Response to Anonymous Referee #3

First of all, we thank the referee for submitting their helpful and productive annotations, which lead to improvements and clarifications within the manuscript.

We prepared a revised manuscript that addresses the questions and comments of the referees. Furthermore, below we explicitly respond to each of the items raised in the comments of anonymous referee #3. These comments are indicated in *italics,* whereas the author's response is presented in blue. Changes in the manuscript are given in green; changes to the supplement are given in purple. A response with "Okay." means we accepted the reviewers' suggestion and implemented it in the manuscript. The differences are also highlighted in separate PDFs using latexdiff. All line and page numbers refer to the ACPD manuscript version, not the revised manuscript.

Interactive comment on "Ice nucleating particle concentrations of the past: Insights from a 600 year old Greenland ice core" by Jann Schrod et al.

Review of Ice nucleating particle concentrations of the past: Insights from a 600 year old Greenland ice core

In this study Schrod et al, present the ice nucleating particle (INP) concentrations from a Greenland ice core spanning the past 600 years. The collected data set shows that the concentration of INPs has been rather consistent over the past 600 years. However, since 1960, the concentration and variability in INPs has increased. This has led the authors to suggest that human activities may be influencing INP concentrations, which could have significant impacts on future cloud radiative forcing. I appreciate that the authors are very careful in not over interpreting their results and are very thorough in addressing potential issues with conversions and contamination. I support the publication of this manuscript and provide some minor technical revisions. Additionally, I think it would be very interesting to extend the analysis to investigate the role of changing atmospheric circulation and rising arctic temperatures may have on the observed changes in INP concentration in this ice core sample.

General comments:

Although all layers of the ice core were treated the same and likely experienced similar temperature variabilities while accumulating on the ice sheet, it would be worthwhile to mention the recently found impacts of the storage on INPs relative to freshly collected samples. For example see Beall et al., (2020) and Stopelli et al., (2014). As the long term storage of the INPs in the ice may contribute to the observed difference between the ice core samples and precipitation samples shown in (Petters and Wright, 2015).

> We thank the referee for directing our attention to potential storage effects. In fact, all reviewers agree that sample storage may have an important impact to the INP activity of the ice core samples. We now address this effect on several instances throughout the manuscript:

Page 5, line 11: "Hence, it was ensured that samples remained frozen at all times in our laboratory. However, sample vials may have been subject to temperatures between 0 °C and room temperature for up to some tens of hours in total (during repeated cycles of melting, storage and refreezing, non-INP measurements, and transport, etc.)."

Page 9, line 30: "However, recent studies indicate that sample storage (i.e. storage temperature) significantly affects the ice nucleation activity of fresh precipitation samples in the range of -7 °C to -19 °C (Beall et al., 2020). For example, samples stored at room temperature lost on average 72% of their INPs compared to the freshly analyzed samples. An average INP loss of 25% was still observed, even when samples were stored at -20 °C. Storage time did only weakly affect the INP concentrations. Therefore, based on this study a loss of INP activity on the order of a factor of 2 – 5 is possible, if not likely for the ice core measurements presented here. Furthermore, it is likely that the warmer end of INPs were disproportionally affected by these disturbances, while cold-temperature INPs were likely more robust. However, as all the samples experienced the same sample history, relative changes within the ice core can still be interpreted."

Page 10, line 26: "Hartmann et al. (2019) come to the same conclusion that INPs are well preserved in an ice core and a reconstruction of their concentration for past climates is possible. However, as previously stated, storage conditions may have affected the INP activation."

Page 16, line 5: "Considering that the total global agricultural land area is estimated to have increased by a factor of 10 from 1400 to 1992 (Pongratz et al., 2008) combined with the fact that wind erosion has immensely accelerated within the last two centuries (Neff et al., 2008), partly due to intensive grazing by the heavily increasing number of domesticated animals, one could even have expected larger differences between the two data groups. Especially in the temperature range around -15 °C, at which soil dust INPs from fertile agricultural regions are known to be active (O'Sullivan et al., 2015). We can only speculate why we generally did not observe many INPs in this temperature range, and why the significant differences between the two data groups were only observed for temperatures below -22 °C. First, it is possible that dust from anthropogenic practices was not transported to Central Greenland in a detectable amount. According to Groot Zwaaftink et al. (2016), most of the dust input contributing to the dust surface concentration of the Arctic is from Eurasia north of 60° N, North America north of 60° N and Asia south of 60° N. In contrast, North America and Europe south of 60° N, where land-use change and the agricultural expansion are most prominent, contribute only little to the Arctic dust input (below 1%). Moreover, Asian agricultural dust sources may not exhibit the necessary high wind speeds to inject mineral dust into the upper troposphere as required for long-range transport to Greenland. In contrast, mineral dust from the Taklamakan desert is intrinsically linked to dust storms in this area.

Second, the more fragile (biological) INPs may have been deteriorated during sample storage (Beall et al., 2020). As a result, the warm-end of INPs might have been largely lost, leaving only a homogeneous fraction of very stable INPs behind. Figures 8 and 9 present some evidence for this hypothesis. As seen in Fig. 8, we find a much narrower range of frozen fractions for the 10 year samples, hinting at a rather homogenous population of INPs. On the other hand, the variability is much higher for the modern-

day samples, possibly because some of the more fragile INPs were still active. However, as both sample groups experienced the same sample history after coring, this hypothesis would only be reflected by deterioration effects related to the time elapsed since the particles were deposited in the ice. Furthermore, Fig. 9 depicts increasingly greater relative differences in the INP concentration from -30 °C to -24 °C until the warmer end of the data is reached, at which only few samples show ice nucleation activity. This observation could possibly be explained by assuming that the warmer INPs were largely deactivated due to storage effects."

As each of the samples used to probe the concentration of INPs every 10 years only covers a period of 6 months, is the 6 month period roughly the same for each of the 10 yr samples? Based on Fig. 6, the variability over a year (monthly sample from 1463-64) looks to be about an order of magnitude. Therefore, if the 6 months covered by a 10 yr sample differs, some of the variability between the 10 yr samples, albeit a small amount, could be explained.

Theoretically, we selected the sample vials for the 10 year time series, whose midpoints were closest to the same season of a year (e.g. 1950.0). However, the uncertainty in the dating of the ice core effectively does not allow to assume that each sample corresponds to the same season (also the "sample resolution" varies to some degree, see Fig. 1b). Therefore, we agree to the referee that some part of the overall variability can be explained by possibly comparing different times of a year. We added a table to the supplement entailing the sample list (Tab. S1; sample number, depth, estimated year, representative time average, data subset). Also see the following answer. We added a sentence to page 6, line 9:

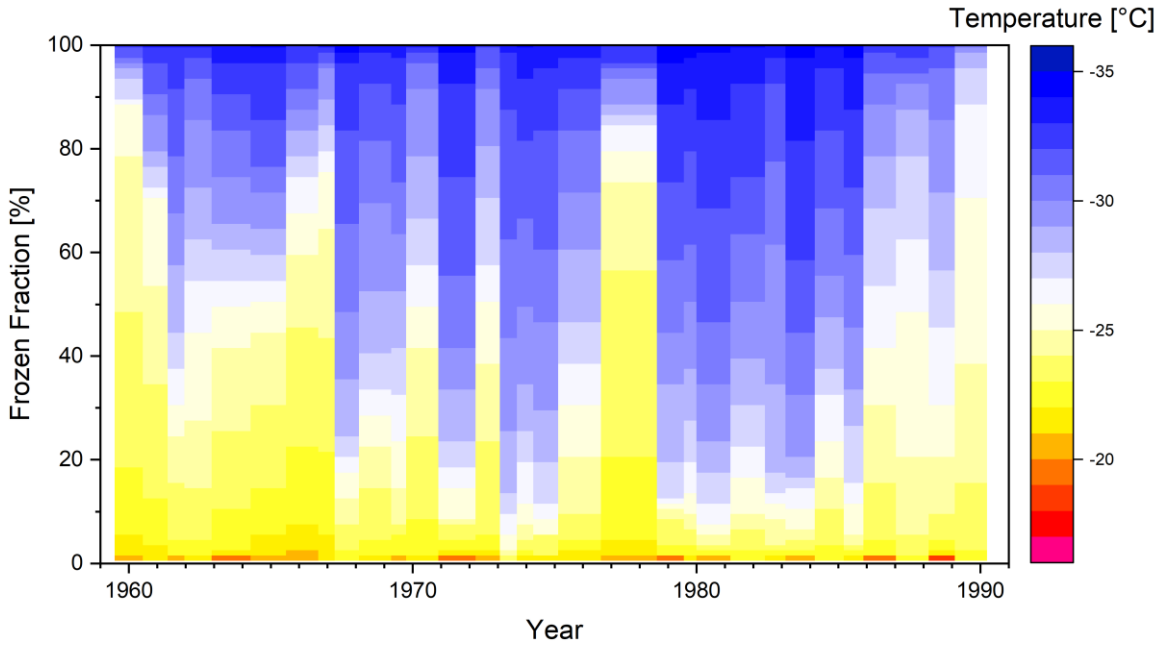
"Whenever possible, we selected samples that theoretically represented the same season(s). However, due to the uncertainty in the ice core dating some of the variability in the INP concentration may be attributed to seasonal differences."

The same question is also relevant for the modern day samples (Fig. 7) where there are some years with higher activity than others. It would be important to know if the yearly samples (actually only 6 months) cover the same 6 month period for each year.

The same procedure was applied to the modern day samples. However, due to the higher sampling frequency of the modern day samples the number of samples to choose from was lower. Accordingly, there is somewhat more diversity to be expected for this group with regards of the averaged seasons. We added a few words to page 15, line 10:

"Furthermore, the results could potentially be intrinsically influenced to some degree by differences in sampling frequency and time coverage, as well as samples representing different seasons of the year."

On a related matter we now added an alternative figure to the Supplement (Fig. S2), similar to Fig. 7, but with the original (non-interpolated) time coverage:



Here it is shown that the Anthropocene samples are significantly different from the preindustrial samples. This is a very interesting finding and something that the authors suggest may be due to a change in the dust due to desertification, and other anthropogenic related aerosols that reach the Greenland ice sheet. Although these seem like possibilities, it would be interesting to discuss the potential influence from changes in atmospheric circulation patterns such as the NAO (Pinto and Raible, 2012).

> We regard changes in the emission strength much more likely than changes to atmospheric circulation patterns. To our knowledge, there is no clear evidence from aerosol tracers or models suggesting that there were strong anthropogenic circulation changes in Greenland yet. However, some changes in transport patterns cannot be entirely disregarded. In fact, we address this on page 10, line 4 – 8. Related effects on dry and wet deposition, which may be caused by a change in atmospheric transport patterns, and the relevance to the interpretation of the INP results are described on page 11, line 20 – 24. Also see following answer.

Additionally, it has been shown that precipitation effectively removes precipitation (Stopelli et al., 2015) and as the ice core site is at a high altitude arctic site, it may be extremely sensitive to the temperature and amount of precipitation that falls (removal of INPs) upstream of the site. The fact that an overall increase in IN activity has been observed in more recent, warmer years may be consistent with warmer air masses precipitating over the ice sheet where fewer INPs have been removed upstream compared to previous (colder) years. Therefore, it may be worthwhile to compare the INP concentrations with the reconstructed temperature record over the same period from the ice core.

> We assume the first sentence was meant to read: "it has been shown that precipitation effectively removes INPs" (?). We recognize that temperature and precipitation are two dominant factors determining the deposition efficiency and therefore the amount of INPs in the accumulated snow (see sections 2.9 and 2.10). The suggested idea to compare the warming climate via a reconstructed temperature record to the INP concentration is definitely an interesting thought. Yet, we feel it is beyond the scope of this manuscript and could be explored further in a follow-up study, which might include a modelling aspect.

We added a paragraph to the discussion in section 3.1 including the last two points of the referee:

"Now the question arises, what factors may have caused these significant differences in INP concentrations. Several hypothetical explanations come to mind. First, the changing climate may have influenced both the deposition pathways and their efficiencies (cf. sections 2.9 and 2.10). But, at least locally, the accumulation rate at B17 does not show a change between modern and pre-industrial times. Further, changes to relevant large-scale atmospheric circulation patterns are essentially unknown for the investigated time period. [...]"

Minor comments:

- *Page 3, line 3: Consider adding the following references: Grawe et al., (2016, 2018); Kanji et al., (2020); Ullrich et al., (2016)*

  Okay.

- *Page 3 line 14: Consider adding the following references: Hill et al., (2016); Steinke et al., (2016)*

  Okay.

- *Page 3 line 20: It is highlighted here that the dominant dust sources in Greenland ice cores come from Chinese deserts and the Taklamakan. Therefore, it would be worthwhile to discuss the observed ability of these mineral dusts to act as INPs. Do they match in terms of INA with the observed INPs found in the ice cores (it seems like they do)? Consider mentioning previous studies on INPs from this region such as Boose et al., (2016); Field et al., (2006); Paramonov et al., (2018); Ullrich et al., (2016).*

  We agree that a short discussion about the ice nucleation activity of the mineral dust from the relevant desert regions is an interesting addition. We thank the reviewer for the suggested literature. The manuscript now reads:

  "Mineral dust from China, and the Taklamakan desert in particular, has been characterized in several laboratory ice nucleation studies (Field et al., 2006; Niemand et al., 2012; Boose et al., 2016; Ullrich et al., 2017; Paramonov et al., 2018), which revealed a relatively high ice active site density in the temperature range below -25 °C, comparable to other natural deserts such as the Sahara (e.g. Niemand et al., 2012; Boose et al., 2016)."

  It is, however, difficult to assess how well these laboratory measurements with pure dust from the Chinese deserts match to the observed INP spectra in the ice core. Most times, laboratory studies provide the active site density n_s as their metric for ice nucleation activity. We don't have a good enough characterization of aerosol particles within the ice core samples to estimate a reliable n_s value, which makes the comparison difficult. Assuming that all particles counted by the CFA measurements have a spherical diameter of 1.2 µm we can estimate the active site density to be on average $1.5 \pm 6.1 \times 10^{10}$ m^{-2} (range: $1.4 \times 10^{8} - 6.3 \times 10^{11}$ m^{-2}) at -25 °C and $8.4 \pm 13.3 \times 10^{10}$ m^{-2} (range: $4.4 \times 10^{9} - 1.0 \times 10^{12}$ m^{-2}) at -30 °C. Obviously, this assumption is flawed, as there will be smaller particles that could not be counted by the CFA measurements, which would add to the total aerosol surface area, as well as

particles that were larger than 1.2 µm, which were here assumed to have this lower size. However, the estimated n_s values are indeed in the range of those presented in the literature for the Taklamakan desert and other Chinese deserts. We added a paragraph to section 3.4:

"Moreover, evidence presented in section 3.3 and Tab. 1 indicated that the long-range transported dust from East Asian deserts influenced the freezing characteristics of the ice core samples. Laboratory studies characterizing the ice nucleation activity of mineral dust from the Taklamakan desert and other Chinese deserts report active site densities ns at -25 °C of approximately 1 x 10^{10} m^{-2} (Niemand et al., 2012; Ullrich et al., 2017) and between 1 x 10^{10} to 1 x 10^{11} m^{-2} at -30 °C (Niemand et al., 2012; Boose et al., 2016; Ullrich et al., 2017; Paramonov et al., 2018). We can only roughly calculate n_s from the CFA particle measurements. Lacking a solid particle size distribution measurement, we assumed all counted particles to have a spherical diameter of 1.2 µm. This assumption is obviously flawed, as particles smaller than 1.2 µm were not counted by the CFA measurements, and larger particles were assumed to have this lower size. With this rough assumption, we find an average n_s of 2 ± 6 x 10^{10} m^{-2} at -25 °C and 8 ± 13 x 10^{10} m^{-2} at -30 °C, which is in surprisingly good agreement with the literature."

- *Page 6 line 14: change "must" to "does"*

  Okay.

- *Page 6 line 20-21: why was the seasonal variability explored in the 1463? Is there a reason for choosing this period? Wouldn't a more recent year make it easier to identify the months of the year as the ice is less compact?*

  There was no particular reason why the year 1463 was explored specifically other than opportunity. The INP analysis was done after CFA and IC measurements were already performed. Particularly, the CFA decontamination step determined the resolution of the samples. There were only two periods with samples of near monthly resolution (average: approx. 10 samples per year) from which seasonal cycles could be established: 1744 – 1763 and 1454 – 1468). The latter period was chosen for being unaffected by the industrial revolution. The exact samples were chosen more or less at random. (The chosen samples were in the center of the period and preliminary CFA data showed a clear annual signal.) But we agree with the reviewer that it would be very interesting to investigate the seasonal resolution of more recent years in future studies (also see page 19, lines 2 – 4). We added a sentence to page 16, line 3:

  "There was no particular reason why this year was explored specifically. As the CFA decontamination step determined the resolution of samples, there were two periods with samples of near monthly resolution from which seasonal cycles could be established (1744 – 1763 and 1454 – 1468). The latter period was chosen for being unaffected by the industrial revolution."

- *Page 6 line 28: "hast" should be "has"*

  Okay.

- *Page 7 line 5: consider rephrasing "picked up" to "pipetted"*

  Okay.

- *Page 7 line 7-8: Why is FRIDGE kept at 14 C initially? Based on what was stated earlier, the samples were defrosted at 6 C, so why wasn't FRDIGE set to 6 C to minimize the temperature range a sample was exposed to. Granted, all of the samples experienced the same treatment so this likely has no impact on the overall comparison between samples.*

  The initial temperature was set to 14 °C for practical reasons and is based on the experience of the operators. While pipetting the droplets, the chamber needs to be partially opened. When the chamber is open the flow of dry synthetic air did sometimes not suffice to prevent condensation on the surface of the wafer substrate if the temperature was set to a cooler temperature (depending on ambient conditions). Overall, we don't think that the short amount of time during pipetting altered the freezing spectra substantially. (However, other storage effects may be more relevant, see other responses and specifically the comments of reviewer 2.)

- *Page 7 line 8-10: Do you mean that the Lauda cryostat was used to dissipate heat from the Peltier element. Please rephrase this sentence to make that clearer.*

  Yes. The manuscript now reads:
  "The temperature ramp was implemented by a PID-controlled Peltier element. A cryostat (Lauda, Ecoline Staredition RE110; ethanol coolant) was used to dissipate the heat from the Peltier element."

- *Page 7 line 11: Does the synthetic air flush change the size of the droplets during the experiment via evaporation? If yes, would this be significant enough to increase the concentration of solutes in a droplet such that it may lead to a freezing point depression in the samples? In theory, the colder the cell gets (the longer the experiment lasts) the more concentrated these solutes would become.*

  Judging from measurement images we can't say for sure if or how much of the droplet size is shrinking due to evaporation. As for freezing point depression, CFA and IC measurements indicate that solutes such as Na^+ and Ca^{2+} are on the order of 10 to 100 ng/mL, which is very low. We agree to the referee that the possible effect of a freezing point depression will increase with shrinking droplet size, however we don't think this will have a significant effect on the overall results.

- *Page 7 line 18: Here you mention mL of meltwater but then use mLice when reporting INP concentrations. Consider making the terminology consistent.*

  Okay.

- *Page 8 line 6: Why was the SEM analysis conducted on the samples after being filtered (400 nm pore size) when the highest correlation between INP concentration and particles concentrations was for particles larger than 1.2 microns? Do these large particles make it through the filter?*

  We believe, the reviewer misunderstood the SEM preparation procedures: The sample water was pumped through a 400 nm pore size filter using a water jet vacuum. Then these filters were then analyzed with SEM. Large particles will therefore be present during the SEM analysis, whereas smaller particles will be lost.

- *Page 8 line 27: Check if "microscopical" should be "microscopic" in this case.*

  Okay.

- *Page 9 line 29: Here it is mentioned that the freezing and melting of the same droplets does not influence the ice nucleating ability of the samples. As previously mentioned in the general comments, it might be worthwhile to mention other studies where it was shown that over longer periods, the storage and repeated melting and freezing of samples influenced the ice nucleating ability of samples.*

  We thank the reviewer for pointing out the possible deactivation of INPs by storage, etc. We will add to the manuscript at the suggested lines (and elsewhere):

  "However, recent studies indicate that sample storage (i.e. storage temperature) significantly affects the ice nucleation activity of fresh precipitation samples in the range of -7 °C to -19 °C (Beall et al., 2020). For example, samples stored at room temperature lost on average 72% of their INPs compared to the freshly analyzed samples. An average INP loss of 25% was still observed, even when samples were stored at -20 °C. Storage time did only weakly affect the INP concentrations. Therefore, based on this study a loss of INP activity on the order of a factor of 2 – 5 is possible, if not likely for the ice core measurements presented here. Furthermore, it is likely that the warmer end of INPs were disproportionally affected by these disturbances, while cold-temperature INPs were likely more robust. However, as all the samples experienced the same sample history, relative changes within the ice core can still be interpreted."

- *Page 12 line 22: Remove extra "/" after gprecip in first term of equation*

  Okay.

- *Page 14 line 8: please specify that this is the concentration at -20 C as mention of -20C comes two sentences earlier.*

  Actually, page 14, line 8 gives the INP concentration at -25°C, which is mentioned two sentences earlier. We believe the structure of the paragraph is clear without repeating the temperature in every sentence.

- *Page 16 line 10-11: How do these large particles make it through the 400 nm pore sized filters described in the methods?*

  See comments above.

- *Page 16 line 27: Here it is mentioned that there is a seasonal cycle in INP and although the variability is significantly less than the over the entire period of the study, it may be worth mentioning if the 6 month samples are taken to over the same 6 months in every time point (as said in the general comments).*

  See comments above.

- *Page 17 line 15-25: Could some of the differences in the INP concentrations be due to the droplet size used in the studies? Perhaps the small droplet volume in this study makes the measurement of rarer INPs less quantifiable. Additionally, could location differences between sampling sites, lead to differences in the number and efficiency of INPs removed upstream of the sites (Stopelli et al., 2015). For example, Svalbard often experiences periods of relatively warm air masses laden with INPs that would*

precipitate out before reaching the high altitude location of this core. These points, although briefly mentioned, could be expanded on.

Drop size used in Hartmann et al. (2019) was 1 µL (LINA) and 50 µL (INDA). Our droplet size of 2.5 µL was therefore somewhere in the middle of those. We therefore think that the droplet size should not have biased the comparison greatly. Of course, the droplet size determines the effectively observed freezing range, but in the Vali (1971) equation of the cumulative concentration it is accounted for. However, generally speaking we agree to the reviewer that a small droplet volume might make it less likely for rare INPs to be quantifiable.

Geographical differences on the INP number and deposition efficiency between the core sites are well within the realm of possibility. Additionally, we now add possible storage effects as a further possible reason for the different concentration range observed. We expanded upon the lines, which now read:

"This disparity may arise from experimental (droplet volume, etc.), methodological (e.g. sample storage conditions) and or geographical differences, which may affect the deposition mechanisms and efficiency."

Literature

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