstedt et al., 2018; Larsen et al., 2017; Moffett et al., 2018).

Exploratory calculations, using our freezing data, suggest that the concentrations of INPs from the ocean in the marine boundary layer range from ~10^{-4} L^{-1} to < 10^{-6} L^{-1} at -10 ° C. Furthermore, only the most active samples we studied gave calculated INP concentrations as high as observed in previous measurements of INPs in the marine boundary layer (DeMott et al., 2016; Irish et al., 2019). However, these exploratory calculations have caveats that need to be considered in future studies.

Data availability

Underlying material and related items for this manuscript are located in the Supplement.

Author contribution

AKB, JPDA, LAM, and VEI conceptualised the research. VEI, MB, MA, and RC collected the samples. SJH, YX, MG, LAM, and MA provided additional data. VEI analysed the data. VEI, SJH, MG, LAM, and AKB wrote the publication. All co-authors reviewed the paper.

Competing interests

The authors declare that they have no conflict of interest.

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Station number	Sampling start time (UTC)	Location
Station 1	20th July 2016 18:30	60°17.921N 062°10.750W
Station 2	28th July 2016 15:30	67°23.466N 063°22.067W
Station 3	1st August 2016 13:30	71°17.200N 070°30.236W
Station 4	6th August 2016 13:30	76°20.341N 071°11.418W
Station 5	8th August 2016 11:00	76°43.777N 071°47.267W
Station 6	9th August 2016 14:30	76°18.789N 075°42.963W
Station 7	11th August 2016 17:00	77°47.213N 076°29.841W
Station 8	13th August 2016 10:30	81°20.041N 062°40.774W
Station 9	15th August 2016 14:00	78°18.659N 074°33.757W
Station 10	21st August 2016 10:00	68°19.199N 100°49.010W
Station 11	23rd August 2016 10:30	68°58.699N 105°30.022W

Table 1. Sampling times and geographic coordinates for the eleven stations investigated.

	Bulk T_{10}-value		
	r	p	n
Heterotrophic bacterial abundance	**-0.77**	**0.003**	**11**
Total phytoplankton abundance (0.2 - 20 µm)	0.19	0.287	11
Salinity	**-0.83**	**0.001**	**11**
Temperature	0.20	0.285	10

Table 2. Correlations between biological and physical properties of bulk seawater and T_{10}-values for 2016. Values in bold indicate results that are statistically significant.

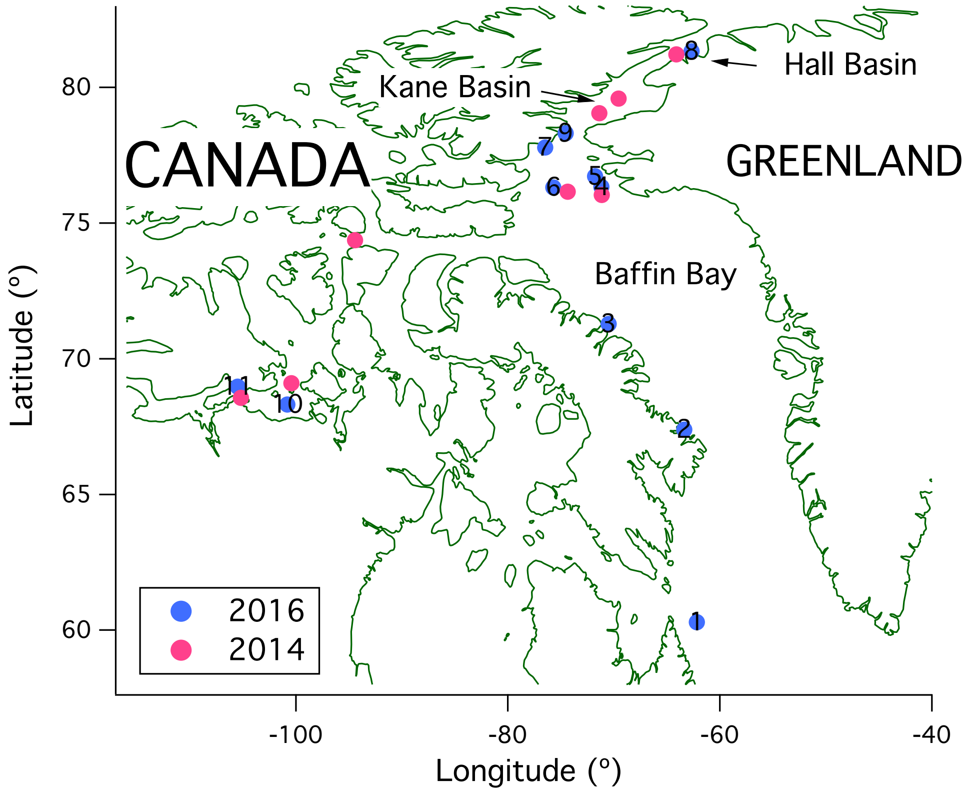

Figure 1. Map showing locations of microlayer and bulk seawater sampling in 2014 (pink) and 2016 (light blue with specific station numbers in black).

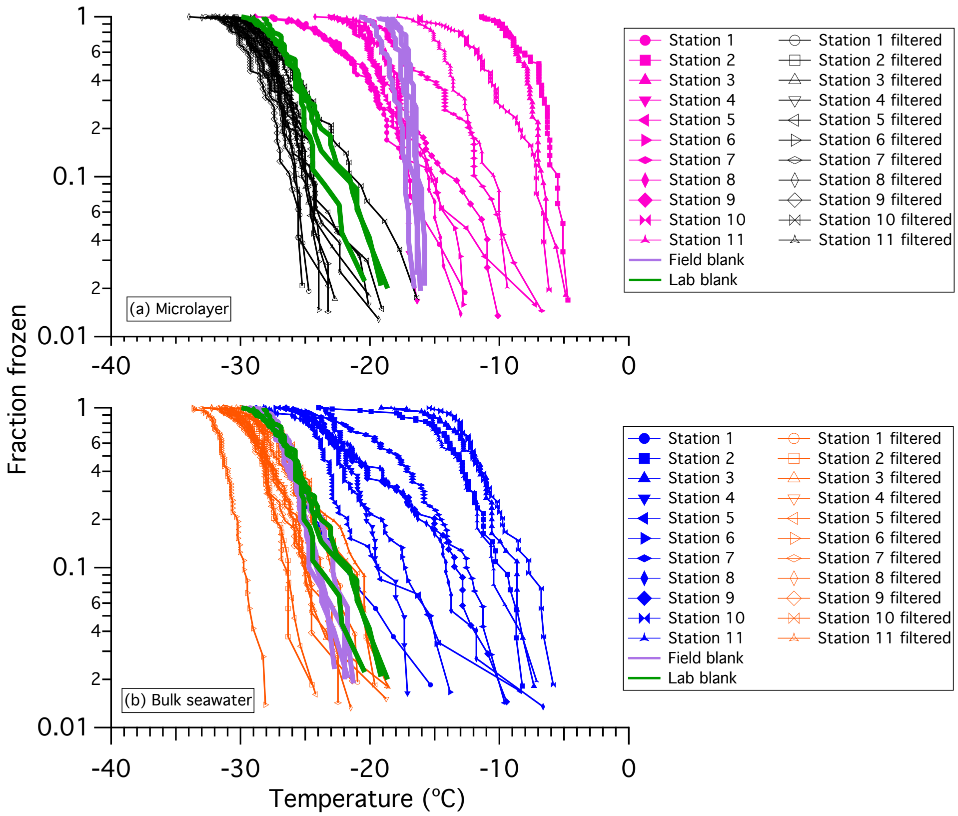

Figure 2. Fraction of droplets frozen (in the immersion mode) versus temperature for (a) the microlayer, and (b) bulk seawater. Each line shows the results for 3 replicate experiments of a sample or a sample passed through a 0.02 µm filter, with a total of between 45 to 60 freezing events in each set. Each data point corresponds to a single freezing event in the experiments. Also included are the laboratory blanks (ultrapure water passed through a 0.22 µm filter), and the field blanks (ultrapure water sampled through the sampling catamaran). All microlayer and bulk seawater freezing points were corrected for freezing point depression to account for dissolved salts in seawater (Section 2.2.3). The uncertainty in temperature is ± 0.3 °C.

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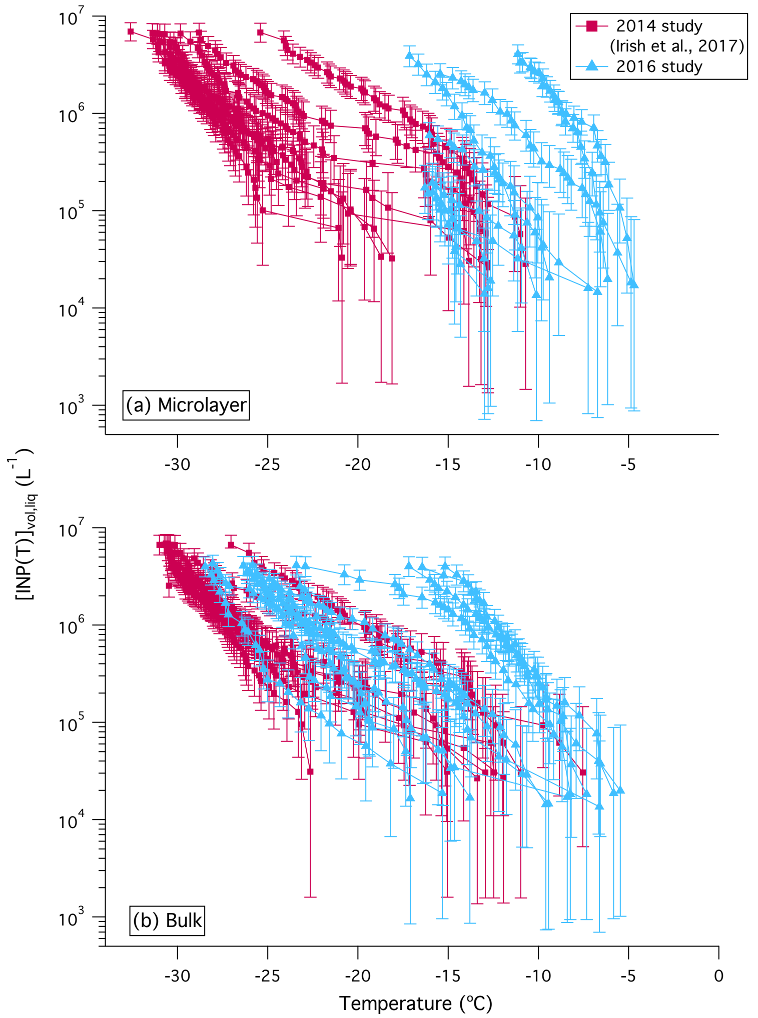

Figure 3. Comparison of the concentrations of INPs, *$[INP(T)]_{vol,liq}$*, in (a) the microlayer and (b) bulk seawater samples from the 2014 (pink squares) and 2016 (blue triangles) studies. All data were corrected for freezing point depression. Error bars represent the statistical uncertainty due to the limited number of nucleation events observed in the freezing experiments (Koop et al., 1997). Only freezing data that was at warmer temperatures than the field blanks are included.

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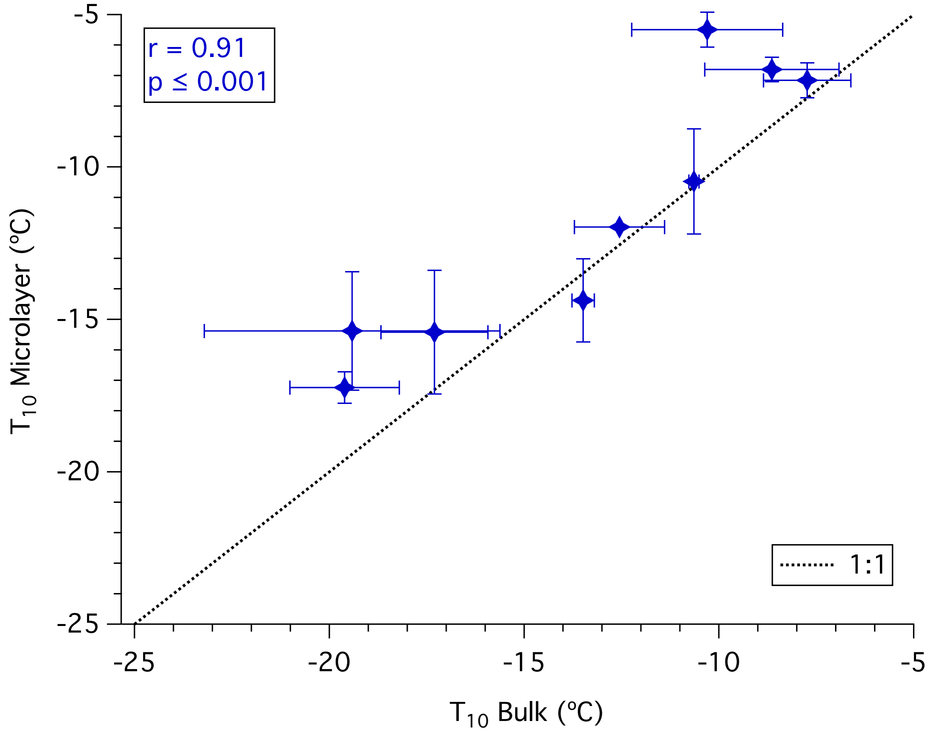

Figure 4. Relationship between T_{10}-values for microlayer and bulk seawater samples with a 1:1 line for reference. Data points are the average T_{10}-values from three repeat experiments. Error bars are the 95% confidence interval for three repeat experiments. Only freezing data that was at warmer temperatures than the field blanks are included.

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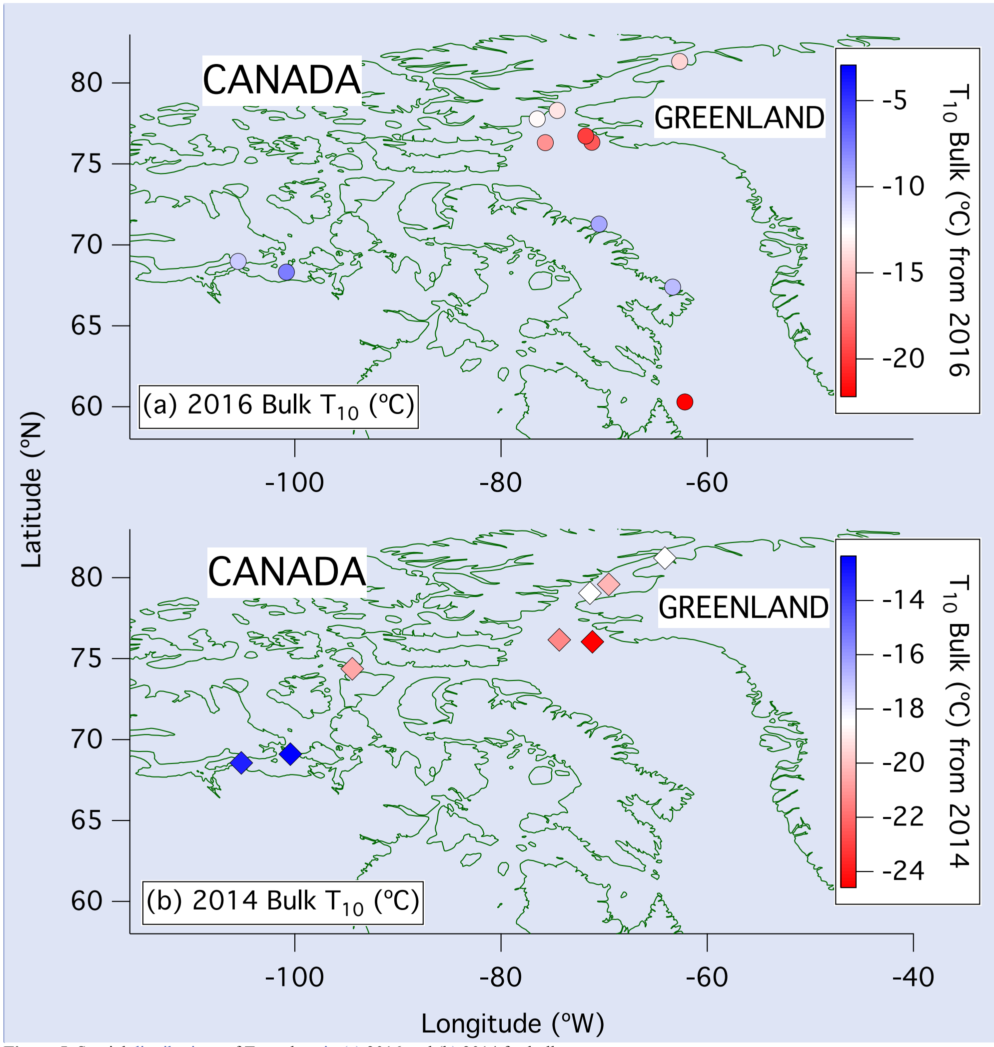

Figure 5. Spatial distributions of T_{10}-values in (a) 2016 and (b) 2014 for bulk seawater.

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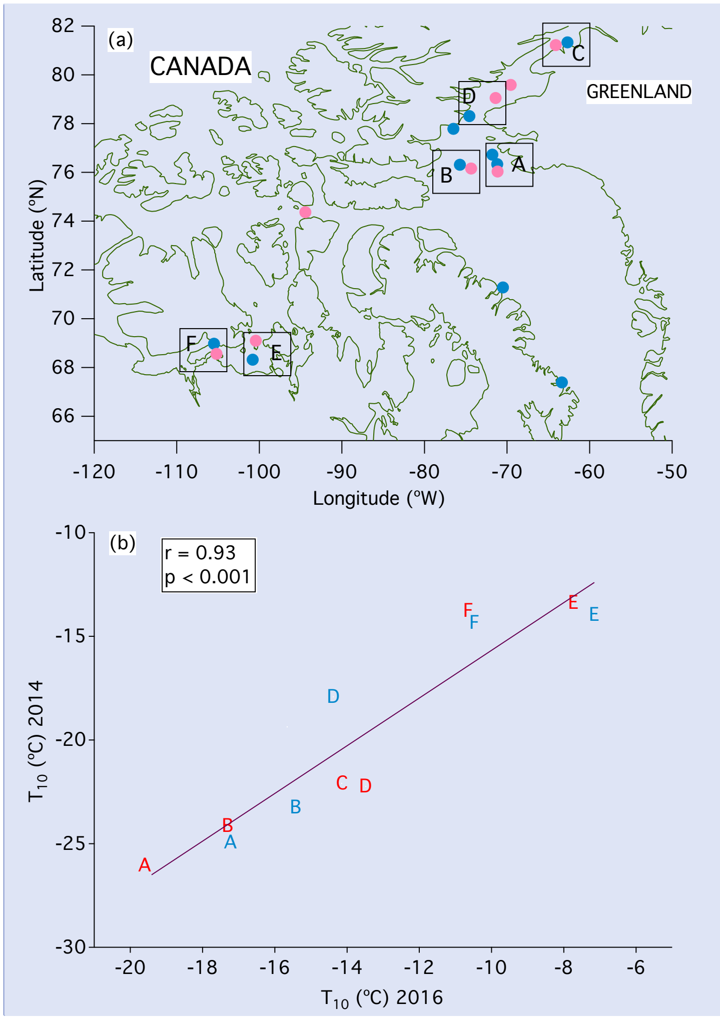

Figure 6. (a) Map showing regions of similar sampling locations in 2014 (pink) and in 2016 (blue). Sampling sites in 2014 that were near sampling sites in 2016 were paired together (indicated with boxes in the figure) and assigned letters A-F. Although there are two stations in box A for 2016, we only used data for the station that was closest to the one in 2014. (b) Relationships between T_{10}-values for microlayer and bulk seawater samples in 2014 and 2016 for similar sampling locations. The letters plotted in (b) indicate the locations in (a). Red letters represent bulk seawater data and blue letters represent microlayer data. Only freezing data that was at warmer temperatures than the field blanks are included.

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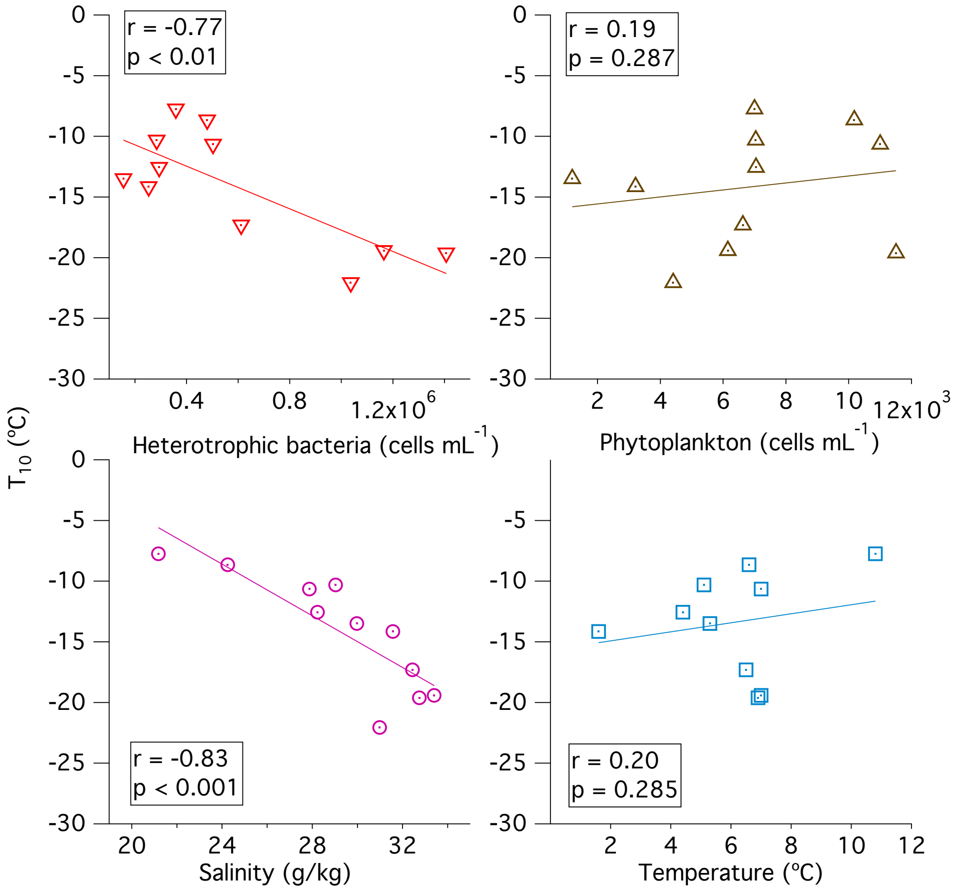

Figure 7. Relationships between T_{10}-values, and biological or physical properties of bulk seawater during the 2016 expedition. Phytoplankton include 0.2-20 µm photosynthetic eukaryotes and cyanobacteria.

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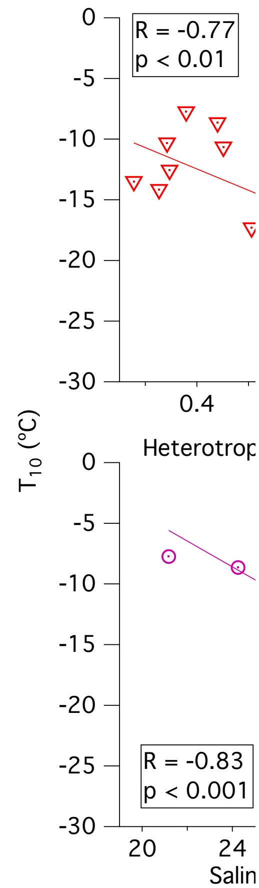

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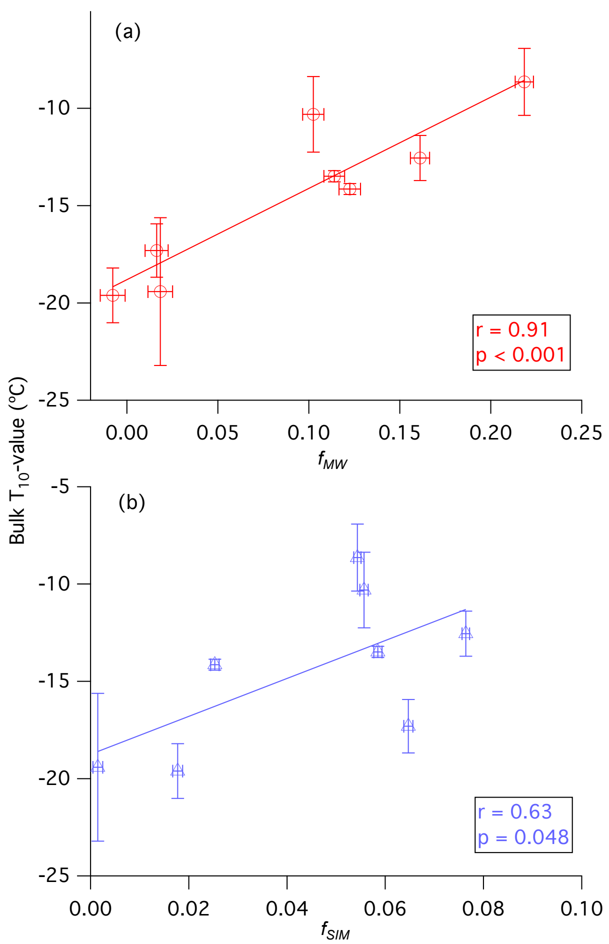

Figure 8. Relationships between T_{10}-values for bulk seawater and (a) the water volume fractions for meteoric water, f_{MW}, and (b) the water volume fractions for sea-ice melt, f_{SIM}. The x-error bars are due to the uncertainties in seawater salinities and seawater $\delta^{18}O$ values used for calculating f_{MW} and f_{SIM}. For further details see Section 2.4. The y-error bars correspond to the 95% confidence interval for three repeat experiments.

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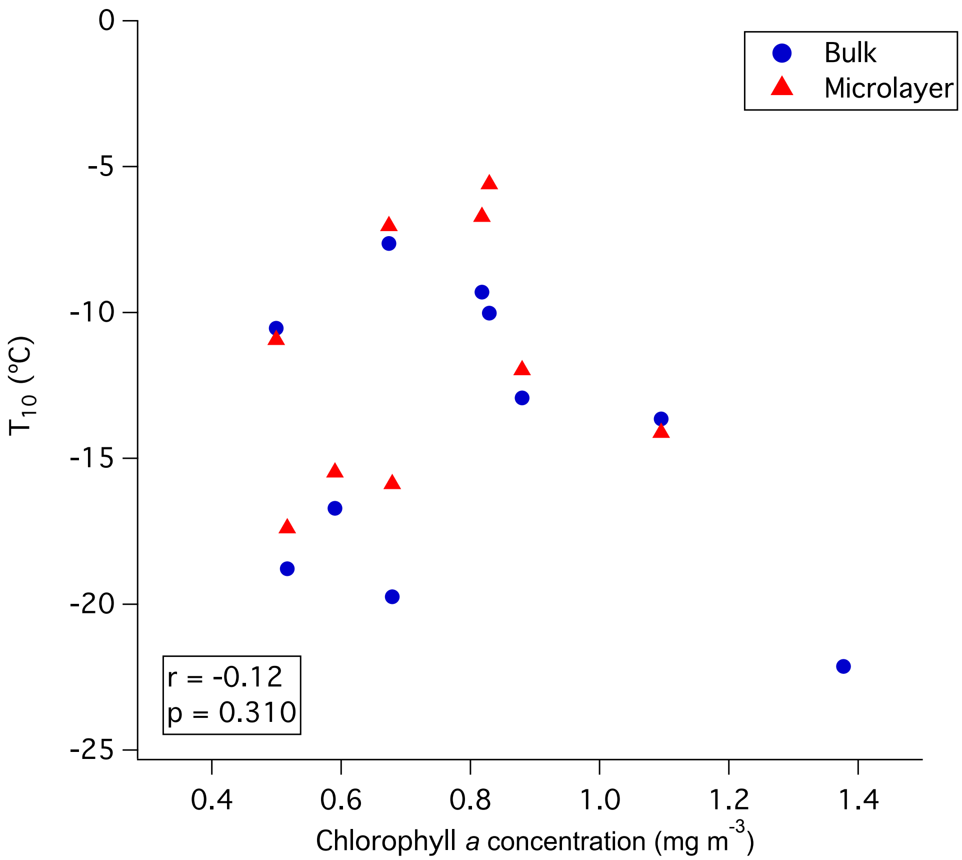

Figure 9. Relationship between satellite-derived chlorophyll *a* concentrations, and the T_{10}-values of microlayer and bulk seawater for 2016. Only freezing data that was at warmer temperatures than the field blanks are included.

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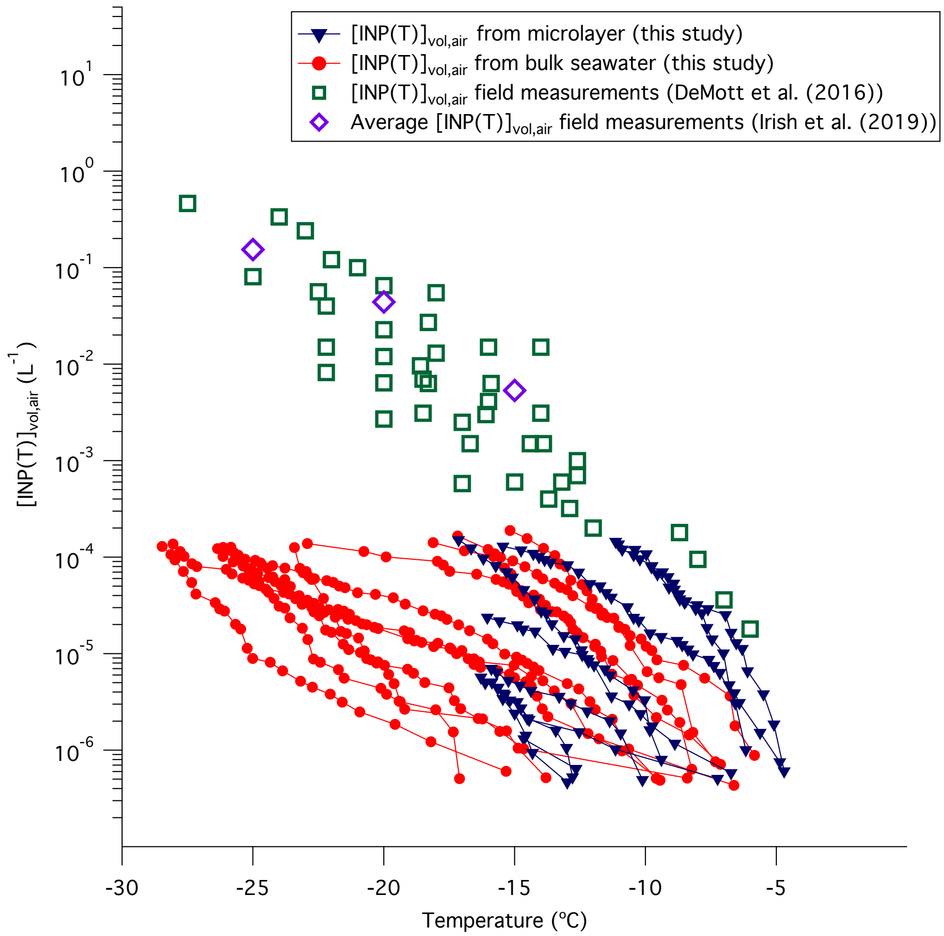

Figure 10. Plot of calculated $[INP(T)]_{vol,air}$ as a function of temperature based on our freezing data and an assumed sea salt aerosol concentration of 1 µg m^{-3}. Also included are measured $[INP(T)]_{vol,air}$ from several recent field campaigns in the marine boundary layer reported in DeMott et al. (2016) and Irish et al. (2019). Only freezing data that was at warmer temperatures than the field blanks are included.

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