Response to Anonymous Referee #2

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 #2. 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.

The authors have made a great effort in trying to reconstruct from the analysis of an ice core the atmospheric concentration of ice nucleating particles (INPs) in the atmosphere over Central Greenland between the years 1370 and 1990. It is only the second such attempt, after a similar but less comprehensive study published last year by another group. Overall, the manuscript is clearly written. Everything is well explained. The text is easy to follow. Data are arranged in a meaningful way in Tables and Figures. Half of the main text is description of methods. Interpretation of results is cautious, if not hesitant. It is here that I see some room for improvement, apart from a few other, minor issues.

The most surprising outcome of this study, from my point of view, is the narrow range of INP concentrations in ice and atmosphere during a period in which Earth has seen a tenfold increase in land area used for agriculture (Pongratz et al., 2008). Ploughing of the North American prairies and the Russian steppes during the past two centuries has greatly accelerated wind erosion with drastic consequences, like the harvest failure of 1891 in the Russian steppes (Moon, 2005) and the Dust Bowl situation in the USA during the 1930s. Also intensive grazing by exploding numbers of domesticated animals has had its share in fostering wind erosion during that time (Neff et al., 2008). Other than desert dust, soil dust from more fertile land carries INPs active at moderate supercooling (O'Sullivan et al., 2014). Therefore, I would have expected to see growing number concentrations of INP active at temperatures at around -15 °C or warmer in samples deposited over the last two centuries. However, this does not seem to be the case. Only 3% of all samples, each consisting of 0.5 mL of melted ice, contained INPs active at -15 °C. There are at least two plausible explanations for this observation. First, it could be that anthropogenically caused dust in the midlatitudes was not transported in detectable quantities to the Arctic and deposited in Central Greenland. The overwhelming majority of dust and INPs deposited in the Arctic probably originates from regions north of 60 °N in America and Eurasia, latitudes not much affected by landuse change in the past. Regions in North America located south of 60 °N probably contribute less than one percent to the total surface dust concentration in the Arctic (Groot Zwaaftink et al., 2016, Table 3 therein). Thus, *large-scale landuse change and increased wind erosion of fertile soils in the midlatitudes following the colonisation of North America by settlers mainly from Europe may indeed not have had a marked effect on INPs deposited in Central Greenland, although it clearly increased dust deposition in the midlatitudes (Neff et al., 2008).*

> We greatly appreciate the interesting and well-presented, detailed remarks, and suggested literature by the reviewer regarding the potential anthropogenically enhanced source of soil dust INPs. We fully agree to the statements made by the referee. We also list soil and desert dust due to desertification, land-use change, the expansion of agriculture and related practices, and consequently higher erosion rates as one of our main candidates for anthropogenic INPs (Page 3, lines 6 – 24). We added a paragraph to the discussion in section 3.1 (see following answer).

Another explanation for landuse change over the past centuries not being reflected in the INP record of the analysed ice core could be a loss of IN-activity, in particular the loss of biological INPs that dominate the spectrum at temperatures warmer -15 °C in ice or during sample preparation, in particular during melting of the core and while the samples were in liquid form. Since Hartmann et al. (2019) found clearly enhanced INP activity between -5 °C and -15 °C even in some older sample (year 1484), sample preparation may be the more relevant issue. It would be interesting to know the temperature on the hot side of the instrument in which the ice core was melted. Further, for how long, in total, were samples in liquid form between the first melting of the core and INP analysis? Evidence pointing at a partial loss of INPs is in Figure 9 of the manuscript in discussion. It shows from -30 °C to -24 °C increasingly larger INP concentrations in the modern, as compared to the older samples. The relative difference between modern and older samples collapses quickly towards the warmer end of the temperatures scale. I would have expected this difference to continue increasing further until the warmest temperature is reached at which INPs are detectable. Maybe there is no difference at warmer temperatures detectable today because INPs active above -22 °C had lost their activity before INP analysis? In my experience, any challenge put to a population of INPs, such as warming or storage in water, always leads first and foremost to a loss of those INPs that are active at the warmest temperature. The warm temperature "bulge" in a cumulative INP spectrum disappears with increasing severity or duration of a challenge, resulting in the cumulative spectrum approaching a linear shape on a log-scale. The same applies to certain mineral INPs (Harrison et al., 2016, their Figure 4a, top panel). Partial deactivation most likely results in the remaining part of the INP population becoming increasingly homogenous, a guess supported by Figure 8 in the discussed manuscript: the distribution of frozen fractions at a specific temperature was much narrower for the older samples (pre- 1960) as compared to the modern samples (1960 to 1990). The majority of fragile INPs, which may have been present at the time of deposition, and still are to some extent in the samples from 1960 onwards, may have been lost, leaving behind a relatively homogenous population of very stable INPs. To summarise, very limited dust transport from the midlatitudes, where most landuse change has happened in past centuries, and deactivation of INPs active at temperatures warmer than -20 °C may explain why the concentration of INPs (Murray et al., 2012). Deactivation might have happened during decades and centuries in the ice core is confined to a narrow range and does not reflect the growing human impact on land over the past few centuries. These considerations are of cause speculative, but I hope they encourage the authors to push their interpretation a bit further.

> We thank the referee for their interesting and inspiring thoughts, and the encouragement to deepen our interpretation of the data. Both ideas presented by the reviewer appear probable to us. The reviewer's argument for a partial deactivation of

the warmer end of INPs from the interpretation of the freezing spectra and INP concentrations in Figs. 8 and 9 are convincingly portrayed. As a consequence we retraced the conditions of storage and melting of the samples as well as possible. In fact, we come to the conclusion that the suggested partial deactivation of INPs is at least possible. Although care was taken during and before INP measurements were made in our laboratory, 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 and refreezing, supporting measurement, and transport). For example, during the CFA decontamination step the ice core is melted in the typically temperature range from 12 – 25 °C depending on the density of the ice and the desired meltspeed. Unfortunately, the exact times and temperature conditions during storage, etc. are difficult to assess in retrospect. We recognize the need to decrease the time samples were in an unfrozen state in future studies.

We added the following text passages to 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."

Minor issues

- *Page 9, lines 19-20: I am always at a loss when told that results "...should be interpreted with care." Is not every interpretation or conclusion based on empirical evidence a preliminary one and absolutely true statements only to be found within closed systems (mathematics, logic)?*

  The reviewer is obviously right with their remark. The phrase in question is only added to sensitize the reader about the lower temperature part of the data, because we did not subtract a background as is otherwise common practice (Page 9, lines 6 – 17).

- *Page 9, line 32: Why use the number of frozen droplets and not the number of INPs in the assay (INPs in 195 droplets) as the criterion from which to estimate uncertainty?*

  We believe both phrasings mean the same thing. The most active INP within a droplet will initiate the freezing of said droplet. Therefore, the number of frozen droplets is related to the number of active INPs. The uncertainty specifies an upper and lower range in the number of droplets that are expected to freeze within a 95% confidence interval at a certain temperature.

- *Page 15, line 26: The data has a lognormal distribution. Was it log-transformed before the t-test?*

  The data was not log-transformed in the reviewed version of the manuscript. Transforming data yields similar results: We observed significant differences in the average (log-transformed) INP concentration for -23 °C ($p < 0.00011$), -24 °C ($p < 0.000002$), -25 °C ($p < 0.00005$), -26 °C ($p < 0.0011$) and -27 °C ($p < 0.02$).

- *Conclusions section: Effects of INPs on cloud radiative properties are mentioned and I wonder whether the very small number concentrations found in the ice core, and the difference between 1960 to 1990 or before, are indeed in a range where they might lead to differences in radiative properties?*

  Answering this interesting question is beyond the scope of this paper. However, we believe it is worth exploring in future studies, e.g. by atmospheric modelling (page 19, line 13 – 15).

- *Regional sources and geographical differences in INPs may not only be accessible through the analyses of ice cores but also through modelling approaches making use of historical records of land cover.*

  We agree with the reviewer and refer to the very last sentence of our manuscript (Page 19, lines 13 – 15). The addition of modelling studies based on historical records of land cover definitely seems like an interesting approach, which we did not consider before. We modified the manuscript, which now reads:
  "Finally, a modeling study could help identify (possibly anthropogenically altered) INP source regions (e.g. based on historical records of land use cover) and estimate the potential atmospheric impact that could be expected from a threefold increase of INPs at −24 °C since the mid of the twentieth century, as it was seen in this study."

- *Figure 1b: Would it be possible to indicate the season for samples with time coverage below one year?*

  Unfortunately, the dating of the ice core is not precise enough to establish this information in an absolute sense. Furthermore, the seasonal distribution of snow fall is not known. See also the responses to reviewer 3 and the new Tab. S1 that entails the detailed sampling list (including the best estimate for the year and the sample averaging time).

- *Figure 2: I would like to see more than one background measurement.*

  We added more background freezing spectra to Fig. 2 (as well as the least active ice core freezing spectrum, as suggested by reviewer 1).

Literature

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