

Prof. Barbara Ervens

Co-Editor of Atmospheric Chemistry and Physics

Dear Barbara,

Listed below are our responses to the comments from the referees 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]). Author's responses are offset in blue below each referee statement with matching numbers (e.g. [A1]). Page and line numbers refer to the online ACPD version. We thank the referees for carefully reading our manuscript and for their helpful comments!

Sincerely,

Allan Bertram,
Professor, Department of Chemistry
University of British Columbia

Anonymous Referee #1

Si et al. investigated the concentrations of ice nucleating particles (INP) at Alert, Canada for three weeks in 2016. This study measured INP concentrations in the immersion freezing using the droplet freezing technique. The presented INP concentrations are within the ranges of previous INP measurements in the Arctic. Complementary measurements of tracers for mineral dust, sea spray aerosol, and anthropogenic aerosols were also conducted. The correlations of INPs with these tracers are also investigated. The subject of this manuscript is within the scope of this journal. There are some minor issues and comments that the authors may want to address or consider in the revision.

[1] P4, L17-18, the particles were exposed to RH above water saturation, to what extent? Is there an estimation?

[A1] A humidified gas flow with a dew point of approximately 3 °C was passed through the flow cell. When the flow cell was at 0 °C, the particles were exposed to a RH with respect to liquid water of approximately 115 %. To address the referee's comments, this information will be added to Sect. 2.2.2 in the revised manuscript.

[2] P4, L28 to P5, L11, it is not very clear how the upper and lower limits were calculated and how the freezing of non-spot droplets was considered in the INP calculation. It may be easy for reader to understand or to use such method if example can be provided in the supplement.

[A2] To address the referee's comment, the description of the calculation of INP concentrations and their uncertainties will be improved in the revised manuscript.

[3] The spots of particles may contain more than one INPs. When cooling the droplet, the first or most efficient INP will trigger the freezing. Once the droplet freezes, it won't freeze again at lower temperature. This could lead to the underestimation of INP concentration. Please comment on this issue.

[A3] Equation (1) does not underestimate the INP concentrations due to the issue raised by the referee. Equation (1) represents the cumulative nucleus spectrum or the concentrations of INPs active at all temperatures warmer than temperature T. This equation was derived by integrating the differential nucleus spectrum. The use of Eq. (1) to quantify the concentrations of INPs active at all temperature warmer than temperature T from droplet freezing experiments has previously been justified using Poisson's law and Monte Carlo simulations. To address the referee's comments, this information will be added to the revised manuscript.

[4] P6, L30-31, although the equation 3 is the standard method to calculate nss-so4, how the Cl depletion in sea salt particles will affect these calculations.

[A4] To address the referee's comment, we have calculated $[\text{nss-SO}_4^{2-}]$ using a method that does not rely on $[\text{Cl}]$. Specifically, we calculated $[\text{nss-SO}_4^{2-}]$ using the following equation:

$$[nss - SO_4^{2-}] = [SO_4^{2-}] - 0.25[Na^+],$$

where Na^+ comes solely from sea salt and is not affected by Cl depletion (Balasubramanian, 2003). The difference between the concentrations of $nss-SO_4^{2-}$ based on Cl^- and the concentrations based on Na^+ is less than 5 %. This difference will be mentioned in the revised manuscript.

[5] P8, L31 to P9, L2, the manuscript states this assumption, it would be useful if the authors can add a short discussion on the potential bias this assumption may lead to the correlation analysis.

[A5] In the revised manuscript, we will comment on the potential implications of this assumption.

[6] How the non-INP affect the freezing data when dissolve in the droplets, this is due to sampling method (collecting a spot of impacted particle vs. individual particles), such as salts including NaCl? This may need additional discussion.

[A6] The referee is correct that the method of collection and formation of droplets results in the soluble material, such as salts including NaCl, being mixed with mineral dust particles within the same droplet. In the atmosphere, however, the soluble material may not be mixed with the insoluble material. Studies of the mixing of soluble material with mineral dust during the same time of the year and at the same location are needed. To address the referee's comments, this information will be added to Sect. 3.4 in the revised manuscript.

Anonymous Referee #2

Review for “Concentrations, composition, and sources of ice-nucleating particles in the Canadian High Arctic during spring 2016” by Meng Si and co-authors, submitted to ACPD:

The manuscript reviewed herein is a well written, up-to-date and informative piece of work. Impactor samples were taken in the Arctic and analyzed wrt. atmospheric concentrations of ice nucleating particles. The results were brought into context with information on the chemical composition and on air mass origin. INP that were ice active at -25°C were shown to correlate with mineral dust particles, with the Gobi desert being a possible source. For INP ice active at higher temperatures, no correlation was found, although sea spray and anthropogenic tracers were tested.

There is a number of (mostly smaller) issues listed below. Other than that, the manuscript well merits publication in ACP once these issues have been tackled.

[7] Abstract: p1, line 17: Add “at that temperature” behind “INP population”, as this is likely not the case at higher temperatures.

[A7] To address the referee’s comment, we will specify the temperature after “INP population”.

[8] Also, mention that you examine immersion freezing – best do that already in the abstract, and/or maybe again later.

[A8] To address the referee’s comment, we will indicate earlier in the abstract that we examined immersion freezing.

[9] And either here or maybe in the methods section, mention how many separate samples you analyzed for INP concentrations. I did not know what to expect until I saw Fig. 2.

[A9] To address the referee’s comment, the number of total samples collected for INP analysis will be mentioned in the Abstract and again in the Methods.

[10] Introduction: p2, line 31 ff: It should become clear that different ice active substances are ice active at different temperatures. Sea spray, anthropogenic aerosol and mineral dust all are a bit intermingled, here. Please make this clearer.

[A10] To address the referee’s comment, the introduction will be modified to make it clear that different ice active substances are ice active at different temperatures.

[11] Methods: p3, line 17: It is not clear to me why there are three circular glass slides on the second stage? It sounds as if they are there simultaneously? Or did you only use three during the whole time? Please clarify!

[A11] Three hydrophobic glass slides were located on the second stage simultaneously. As a result, each sample consisted of three hydrophobic glass slides.

This will be clarified in the revised manuscript.

[I2] p4, line 20: It is crucial what happens to the RH during cooling, in terms of the effect of RH: did the droplets grow or shrink during this phase, if yes, to which extent? (They might get in touch with each other, or they might dry out, as the two extreme ends of what could happen.) Is that prevented somehow? How? A bit of text discussing this should be added here.

[A12] If no gas is passed through the flow cell during cooling, the droplets tend to grow by condensation. To prevent the growth, a small flow of dry helium ($\sim 0.2 \text{ L min}^{-1}$) was passed through the flow cell during cooling. To address the referee's comments, this information will be added to the Sect. 2.2.2 in the revised manuscript.

[I3] p4, line 28 ff: Do really several separate droplets form on one spot? How large is such a spot? You may want to give this number here.

[A13] The diameter of each spot was approximately $110 \mu\text{m}$. This information will be added to Sect. 2.2.2 in the revised manuscript.

[I4] p5, line 5 ff: Freezing of “non-spot droplets” may come from impurities on or in the glass, particularly as particles as small as 180 nm may not be very ice active. And if this is the case, your way of analyzing the data leads to an overestimation. Did you try the experiment on a “field blank” glass (glass slides treated as the ones used for sampling, including to put them into the sampler, just without turning on the air flow)? Are those “blanks” you mention on p5, line 20 such “field blanks”? How do the data from your “blanks” compare to the number of “non-spot droplets”? And should not the counts obtained from the “blanks” be subtracted from the counts of the samples, instead of adding “non-spot droplets” to the counts of the samples?

[A14] The blanks mentioned on P5, line 20 and shown in Fig. 2 refer to field blanks (treated exactly as the referee described) and lab blanks (glass slides that were cleaned in the lab the same way as the ones used for sampling in the field). Lab and field blanks shown in Fig. 2 are consistent with lab and field blanks determined in another study using exactly the same techniques described in the current study (Irish et al., 2018). In short, rarely do we see freezing at $-25 \text{ }^\circ\text{C}$ or above in the field or lab blanks. In the current study, we report INP concentrations at $\geq -25 \text{ }^\circ\text{C}$. Thus, any freezing events of non-spot droplets that happened at $\geq -25 \text{ }^\circ\text{C}$ were most likely not from impurities on or in the glass substrates. We assume that non-spot droplet freezing is due to INPs $< 0.18 \mu\text{m}$ not being focused into the spots, or that a small fraction of the INPs $\geq 0.18 \mu\text{m}$ may not be concentrated into the spots due to rebound from the substrate. To address the referee's comments, this information will be added to the revised manuscript.

[I5] p5, line 14 ff: The number 300 confused me. Is that the number of impactor spots that were sampled on that stage? If yes, please clarify! Also, above you discuss a number of sources for uncertainty (several droplet on one spot, merging droplets, . . .), and here now you say that the uncertainties were derived based on Koop et al. (1997). So were

these issues (several droplet on one spot, merging droplets, . . .) not considered for the uncertainty?

[A15] 300 is the number of nozzles in the nozzle plate of the impactor, and consequently, the number of spots generated on the second impactor stage below the nozzle plate. The uncertainties based on Koop et al. (1997) account for the uncertainties due to the limited number of freezing events detected. The overall uncertainty reported in the manuscript includes this uncertainty as well as the uncertainties discussed earlier. This will be clarified in the revised manuscript.

[I16] p5, line 19: More information on the background measurements is needed. Right now, you basically only show this background data in Fig. 2, but it is not said if it had been subtracted, and depending on if you did or did not subtract it, why it was done how it was done. This should be added here.

[A16] To address the referee's comments, more information about the background measurements (i.e. blanks) will be added to Sect. 2.2.2 in the revised manuscript.

[I17] p6, line 13 ff: I now know that it is discussed later that the daily filter samples described here have a different time resolution than the samples taken for INP analysis (p-8, line 31). This confused me when reading it for the first time, and it would be good to mention already here, that this is the case and that it is discussed later. At the later discussion of this issue, it would be good to mention if air mass trajectories were at least similar throughout the whole days when you sampled. For days when that was not the case, less correlation between INP and any information on chemical composition should be expected.

[A17] Thank you for pointing this out. We will mention earlier (P6, Line 13) that daily filter samples had a different time resolution than the samples taken for INP analysis. In addition, we will add to the Supplement air mass trajectories initiated every 2 h to illustrate the variability in air mass trajectories over the 24 h filter sampling periods.

[I18] Results and discussion: p9, line 27: "The North Pacific Ocean is not likely the source of mineral dust either." The high signal in Panel D of Fig. 9 confused me in the beginning. But after looking at the plots a bit, I now assume that it originates in the fact that this Pacific region gets its high signals as it has small signals in both, plot B and C. So it would be the result of bad statistics (dividing a small signal by yet smaller signals).

But still, would not all regions in B have to have higher concentrations as those in C? C, as I understand it, is a subset of B, and yet, there are regions in C that indicate larger concentrations, which cause the high values in the Pacific in D. - How can this be? Please explain the latter, and also mention that high values in the Pacific in "D" come from the division of small signals by small signals, if that is the case.

[A18] This section will be revised for clarity.

[I19] p10, line 12-16: I agree that you show that mineral dust contributes INP that are ice

active at -25°C . You also show that INP that are ice active at higher temperatures have other sources (as they do not correlate with mineral dust). So the statement you make here is a bit twisted, as you do not show what contributed the INP that are ice active at the higher temperatures, which is the temperature range for which INP from sea spray (generally assumed to be biogenic in origin) may be ice active. And for mixed phase clouds INP active at higher temperatures might be even more important than INP active at -25°C . Please correct your statement here accordingly, particularly the last sentence.

[A19] To address the referee's comments, we will specify the temperature to make the statement more accurate.

[20] p10, line 21 ff: It is VERY well known that salt in general causes a freezing point depression (that's why salt is put on icy roads in winter time). That is why I was somewhat surprised by that part in general, as I would not consider this a new result. There is also other older work on that, not for NaCl but for salts and other soluble material in general, on the temperature depression of ice nucleation for minerals (Koop & Zobrist, 2009, Wex et al., 2014), in which even more general ways of describing this suppression are given. Although this originates from laboratory studies, it may merit including that and mentioning that your results is not such an astonishing finding. Also, as you know the salt concentrations on the filters, it would be interesting to see how much freezing point depression could be expected from that. This is easy to do, and, albeit only being an estimate, it could show if an effect may be expected at all.

[A20] To address the referee's comments, we have estimated how much the NaCl can decrease the freezing temperatures of mineral dust by the well-known freezing point depression mechanism, which involves the salt changing the water activity in solution. The maximum concentration of NaCl in our freezing experiments was $\sim 0.03 \text{ mol L}^{-1}$, which would only cause a freezing point depression of $\sim 0.1^{\circ}\text{C}$. Since this number is within the uncertainty of our measured freezing temperatures, it is too small to explain the negative correlations shown in Fig. 11 and Fig. 12. On the other hand, very recent studies have illustrated that trace amounts of NaCl can lower the freezing temperature of feldspar (a type of mineral dust) by surface specific interactions between the solute (NaCl) and the mineral dust surface, and the decrease in freezing temperature by this mechanism is more than expected based on traditional freezing point depression mechanism (Whale et al., 2018). Additional discussion will be added to Sect. 3.4 in the revised manuscript to make it clear that our results cannot be explained by the traditional freezing point depression mechanism.

[21] p11, line 17: Do you mean "at any of the three temperatures"?

[A21] This statement will be revised to improve clarity.

[22] p11, line 19ff: As you discuss other non-Arctic studies here, you may want to include a recent study on INP in Beijing, where it is also said that: "All these results indicate that Beijing air pollution did not increase or decrease INP concentrations in the examined temperature range (down to -25°C)." (Chen et al., 2018).

[A22] Thank you for the suggestion. This reference will be added to the revised manuscript.

[23] Figures Caption of Fig. 9: What do you mean by “for all mineral dust sampling periods”? The time when samples were analyzed wrt. INP concentrations? Please clarify, here or in the respective text.

[A23] This figure caption will be revised to improve clarity.

[24] Supplement There is a supplement with nothing else than one table that is not even large. This should be included in the main manuscript. It makes no sense to have a separate document for so little of information.

[A24] Additional plots will be added to the Supplement to address Comment *[17]* above. Hence, a Supplement will be necessary.

Literature Chen, J., Z. Wu, S. Augustin-Bauditz, S. Grawe, M. Hartmann, X. Pei, Z. Liu, D. Ji, and H. Wex (2018), Ice nucleating particle concentrations unaffected by urban air pollution in Beijing, China, *Atmos. Chem. Phys.*, 18, 3523–3539, doi:10.5194/acp-18-3523-2018.

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Wex, H., P. J. DeMott, Y. Tobo, S. Hartmann, M. Rösch, T. Clauss, L. Tomsche, D. Niedermeier, and F. Stratmann (2014), Kaolinite particles as ice nuclei: learning from the use of different kaolinite samples and different coatings, *Atmos. Chem. Phys.*, 14, 5529-5546, doi:10.5194/acp-14-5529-2014.

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