Response to Anonymous Referee #1

First of all, we thank the referee for submitting helpful and productive comments and annotations, which have led to improvements and clarifications within the revised manuscript we submit with this review response.

We have prepared a revised manuscript that addresses the questions and comments of all referees. Furthermore, below we explicitly respond to each of the items raised in the comments of anonymous referee #1. 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 accept the reviewers' suggestion and have implemented it within the revised manuscript. The differences are also highlighted in separate PDFs using latexdiff. All line and page numbers refer to the ACPD manuscript (version 2), not the revised manuscript.

Review of "Long-term INP measurements from four stations across the globe" by Schrod et al.

General comments:

The authors made enormous amount of efforts tackling the current challenges of the INP research community – wide spatiotemporal coverage of ambient INP measurements. This reviewer is impressed with a comprehensiveness of this work (for 1212 samples) as well as persistence and articulation of the authors, and supports publication of this manuscript in ACP. The results and discussions provided in this manuscript tightly fit in the scope of ACP. The reviewer has only technical (some are minor) suggestions to make (see below). But, the reviewer noticed different writing styles/tones involved over different sections (before/after Sect. 2.3.). Consistency in writing will improve the readability as well as importance of this paper even more.

We are grateful for the positive feedback of the reviewer. We hope to improve the readability (and substance) of the manuscript by implementing the suggestions of the reviewer.

Specific and technical comments:

- *P1L4: → Unfortunately, only a few ...*

  Okay.

- *P1L14-15: This statement introduces a multitude of perspectives – one may consider physicochemical properties have negligible impact on INP abundance/propensity, thereby ambient INP estimation could be rather simple than 'complex'. This may be true and somehow supported by what the authors found (i.e., P1L9-11 & P1L18-19; great statements, by the way). Perhaps, incorporating this counter-thought (on top of*

what already exists) in an abstract and other parts in the main text would increase the readability/flexibility to both authors and readers.

Admittedly, one could argue as the reviewer proposes here. We argue for a "complex" and unresolved interplay of factors determining the INP concentration as we did not find an individual parameter (i.e. particle number concentration > 0.5µm, PM_{10}, etc.), which managed to predict the number of INPs to a satisfyingly high degree at any one site let alone all sites. Hence, we think that the observed high short-term variability is a clear sign that we do not sufficiently know all processes involved, or at least that the supporting physical and chemical parameters at hand did not cover all relevant aspects of the ice nucleation process.

- *P2L6-8: Depending on ... - the reviewer is not sure if this statement is adding any meaningful aspects in this paper. The authors may consider removing this statement. The CCN is not discussed in tandem with INP much in this manuscript.*

  Okay.

- *P2L9: Non-biological organics are deemed to be overlooked here. The authors may review Knopf et al. & Kanji et al.?*

  We now include non-biological organics in the list. The sentence now reads:
  "Known species of INPs include mineral dust, soil dust, primary biological aerosol particles of terrestrial and marine origin, as well as organics and glassy aerosols (Kanji et al., 2017)."

- *P2L19: Vertical distribution – very good point. This is somehow one of the things INP community has been missing for a long time in the reviewer's opinion. This should be pointed out in the outlook section?*

  We agree with the referee that vertical distributions of INP need to be explored more by the community, as INP concentrations at heights where clouds form may differ significantly from those at ground level (e.g. Schrod et al., 2017). We added a paragraph to the outlook (see later).

- *P2L21: ...in identifying globally relevant INP... → ...in identifying some or potentially atmospheric-related INP...*

  We changed the phrasing to:
  "...in identifying some of the INP species of global relevance..."

- *P3L1: The reviewer totally agrees with this statement. This statement is a nice complement to previous studies. Nice writing.*

  Thank you.

- *P3L2-17: Perhaps summarizing the examined temperature and the n_INP ranges from these previous studies in a tabular format with minimum explanation instead of prolonged texts would increase the readability of this section.*

  We understand the argument for a better readability, yet we feel that the paragraph and the entailed efforts made in the early years of ice nucleation research deserve some space in a manuscript, highlighting the importance of long-term INP measurements.

- *P3L20-21: Yes. This is a very good motivation statement. Good job.*

  Thank you.

- *P4L6-8: Seeing long/lat coordinates for these locations in their first appearances would be nice. The reviewer is aware these coordinates appear later on. This is just a suggestion from the reader's perspective. The authors can decide what to do.*

  We have added the coordinates within the introduction as well.

- *P4L11: Please clarify what "semi-automated" really means. Please also clarify how the samples were stored while transporting here. Frozen at a certain temperature all the way? The reviewer is aware that the authors mention an insignificance of storage method on their INP characterization in P5L18-19. Perhaps, transportation and storage discussion can be combined here or P5?*

  We think there is no need to add a very detailed description of these sampling related specifics here in the introduction. Much of these questions are answered (i.e. "semi-automated" sampling) within the following section (see section 2.2 Aerosol sampling). We will, however, add to this section, addressing the items raised by the referee. P5L19:

  "Since a frozen storage and transport could not be logistically guaranteed for all sites and for all times, samples were stored and transported at ambient temperatures, which may have affected the warm end of (biological) INPs."

- *P4L17: factors could include local dynamics, thermodynamics, large scale meteorology, and/or a combination of any?*

  All these factors surely influence ice nucleation in the atmosphere, yet we largely did not consider these in the analysis as we feel they are outside the scope of this manuscript. When formulating this sentence we were mainly thinking about aerosol species and sources.

- *P4L26-27: So is this correction incorporated/applied in relevant INP # in this study? Please state it if so.*

  Yes, it is. The sentence now reads:

  "The PEAC7 collection efficiency has been found to be about 60%, independent of particle size (Schrod et al., 2016). Accordingly, a correction factor of 0.6 has been applied to the data."

- *P4L27-: It would be meaningful to have a discussion of all inlets configuration and properties (e.g., length, flow rate – if any, cut-size – if an impactor was used in part, transmission efficiency, transmitted aerosol particle size range etc.) from individual sites here (rather than in Sect. 2.3). Maybe, the authors can use a table summarizing the inlet config. characterization (if done/any). Also, listing previous INP research done at the sites would be meaningful info for the readers.*

  We recognize from both reviews that more care should have been taken when describing the inlet configurations. Unfortunately, only the particle losses at AZ have been quantitatively characterized (Moran-Zuloaga et al., 2018, see section 2.4.1). Regrettably, we don't think a thorough inlet characterization is feasible at this point as the sampling devices are no longer at the sampling sites. We will add a paragraph that mentions this shortcoming more clearly. P4L27:

"No inlet size-cutoffs were used for the results presented here, and thus we expect to sample the complete particle spectrum, except for the usual particle losses that may occur for large particle sizes. The exact aerosol inlet configuration differed substantially between sites and was mainly predetermined by the local observatory facilities. Unfortunately, these inconsistencies may lead to some aerosol sampling artifacts with respect to the absolute particle losses. The individual sampling configurations are described in section 2.4 and Tab. 1."

Table 1. Main characteristics of the geographic sampling location and inlet configuration at the sites.

	AZ	MQ	TO	SB
Geograph. coordinates	2.144° S, 59.000° W	14.735° N, 61.147° W	50.221° N, 8.446° E	78.908° N, 11.881° E
Altitude [m AMSL]	130	487	825	474
Climate	tropical	(sub-)tropical	temperate	Arctic
Continental / marine	continental	marine	continental	marine
Mountain site	no	yes	yes	yes
Predominant vegetation	tropical rainforest	diverse (i.e. ranging from alpine to tropical rainforest)	coniferous forest	low-growing tundra (summer) / snow-covered (winter)
Anthropogenic impact	near pristine to polluted	remote to polluted	rural to polluted	near pristine to polluted
Inlet type	Total Suspended Particulate (Moran-Zuloaga et al., 2018)	1/4" tube, rain shield (no characterized inlet)	HORIBA ASS-370 type (ÖNORM, 2007)	Whole-air (Karlsson et al., 2020)
Inlet height [m AGL]	60	2	11	7.5
Isokinetic flow splitter	yes	no	yes	yes
Length of tubings to PEAC7 [m]	1.5	2	1	2

We added to P9L14 (TO):
"Samples were collected from the upper level of Atmospheric Physics Laboratory at the hilltop. The aerosol inlet was at 11 m above ground. A main flow of ambient air was pumped through a Horiba ASS-370 type inlet (ÖNORM, 2007) with a 40 mm I.D. x 7 m length stainless steel tube into the laboratory. The PEAC7 collected aerosol isokinetically at 2 l min^{-1} from the main flow through a nozzle of 2.2 mm diameter."

We added to P9L23 (SB):
"A whole air inlet was used for aerosol particle sampling according to the ACTRIS guideline for stations that are often embedded in clouds. The flow through the inlet was kept constant to ensure near isokinetic sampling conditions. A short description about the inlet characteristics of the Zeppelin Observatory can be found in Karlsson et al. (2020)."

As for previous INP research at the sites: This part is discussed in the respective sections 3.2.1, 3.2.2, 3.2.3 and 3.2.4 when available.

- *P5L2: "for use within an INP monitoring network" seems misleading – sounds like a strong promotion. The reviewer suggests altering this to → to collect aerosol particles*

at multiple field sites for subsequent offline INP analysis. This way, the tone would be reduced, and the point can be made for the concurrent work.

Okay.

- *P5L12-13: Please elaborate the difficulties a bit further.*

  The sample substrates need to be thoroughly cleaned before use as contaminant particles may introduce significant background freezing. This is a problem observed especially at lower temperatures (i.e. ≤ -30 °C). During the stated time frame we struggled to meet the workload associated with the cleaning procedure and INP analysis. As a result we were only able to guarantee clean (low background) substrates for temperatures ≥ -25 °C. The manuscript now reads:

  "Between October 2015 and February 2016 some unexplained contamination in the process of wafer cleaning prevented to clean substrates to below the desired background level of INP at the lowest temperature. As a consequence no data below -25°C are available for this period."

- *P5L13: Representativeness of local noon & short sampling time is questionable (the reviewer is aware that the discussion is given later on). On the other hand, the reviewer supports the best practice of pursuing consistency with this strategy employed by the authors for this study. Perhaps, such should be mentioned here to justify the strategy. The readers will understand.*

  We added the following to the description of the sampling strategy:

  "However, the level of representativeness of the deployed sampling strategy is difficult to assess (see discussion). Yet, the pursued sampling protocol ensured a consistent data base."

- *P6 Sect. 2.3.: Very informative and detailed. But, this section seemingly better fits as SI in the reviewer's opinion. Especially, P6L20-P7L10 & P7L23-P8L20 seem not relevant to the main focus of this study. Putting a subset in SI at the least would even increase the readability – the reviewer's suggestion is based on the readers' perspective.*

  We understand that the site descriptions are unusually long in comparison to other studies, but we feel it is important to this manuscript to emphasize the contrasting features of the measurement stations by including a rather thorough characterization here. Especially, as one of the main findings emerging from this study is that the deposition INPs do not seem to differ all that much from site to site, despite these differences.

- *P10L15: Delete (incomplete).*

  Okay. Note that we try to address the matter of nucleation mechanisms addressed more clearly in the revised manuscript in response to the feedback of reviewer 2.

- *P10L10-11, 16-12, and 27-29: The reviewer is impressed with these statements. Congratulations on finding these.*

  Thank you.

- *P11L1: Besides storage effects, inconsistency in inlet configurations and IN mechanisms can also play a role in the reviewer's opinion. If a proper inlet is not used for aerosol particles sampling, sampling efficiency of the sampler could be affected by local*

turbulence and other dynamic/thermodynamic conditions (e.g., sampler port get frozen/clogged). These points should be incorporated, otherwise the readers might be misled.

We added the following to P11L1:

"Furthermore, differences between the inlet configurations of the individual sites may have influenced the particle sampling process (see section 2.2)."

- *P11L7-8: Add reference(s) for bio-INPs that the authors are mentioning here or elaborate it.*

  We have added to this text passage:

  "For example, O'Sullivan et al. (2018) found that immersion INP concentrations at -20 °C at a northwestern European site were reduced by more than a factor of 2 in 59 % of the cases when samples were heated to 100 °C. For warmer temperatures the reduction was found to be significantly higher."

- *P11L9-16: So what is the implication of such a strong IS dependence? Are the authors trying to point out the condensation/droplet freezing is more predominant as compared to deposition?*

  As reviewer 2 (Paul DeMott) points out, an INP activation spectrum that is not dependent on temperature implies that immersion mode INPs were not represented in the data. We will try to address this point more clearly in the revised manuscript (see the revised text in section 2.1 and 2.3.1, and the responses to reviewer 2).

- *P11L19-22: This part is speculative. The reviewer sees lots of "may" words. But, it does justify that the sentence can remain speculative. Please introduce some references/ citations to support the authors' idea at the least.*

  We agree that the part is speculative and we believe the chosen phrasing makes this clear to the reader. Section 2.4 lists some references that indicate that long-range transport of mineral dust is a regular feature of the AZ and MQ sites.

  We added a sentence (P11L22):

  "Our view of a generally higher abundance of mineral dust at the low latitude sites MQ and AZ as compared to the high latitudes of SB and TO is supported by dust observations from surface stations (Prospero et al., 1996), remote sensing (Kaufmann et al., 2005) and models (Zender et al., 2003; Lee et al., 2009)."

- *P11L28-29: Yes. The reviewer agrees.*

  Good.

- *P12L8: That said, –> However (too informal for a scientific journal).*

  Okay.

- *P12L8-9: The source of INPs is important, but how aerosol particles are sampled at the sampling location through what sort of inlets is also an important source of potential data variation. See the reviewer's comment regarding an inlet above.*

  We agree. See previous responses.

- *P12L16: which one is bimodal? Please clarify this in the text.*

  There is no clear indication of a bimodal frequency distribution, yet, as stated, some of the data hint at it (e.g. SB).

- *P12L19-19: distribution analysis with higher sensitivity at high Ts would be a good future work (may be incorporated in depth in an outlook section?).*

  We agree with the reviewer that future works could focus on the frequency distribution of the INP concentrations for warm temperatures. Furthermore, we would like to point the reviewer to a publication by Welti et al. (2018) that shows a similar figure for INP measurements in the subtropical marine boundary layer at temperatures up to -8 °C. We have added a paragraph to the outlook (see later).

- *P12L27-29: This sentence is running too long, diluting an important message. The reviewer suggest breaking it down and carefully reformulate this sentence.*

  We rephrased the sentence:

  "Therefore, local species of plants or bacteria may be less likely to have evolved traits that induce freezing. It has previously been posited that some microbiology (e.g. bacteria like *Pseudomonas syringae*) gain an evolutionary advantage by being able to induce freezing (Morris et al., 2014)."

- *P13L9-10: background air masses mean local ambient T and RH etc.? The authors may want to add "More discussion of insignificant role of local sources is provided in the next section" or something similar to smoothly guide the readers to e.g., P13L31.*

  We are not sure what is meant by reviewer's first comment. We believe that the data supports the idea that the measured deposition INP concentrations are largely determined by large-scale background air mass movements. The ambient conditions (T and RH) define if and how many INPs will be activated to ice crystals.

  We have added a short sentence to guide the reader to section 3.2:

  "More discussion of the site specific local sources and characteristic features is provided in the following section."

- *P14L1-13: Though the reviewer finds this part (bio aerosol - INP - precipitation interactions) very interesting, some parts sound speculative simply due to the lack of sufficient data – e.g., rain intensity, wind/gust condition, rain duration etc. etc. What is discussed in this sub-section seems supplementary, not the main point of this study. The reviewer suggests either elaborate it rigorously or eliminate it completely.*

  We believe that although we cannot present sufficient evidence for the importance of biology-precipitation interactions in our data, the discussion would lack a potentially substantial INP feedback for AZ, if we completely removed the discussion. We have shortened some of the text passages. The manuscript now reads:

  "[...] Another way to interpret the anti-correlation of AF and biomass burning markers is by coupling the metric to precipitation rates. There are several intricate interactions of note here. On one hand more precipitation leads to higher aerosol particle (and INP) removal by wet deposition. Moreover, enhanced precipitation during the wet season can largely prevent wild fires and the accompanied particle emissions in the first place. On the other hand, it has

been postulated previously that precipitation may be a driver of biological INPs (Huffman et al., 2013), and large tropical rainforests like the Amazon have been highlighted in that regard (Morris et al., 2014). However, the processes responsible for the release of the biological particles have not yet been deciphered in detail."

- *P14L18: likely → presumably*

  Okay.

- *P14L24: Then, the local source seems important... This seems contradicting to the point made in P13L9-10. Please clarify.*

  On one hand we observed that during a distinct LRT episode INP concentrations were significantly correlated to mineral dust particles. However, even when no clear dust transport was registered (e.g. by back-trajectory analysis and particle measurements), electron microscopy analysis of six samples indicates that mineral dust is responsible for about half of the INPs at AZ. Therefore, we argue that there seems to be a well-mixed and diluted background concentration of mineral dust INPs at all times present at AZ. We have rephrased the text to make our argument more clear:

  "However, mineral dust may be a relevant INP in this region even in the absence of distinct LRT events: An analysis of the average composition of INPs of six samples (4 in April 2016, 2 in December 2016) using scanning electron microscopy (SEM, Figure 9), identified that nearly half of the particles that activated to ice crystals in FRDIGE were mineral dust. This finding suggests that there seems to be a well-mixed and diluted background concentration of mineral dust INPs at all times present at AZ. The diameter of most of the INPs investigated by SEM in this study was between one and a couple of micrometers (Figure 9b)."

- *P14L29-31: Very good statement.*

  Thank you.

- *P16L5: Given → Due to*

  Okay.

- *P16L5: ...atmosphere, the Arctic...(comma)*

  Okay.

- *P16L13-27: The authors may consider mentioning about a more recent study by Rinaldi et al. (2020 - https://acp.copernicus.org/preprints/acp-2020-605/). The reviewer believes that findings of Rinaldi et al. (Ny-Alesund, Gruvebadet station through a semilaminar flow TSP inlet during 2018) are consistent with what is presented in this study (2015-2017). Another place to potentially add Rinaldi et al. is on P17L11 in addition to Welti et al. (2020).*

  We thank the referee for the suggested reading. We have added a paragraph:

  P16L23: "However, a recent study by Rinaldi et al. (2020) did not observe a distinct seasonal signal in their INP measurements between -15 °C and -22 °C in the spring and summer of 2018 in Ny-Alesund. Rinaldi et al. (2020) present

INP concentrations from two separate methods, one of which is fairly similar to FRIDGE, addressing the condensation freezing (DFPC) and immersion freezing (WT-CRAFT) modes."

P16L27: "Rinaldi et al. (2020) present evidence that Arctic INP concentrations are influenced by sources of marine biological INPs by providing a spatio-temporal correlation analysis between Chlorophyll-a fields from satellite data and a trajectory model."

- *P16L32: → ... anthropogenic Arctic Haze phenomenon during our study period. The reviewer supports the authors' view, but the authors may want to reduce the tone. Otherwise, it may sound like a personal attack even without an intention. Just a suggestion to be fair on everyone in our community.*

  We meant to achieve quite the opposite effect here. In fact, we are rather a little concerned with the quality of our data due to the lack of a seasonal feature, as is frequently reported by others. We had hoped to get this message across by the last sentences of the paragraph (see P16L33 and following).

  We have added the word "concerning" in P16L34:
  "The concerning lack of meaningful correlations and/or seasonal trends may be in part related to a relatively poor signal-to-noise ratio in our SB measurements."

- *P17L4-9 & P17L22: Very good summary – the reviewer's additional hope is a consistency in an inlet sampling system.*

  We now list inconsistencies in the inlet system as one cause of uncertainty in P17L32:
  "However, when using the presented data one should be aware of the substantial limitations of the conceptual aspect of the approach and the uncertainties that are inherent in the aerosol sampling and INP measurements themselves."

- *P18L17-18: The reviewer disagrees. The finer time resolution of INP measurements for prolonged period of time with a reasonable detection - perhaps by semi-autonomous technique as mentioned towards the end of this section by the authors - is an ultimate goal/outlook for ambient INP measurements in the reviewer's opinion. With a long(er) sampling time, researchers would overlook subtle change in INP episodes or local dynamic condition that has certain roles on INP propensity.*

  We agree with the reviewer and point him/her to the very next lines (P18L19 and following.

There are quite more important things to be listed as more specific future study ideas out of this study (e.g., inlet consistency, P2L19, P12L19-19 etc.). These could be addressed in this section.
Other general outlook can be made, but the authors may look through Murray et al. (2020 -https://acp.copernicus.org/preprints/acp-2020-852/), and adapt the authors' ideas on top? Just a suggestion.

We thank the reviewer once again for sharing this excellent suggested reading. We feel it is beyond the scope of our manuscript even to attempt to fully and satisfyingly include all the listed needs of future INP research as done by Murray et al. (2020). However, we now refer to the paper to direct the interested reader

to the more extensive list. We have added a paragraph to the end of the manuscript:

"In addition to the goal of establishing more long-term global observations of continuous INP concentrations there are certainly other important areas for future research to address. For example, as most measurements are conducted at ground level, we believe there is a need to systematically study the vertical distribution of INPs – for example at heights where INPs are transported over long-ranges and/or where cloud formation occurs. Moreover, more extensive data sets from long-term INP monitoring might shed light on what mechanisms result in the observed log-normal INP frequency distributions (and departures from ideality etc.) as presented here and, for example, by Welti et al. (2018). Murray et al. (2020) has recently enumerated many crucial areas into which future INP research should delve. First and foremost, the authors emphasize the need to accurately implement ice nucleation related cloud-phase interactions in climate models in order to predict future climate scenarios correctly. We gladly refer the interested reader to Murray et al. (2020) for a more extensive list of future ice nucleation related research questions, as is presented in this study."

- *P19L8: Möhler et al. may become publicly available soon. The authors may keep an eye on it, or touch base with Dr. Möhler.*

  We have updated the reference from the Lacher et al. (2019) conference abstract to the newly available Möhler et al. (2020) paper.

- *The reviewer enjoyed reading this paper. Hope some of suggestions/comments made here help the authors (and future readers).*

  We are glad that the reviewer appreciated the manuscript. Again, we thank the reviewer for their valuable suggestions, which will most certainly improve the paper.

Literature

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Response to Referee #2 – Paul DeMott

First of all, we thank Paul DeMott for submitting helpful and productive comments and annotations, which have led to improvements and clarifications within the revised manuscript we submit with this review response.

We have prepared a revised manuscript that addresses the questions and comments of all referees. Furthermore, below we explicitly respond to each of the items raised in the comments of Paul DeMott (reviewer 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 accept the reviewers' suggestion and have implemented it within the revised manuscript. The differences are also highlighted in separate PDFs using latexdiff. All line and page numbers refer to the ACPD manuscript (version 2), not the revised manuscript.

Interactive comment on "Long-term INP measurements from four stations across the globe" by Jann Schrod et al.

General comments:

This paper is excellent as a large compilation of INP data that has been processed in a consistent manner. The effort is to be commended for that reason alone. It is also a very well written manuscript, and with most of the details one would wish for, and the abstract highlights several key points: well mixed populations that do not vary greatly overall between northern and southern continental and marine sites, short-term variability dominating at all sites, certain site specific aerosol drivers of INPs, but no universal driving aerosol property driver, and no indication of anthropogenic influences. Nevertheless, as I read the paper as it is currently organized, I struggled in knowing how to relate the method and results from the standard FRIDGE method to drop freezing assays (or the immersion mode method sometimes applied using the FRIDGE device), which are possibly the most widely used present method. It seems to me that two things are required to assist readers in understanding the nature of the results, and potentially how to consider them in relation to immersion freezing data. First, the title should explicitly describe the basis for INP measurements. In other words, "Long-term deposition/condensation freezing INP measurements. . ." or something to that effect. When one sees the INP versus ice supersaturation data in this manuscript, there is no discontinuity that occurs at water saturation (as the authors readily note), and so it seems apparent that immersion mode freezing is indeed not represented at all. The authors provide a discussion of the dominant mechanisms at play in the data and the likely underestimate in comparison to immersion freezing mode operation of the FRIDGE only very late in the paper. This is critically important in understanding if the findings can be ascribed only to deposition and condensation-freezing mode INPs, or if the same is expected for immersion freezing populations. I suggest in the specific comments that the methods used may indeed limit assessment of strong local/regional impacts, at least for biomass burning. Of course, it will not be possible to make a conclusion about what was not measured, but it should be highlighted as a question for future inspection. This should all be made crystal clear. Hence, the second recommended change is to bring a discussion forward of what types of INPs the data describe, and what types the

generalized results may not describe. It will not detract from the great effort the authors have made to collect large quantities of ice nucleation data from multiple sites and discern answers to some of the key and enduring questions related to INP sources. However, I believe that it will better frame future needs.

We thank the referee his helpful feedback and review. After re-reading the paper and the reviews, we recognize now that it may indeed be difficult to understand for the reader what is measured here and what is not. As a matter of fact, we do absolutely think that we need to explore the differences in our own measurement methods, i.e. FRIDGE standard and droplet freezing mode, to a greater extent. As for the suggested implementations, we agree to the proposed changes. Adding the addressed nucleation mode in the title will immediately help the reader orient themselves. Also, we come to the same conclusion as the referee, that the discussion about the nucleation mode appears too late in the paper and can be better introduced in the methods section as the reviewer proposes in the specific comments.

Accordingly, we have changed the title of the manuscript to:
"Long-term deposition/condensation INP measurements from four stations across the globe".

Furthermore, we now introduce both operational modes of the FRIDGE instrument shortly in a new section 2.1, indicating clearly at the beginning of the methods chapter that only the standard mode has been used in this study:
"2.1 FRIDGE operational modes

The FRIDGE instrument was originally introduced by Bundke et al. (2008) and Klein et al. (2010), but was fundamentally reevaluated and updated by Schrod et al. (2016). Since this effort FRIDGE has participated in laboratory intercomparisons (Hiranuma et al., 2015; DeMott et al., 2018; Hiranuma et al., 2019) and field campaigns (Schrod et al., 2017; Thomson et al., 2018; Gute et al., 2019; Marinou et al., 2019). In its original design FRIDGE serves as an isothermal static diffusion chamber for offline analysis of ice nucleation. In this standard operation mode FRIDGE analyzes deposition and condensation freezing INPs on substrates that had been laden with atmospheric aerosol particles by electrostatic precipitation. To avoid confusion, we point out that the FRIDGE instrument can in fact be modified to serve as a cold stage for droplet freezing assay measurements as well, which was, however, not done for the results presented here."

The former sections 2.1 (2.2 in the revised manuscript) and 2.2. (2.3. in the revised manuscript) then follow, describing the typical procedure during sampling and measurements.

Finally, we have added section 2.3.1, which goes into more detail regarding what kind of INPs were actually measured in this study, i.e. deposition/condensation vs. immersion mode and how these might relate to each other:
"2.3.1 Freezing modes

It should be noted that we cannot predict how our deposition/condensation freezing measurements would translate to the immersion freezing mode in a situation given in the atmosphere. Some conclusions may however be drawn from previous parallel

measurements (unpublished) with the FRIDGE diffusion chamber and the FRIDGE droplet freezing assay in different environments during the FIN-03 (Storm Peak Laboratory, SPL, USA, 2015), GLACE (Jungfraujoch, JFJ, Switzerland, 2017) and PICNIC (Puy de Dome, PDD, France, 2018) campaigns. Daily average INP concentrations (i.e. one day sample and one night sample) covered three orders of magnitude at -25°C. When transforming the INP concentrations to log-space, we find that the two operational modes are well-correlated (R = 0.81, N = 44), with the immersion freezing INPs being on average a factor of 10 higher than deposition/condensation INPs. In fact, the INP concentrations measured in the droplet freezing assay were always higher. One may speculate that both species simply covary for the reason of having the same sources and sinks, or that deposition INPs may represent just a subset of immersion INPs, when observed by FRIDGE, or both. We will present the results of this comparison in more detail in a forthcoming publication, in which we will further investigate how exactly the nucleation modes of both methods are connected to each other.

Except when noted otherwise, the discussion presented in section 3 will focus on the highest ice supersaturation(s) RH_{ice} at each of the three examined activation temperatures (Tab. 2). At these highest saturation conditions, at or slightly above water saturation, we observe the highest INP concentrations. We expect the nucleation mechanism to be a mixture of deposition nucleation and condensation freezing. At lower supersaturations we qualitatively observe trends and variability in INPs that are similar, but at lower absolute concentration levels."

Specific comments:

1) *Introduction*

- *Page 2, Lines 8-9: Is there a reason to separate primary biological aerosol and marine biological aerosols? They are both primary biological aerosols, no? If referring to secondary marine aerosols, you might require evidence that those play any role as INPs.*

  This was rather unintentional. We have rephrased the sentence for more clarity (we included non-biological organics to the list as suggested by reviewer 1):
  "Known species of INPs include mineral dust, soil dust, primary biological aerosol particles of terrestrial and marine origin, as well as organics and glassy aerosols (Kanji et al., 2017)."

- *Page 2, Lines 30-32: I find this statement quickly becoming untrue, with many laboratories now involved in long-term measurements of immersion freezing (e.g., Schneider et al., 2020), some with agency support, and multiple online instruments are in development (or are already there) for automated or semi-automated operation.*

  We thank the referee for the interesting paper, which was not available at the time of submission. We certainly hope that the assessment of the referee proves to be correct, as we think that having more long-term INP measurements publicly available is a crucial step in understanding the spatio-temporal variation of INP concentrations worldwide. As for the sentences in question: We think that at least for the very recent past the phrasing is correct. We fully stand by the first sentence, stating that very few of the published INP

measurements cover multiple seasons or more. We edited the second sentence, adding the assessment of the reviewer:

"A further obstacle to INP monitoring was that many instruments were previously not suited for sustained, long-term monitoring tasks due to their complex and labor intensive operating principles. However, recent developments in INP instrumentation and a shift in sampling focus may lead to more long-term INP measurements becoming publicly available now and/or in the near future (e.g. Schneider et al., 2020)."

- *Page 3, line 30 to end of paragraph: With regard to anthropogenic influences, I do think that there is some literature on this topic. Some is recent, e.g., Levin et al. (2019) found no apparent influence of urban pollution on INPs in studies in CA, USA. Chen et al. (2019) and Bi et al. (2019) discuss urban pollution impacts in Beijing.*

  While we are aware that some literature exists on this topic, we wanted to emphasize in the paragraph that the anthropogenic influence on the INP abundance and efficiency is far from conclusive at this point. We added a sentence to the paragraph (P3L26):

  "Although some recent studies indicate that urban pollution aerosol do not make efficient INPs (e.g. Chen et al., 2018), the overall anthropogenic impact on the INP concentration is still rather inconclusive (see also Schrod et al., 2020)."

2) Methods

- *Page 4, lines 28-29: Have larger particle losses been quantified? This is important, as it is a weakness compared to an open-faced filter for example, and it is not clear as an advantage over the in situ instruments mentioned in the last sentence of the paragraph. For example, Schrod et al. (2016) report collection efficiencies only to 3 microns, which is not measurably much different that impactors used on some in situ devices. And larger particles might be imagined as the most efficient deposition nuclei. While collection of and a role for larger INPs is evident ultimately in Fig. 9 for the AZ site, one wonders if the drop off of INPs at sizes above 2 microns reflects the true contributions in these size classes or is influenced at all by collection efficiencies.*

  We recognize from both reviews that more care should have been taken when describing the inlet configuration. Unfortunately, only the particle losses at AZ have been quantitatively characterized (Moran-Zuloaga et al., 2018, see section 2.4.1). Regrettably, we don't think a thorough inlet characterization is feasible at this point as the sampling devices are no longer at the sampling sites. We will add a paragraph that mentions this shortcoming more clearly. P1L27:

  "No inlet size-cutoffs were used for the results presented here, and thus we expect to sample the complete particle spectrum, except for the usual particle losses that may occur for large particle sizes. The exact aerosol inlet configuration differed substantially between sites and was mainly predetermined by the local observatory facilities. Unfortunately, these inconsistencies may lead to some aerosol sampling artifacts with respect to the absolute particle losses. The individual sampling configurations are described in section 2.4 and Tab. 1."

Table 1. Main characteristics of the geographic sampling location and inlet configuration at the sites.

	AZ	MQ	TO	SB
Geograph. coordinates	2.144° S, 59.000° W	14.735° N, 61.147° W	50.221° N, 8.446° E	78.908° N, 11.881° E
Altitude [m AMSL]	130	487	825	474
Climate	tropical	(sub-)tropical	temperate	Arctic
Continental / marine	continental	marine	continental	marine
Mountain site	no	yes	yes	yes
Predominant vegetation	tropical rainforest	diverse (i.e. ranging from alpine to tropical rainforest)	coniferous forest	low-growing tundra (summer) / snow-covered (winter)
Anthropogenic impact	near pristine to polluted	remote to polluted	rural to polluted	near pristine to polluted
Inlet type	Total Suspended Particulate (Moran-Zuloaga et al., 2018)	1/4" tube, rain shield (no characterized inlet)	HORIBA ASS-370 type (ÖNORM, 2007)	Whole-air (Karlsson et al., 2020)
Inlet height [m AGL]	60	2	11	7.5
Isokinetic flow splitter	yes	no	yes	yes
Length of tubings to PEAC7 [m]	1.5	2	1	2

As we cannot retrospectively quantify the particle losses reliably for the inlet configurations at the stations we deleted the sentence about a possible advantage of not using size-cutoffs (P4L29-31).

Concerning Figure 9, as already mentioned the inlet configuration has been characterized by Moran-Zuloaga et al., 2018, as presented in the supplementary Fig. S1 of that manuscript. Here it can be seen that transmission efficiency from the inlet was calculated to be between 90 and 100 % at 2 µm. Depending on the particle density the transmission drops for larger particle sizes. For example, at 5 µm the transmission efficiency is still between 80 and 90 % for particle densities around 1 g cm^{-3}, but may be as low as about 60% for particle densities of 2 g cm^{-3}, e.g. mineral dust or sea salt. Taking these calculations into account, we believe that the presented INP composition vs. size likely represents the true contributions quite well, at least for the bins up to 5 µm. However, the last bins may in fact be influenced by particle losses to an unknown, but non-neglectable, degree. We added a sentence to P14L28:
"Note however, that the contribution to the larger size bins might be potentially underrepresented due to particle losses from the inlet configuration."

- *Page 5, line 13 paragraph: This description of the aerosol samples had me already wondering about sampler inlets and placement. You might state that this will be covered for each specific site. I do question the statement that 100 L samples provide for "well-resolved ice crystal numbers for a broad spectrum of temperatures..." INP concentrations can span several orders of magnitude from -5 to −35 C . This paper covers a 10C range for data presentation. Finally, is the statement on storage effects necessarily assured for biological INPs that might be exposed to dessicated and higher temperature conditions? This was qualified in Schrod et al. (2016).*

  First part: see previous response.
  Second, yes, although we think a span of 10 °C is still quite good, we agree to rephrase the statement:

"The sampled aerosol particles resulting from this 100 L of air were found to usually generate well-resolved ice crystal numbers in the investigated temperature regime using the FRIDGE analysis system."

Further, we cannot guarantee that biological INPs remained active during storage and transport. We expanded upon the paragraph:
"As a result, several weeks often passed between sample collection and analysis, which may introduce an aging effect. However, in a previous study no effect of storage time on ice nucleation activity was observed within the investigated temperature regime (Schrod et al., 2016). Since a frozen storage and transport could not be logistically guaranteed for all sites and for all times, samples were stored and transported at ambient temperatures, which may have affected the warm end of (biological) INPs."

- *Section 2.2: It is worth carefully explaining the valid activation modes for this work (should be deposition and condensation "freezing" mode on line 22), perhaps by reiterating a few points from Schrod et al. (2016). This first paragraph appears to be the clear place to expound on what is known about the potential underestimations compared to immersion freezing mode INP data as well. Instead, there is only a sentence, "In this context...", which is awkward and defensive considering that the FRIDGE instrument pre-dated many of the droplet freezing assays. The instrument is clearly a tool within the wider array of ice nucleation instrument types, and to my knowledge one of the few well-characterized and documented ones that allows for exploring the full temperature and ice relative humidity space (in the mixed-phase cloud regime) for single samples, in the same manner that droplet freezing assays allow for full temperature spectra. All of the advantages of the technique compared to more labor intensive diffusion chambers and drop freezing assays are well acknowledged. What is missing for this assessment of long-term records at multiple sites is a clear indication of the relation of the modes assessed to immersion freezing. What is known and what remains for future exploration, if the method could be meshed with additional immersion freezing measures?*

  Yes, we agree with the referee. See the response to the general comments section. Furthermore, we have removed the sentence starting with "In this context".

- *Page 5, line 24: The word meaningful seems unnecessary.*

  Okay.

- *Page 7, line 15: An additional question here is if there are any considered additional particle losses in the inlet entry to the sampling system. That is, is sampling from the main inlet isokinetic (or sub- or super-isokinetic) and are any additional large particle losses characterized for that last step in collection? Similarly on page 8, line 23, it says that the sampler and the OPS instruments were connected to a 2 m stainless steel line at OVSM. Were particle transmission efficiencies characterized/expected to be the same at this site? Given the outsized role of larger particles as INPs at some surface sites (e.g., Mason et al., 2016), it seems important to know if the relative collection efficiencies were the same, and what the upper limit might be. I also note no mention of sampling inlet protocol for either TO or SB sites.*

  The inlet sampling configuration of AZ is well-characterized in the supplementary information of Moran-Zuloaga et al., 2018 to which we refer. The

main sampling line is in fact connected to an isokinetic flow splitter that was connected to the PEAC7. The main particle loss mechanism considered is sedimentation of particles >0.5 µm. P7L15:
"An extensive inlet characterization can be found in the supplementary information of Moran-Zuloaga et al., 2018."

We do assume more or less similar particle loss scenarios at the other sites to what is stated in this section, although we, unfortunately, did not characterize the transmission efficiencies at the other sites. Also see previous response.
We now add information about the inlet configurations at TO and SB:

P9L14 (TO):
"Samples were collected from the upper level of Atmospheric Physics Laboratory at the hilltop. The aerosol inlet was at 11 m above ground. A main flow of ambient air was pumped through a Horiba ASS-370 type inlet (ÖNORM, 2007) with a 40 mm I.D. x 7 m length stainless steel tube into the laboratory. The PEAC7 collected aerosol isokinetically at 2 l min^{-1} from the main flow through a nozzle of 2.2 mm diameter."

P9L23 (SB):
"A whole air inlet was used for aerosol particle sampling according to the ACTRIS guideline for stations that are often embedded in clouds. The flow through the inlet was kept constant to ensure near isokinetic sampling conditions. A short description about the inlet characteristics of the Zeppelin Observatory can be found in Karlsson et al. (2020)."

- *Page 7, line 29: A minor note here that it would be interesting to know the vegetative differences in these sites. Images of the sampling sites could also be interesting, for supplemental information.*

  We have added one picture for each site to the supplement (Figs. S1 to S4). Further, we have added Tab. 1, which describes the most relevant site characteristics, including the predominant vegetation.

- *Page 9, line 20: What is meant by "direct influence of sea salt aerosol"? Is the Zeppelin site not within the boundary layer? This is important to know with regard to what influences are being measured there. Sea spray particles would seem as one key source.*

  Yes, sea spray is still expected to be a key aerosol source. Due to the elevated position of the observatory we expect lower absolute sea salt concentrations than what would have be measured at sea level (i.e. the other research stations in Ny-Alesund). The sentence now reads:
  "The mountain top Zeppelin Observatory was chosen for its elevated position, which likely limited the effects of locally produced pollution and of sea spray from the surf zone."

3) Results and Discussion

- *Page 10, lines 10-11: Considering the discussion above about INP mechanisms, this statement about deposition being considered relatively unimportant for mixed phase*

clouds is confusing. Is this not what is measured by the FRIDGE instrument? If the traces of INP versus ice supersaturation are continuous, how to know the difference between deposition and condensation freezing? Is not the highest RH value of processing used here so that the highest INP concentrations assessable are accessed? This is the only way to understand the following statement that "incomplete" condensation freezing is assessed. Again, this may be material to consolidate in the Methods section, where it can be pointed out that an emphasis will be placed on the highest RH values for inter-comparison of site data.

Yes, the results of the highest RH are shown to give the highest INP concentration. The intention here was to say that these concentrations are the closest we can come to immersion freezing in our instrument. We recognize that the phrasing adds more confusion than it actually helps. Therefore we have removed the sentence and moved the paragraph to the methods section (see response to the general comments).

- *Page 10, lines 31-32: It is great that the authors qualify the results regarding timing of the sampling, storage impacts, etc. However, I am not sure what this statement means about long-term trends being better captured by different sampling strategies. Can you expound? Does it mean spreading the sampling periods out across daily periods? Larger volume samples collected over longer time periods? Additional use of immersion freezing methods, as in that study, to investigate if that mode of ice nucleation also shows a lack of long-term trends at sites. Also, please note that the full publication on the noted results is now in press and under review in ACP (Schneider et al., 2020). That study does show trends linked to a regional source. One can imagine that regions close to mineral dust sources also show impacts of a strong regional source, where much higher INP concentrations are noted (e.g., Price et al., 2018). Likewise, higher latitude and polar regions, especially from ship campaigns in the Southern Hemisphere (McCluskey et al., 2018; Welti et al., 2020), appear to represent extraordinarily pristine INP environments. It is simply the case that for the sites selected for this paper and the methods applied, strong cycles are not noted and short-term variability dominated. The extent to which this can be generalized for tropical and mid-latitude regions remains to be seen.*

  Yes, we primarily meant longer sampling periods/larger sampling volumes. For example, Schneider et al. (2020) have used a time resolution of 24 to 144 h at 11 L min^{-1}. However, it would be rather difficult to adapt the FRIDGE standard technique to such long sampling times, as the number of resolvable ice crystals on a substrate is limited. All of the suggestions to implement a different sampling strategy are good ideas, i.e. spreading the total sampling time out over short increments of time throughout a day as well as complementing the standard mode with the FRIDGE droplet freezing mode and longer sampling times. The manuscript has been modified to read:

  "Comparisons with other recently published data sets suggest that long-term trends may be better captured using different sampling strategies (Schneider et al., 2020). The authors of that study observe a clear seasonal cycle of immersion INPs in a boreal forest using 24 –144 h filter sampling at 11 L min^{-1}, which is a much longer sampling period than has been used here. [...]"

We have not intended to overly generalize our results. To clarify we have added the freezing mode in more instances throughout the manuscript when discussing the "INP concentration". For example, P17L10 now reads:

"In spite of the great differences in basically all characteristics that are expected to define the aerosol concentration, composition and source apportionment, we observed fairly similar INP concentrations for all four stations for the methods and sampling strategy applied."

- *Page 11, lines 15-16 and elsewhere: I have a suggestion to consider for demonstrating the spectral differences between sites, and where they are distinguished for given sites. Currently, a temperature spectral plot is not included in the paper, with too much emphasis on ice supersaturation in my opinion. Figure 5 could be made differently or augmented with an additional panel. While sometimes a linear scale is preferable, in this case if you alternately (or additionally) put these data on the same log scale, one could see the temperature differences more clearly. For example, if the y-axis scaled from 0.01 to 10 on a log scale, the temperature spectra becomes evident for conditions near water saturation, which are arguably the most important for clouds.*

  The suggested change to Fig. 5 is appreciated. We have changed it accordingly:

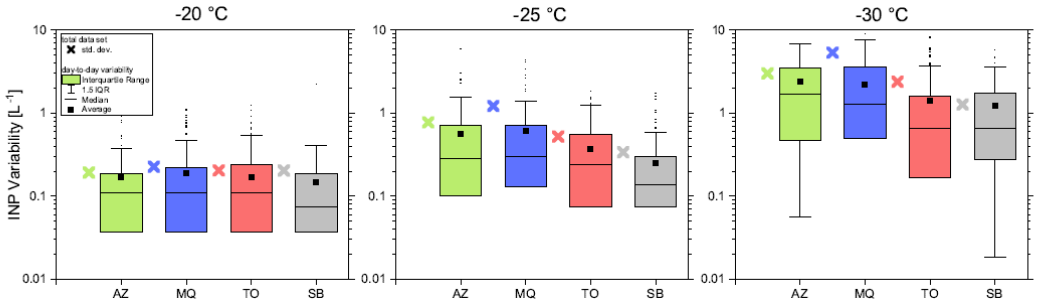

Figure 5. INP variability for $T = -20\,^{\circ}\mathrm{C}$ (left), $T = -25\,^{\circ}\mathrm{C}$ (middle) and $T = -30\,^{\circ}\mathrm{C}$ (right) at $RH_{water} = 101\,\%$. Crosses show the standard deviation of the total data set for each site. Box-plots show the distribution of sample-to-sample differences in the INP concentration of consecutive samples (i.e. day-to-day or every other day). Lower whiskers are not shown when the lower 1.5 IQR is at zero.

- *Page 12, lines 18-19: This comment harps back a little bit to the statement in Methods regarding the large dynamic range of measurements. While 100 L samples are more useful than the smaller sample volumes used in online instruments, the lack of resolution in the −20 C and warmer regime means that there is little or no access to the temperature range where one might expect most sites to be distinguished, considering for example the results shown in Petters and Wright (2015). This is also an important point to remember in the discussion here regarding whether any of the sites are distinguished by apparent biological particle influences. The measurements are just touching the regime of interest.*

  Yes, we agree. We have added a comment on P12L24, when mentioning the potential for biological INPs:

  "However, there is no strong evidence for such a signal in our data overall, possibly due to the comparably low sampling volume. As a result the temperature range of our measurements overlaps only very little with the regime where biological particles nucleate."

- *Page 13, discussion of Fig. 7: Figure 7 is a remarkable figure, and I find it astonishing that local sources do not come into play for either TO or AZ. I wonder if the authors might comment on whether INP removal is also a factor to consider, not only dilution/ mixing out from strong sources, as is inferred in the comment about "background" air masses?*

  It is possible that INPs are removed by either being activated to ice crystals or by deposition processes. However, it is difficult for us to assess how such effects may affect the distribution of INP concentrations found, and particularly if and how local sources are affected differently.

  Generally speaking, we also found the strong log-normal representations to be surprising. We believe that this is an area that deserves further attention within the community. In particular we would like to understand how skewness and departures from log-normality is affected by source function changes and atmospheric processing, but these questions go beyond what we can address in this manuscript.

- *Page 13, section 3.2.1: First, can you please clarify the timing of the "dry season" at AZ? It becomes obvious in Fig. 8, but it would be nice to see it stated in the discussion. And then one has to go back to figures to note the lack of an apparent influence of smoke. The reduction is AF is not really unexpected, right, in consideration of previous results regarding biomass burning INPs? Considering laboratory studies of surrogate and real combustion particles (Petters et al., 2009; Levin et al., 2016; Kanji et al., 2020) and field studies (Prenni et al, 2012; McCluskey et al., 2014; Schill et al., 2020)? Hence, the discussion could be clarified here, including the most recent references. One might even support that for realistic combustion particles, and not only black carbon isolated (Kanji et al., 2020) or contained in real biomass burning particles (Schill et al., 2020), water supersaturations and immersion freezing are required to see the influence of biomass burning on INP concentrations (e.g., Petters et al., 2009; Schill et al., 2020). That is, there are clear impacts of biomass burning on regional INP concentrations already demonstrated in the literature for other regions. I think this discussion needs more specifics than referencing a review paper and a single laboratory study on black carbon surrogates. Activity within the deposition and condensation freezing regime up to water saturation may be quite limited, so this may represent a case where the methods applied in this paper cannot resolve real influences on INPs, or it may indicate that fires are not sources at AZ. I think it is unresolved still.*

  The timing of the dry season is given in section 2.4.1: Dry season: August to November, wet season: February to May, transition periods in between. We will state this in 3.2.1 again now.

  We agree that the obtained results are not unexpected, as we wanted to indicate by including the Kanji et al. references. We will expand upon this point as the referee suggests, adding more references on this matter. We thank the referee for the suggested papers. P13L31 now reads:

  "The observed anti-correlation seems to suggest that aerosol particles from fires are relatively poor ice nuclei; an observation that agrees with previously published findings (Kanji et al., 2017, 2020). Considering the recent literature consensus regarding biomass burning INPs, these results are not unexpected. Biomass burning INPs have been studied in the laboratory investigating both surrogate and real combustion particles (Petters et al., 2009; Levin et al., 2016; Kanji et al., 2020), and in the field (Prenni et al., 2012; McCluskey et al., 2014;

Schill et al., 2020). Although at least a regional impact of biomass burning on INP abundance is reported, the nucleation temperatures are usually close to the homogeneous freezing limit. Some of these studies suggest that water supersaturation is a requirement for biomass burning aerosol to act as INPs (e.g. Petters et al., 2009; Schill et al., 2020). In this regard, our data may demonstrate the limits of what is explorable with FRIDGE. Either biomass burning aerosol is in fact a poor source for Amazonian INPs in the investigated temperature regime or the method simply cannot represent the freezing behavior of these particles accurately."

- *Page 14, lines 17-18: Following in the same line of comment, in fact the INP concentration results herein seem to be a factor of several lower compared to Prenni et al. (2009). It would be good to quantify what is stated presently as "on the low end".*

  Okay. The line now reads:

  "However, our observed concentrations are clustered at the low end of those presented by Prenni et al. (2009) (i.e. a factor of 5 lower at -30 °C), which is presumably due to the different nucleation modes addressed."

- *Page 15, lines 25-26: It is unclear if the conclusion here is that marine contributions to the INPs at MQ are represented in the lower range of values observed?*

  We removed the unclear sentence. The manuscript now reads:

  "[...] They measured INP concentrations of 0.06 L^{-1} at -20 °C and 0.3 L^{-1} at -24 °C, which agrees within a factor of two to our median INP concentrations at -20 °C and -25 °C."

- *Page 15, lines 32-33: Is this correlation with PM10 at TO shown anywhere? Can you at least state the r2 and p values?*

  In the next line we do present the Pearson correlation for -25°C (101%). The R-value is not impressively high, but is significant due to the large number of samples. We have added an indication of the p-value.

- *Page 16, SB section: As I read this section, I wondered about the issues brought forward at the end of the section with regard to signal to noise ratio, and how this influenced the lack of a seasonal cycle. For example, Hartmann et al. (2020) should also be referenced here. They also report winter values consistent with Tobo et al. (2019) and Wex et al. (2019). Hence, one wonders why no seasonal cycle is present in the data here. Is it just noise, or is the baseline potentially somehow even higher than you have estimated from blank data?*

  We have now added a sentence regarding the new measurements by Hartmann et al. (2020), and have added references to the measurements by Rinaldi et al. (2020) who do not find a seasonal shift in Ny-Alesund (suggested by referee 1). P16L23:

  "Very recent measurements from Greenland during March/April 2018 qualitatively agree very well to these concentration levels (Hartmann et al., 2020). However, a recent study by Rinaldi et al. (2020) did not observe a distinct seasonal signal in their INP measurements in the temperature range from -15 °C to -22 °C in the spring and summer of 2018 in Ny-Ålesund. Rinaldi et al. (2020) present INP concentrations from two separate methods, one of which is fairly

similar to FRIDGE, addressing the condensation freezing (DFPC) and immersion freezing (WT-CRAFT) modes."

Unfortunately, it is difficult to add more insight into why we did not observe a seasonal cycle in the SB data. Although some variation in the background concentration is present, we don't think that the baseline is higher overall than we have assumed. Rinaldi et al. (2020) conclude that the discrepancy of their time series with the clear spring-to-summer differences from other observations "likely indicates that the inter-annual variability of meteorological and biogeochemical conditions determining the INP atmospheric concentration over the Arctic is wider and more complex than previously assumed. For sure, the number of observations in the Arctic and their temporal coverage are still too limited to derive general conclusions on the INP concentration trends." In general, we agree with these statements, although it is still possible that we have missed a seasonal shift due to a poorly selected sampling strategy, as stated in the manuscript (see also above).

4) *Conclusions*

- *Page 17, lines 11-13: I find alluding to the Welti et al. paper results to not be a great comparison. In fact differences in the most remote locations were striking compared to mid-latitude and tropical locations in that paper and in other recent ship campaigns (McCluskey et al., 2018).*

  Okay. We have removed the reference.

- *Page 17, line 20: I think you should add "at all sites" when referring to the inability of single parameters to describe results. This is important, as influences were noted at some sites.*

  Okay.

- *Page 18, lines 3-6: This is the discussion point that needs to be introduced earlier in the paper, as I mentioned previously. One even wonders if the processing conditions emphasize certain INP types that are more well mixed in the atmosphere and contain few hygroscopic materials that would limit ice nucleation until strong condensation occurs at most of the temperatures investigated.*

  We agree and have moved the discussion to the methods section as described earlier.

  Second, unfortunately, we did not fully understand the arguments made regarding a potential bias towards more well-mixed INPs in our data, but we don't think that there is clear evidence for this hypothesis present.

5) *Outlook*

- *Page 18, lines 18-19: One wonders about varying sampling times over daily schedules to represent diurnal cycles. However, here, I wonder if it is necessarily true that longer sampling times would reduce short term variability? Would several hour samples reflect less differences than the short sample times used in this study? How do you know?*

  We do not know and this is a bit speculative. We have changed the wording:

"Longer sampling may effectively act as a low-pass filter and thereby reduce the considerable short-term variability in INPs that is observed everywhere."

- *Page 18, lines 21-22: Again I find myself disagreeing with this conclusion that automated and higher frequency sampling methods are too much of a technological challenge. It simply needs impetus and being made a priority, and I would judge that the time has already arrived.*

  We agree with the assessment of the referee and hope that soon such an effort will be made. We have changed the wording:

  "However, such an instrument and/or technique has not been available in the past and will likely present both technological and human resource challenges."

- *Page 18, lines 30-32: A reason that immersion freezing is considered so important is because clouds, and how they form, in many cases determine this result. Could immersion freezing measurements become an integral part of sampling and processing protocol for a device like the FRIDGE? Then all mechanisms except contact freezing would be assessed.*

  The sampling schedule of this manuscript began in 2014, when the immersion mode was not yet implemented. But in future FRIDGE measurements we will study the atmosphere with both the standard mode and the immersion mode setup whenever possible, just as the referee suggests.

- *Page 19, lines 9-10: I find the calling out of a single device to be inappropriate here, from a conference paper no less. Fortunately for this reference, the prime publication on the PINE came out the same day as this review (Möhler et al., 2020). However, automated CFDC instruments are already being built for surface sites (Bi et al., 2019) and under development for aircraft use. I do not understand the statement about a "vital intermediate step".*

  We thank the referee for bringing our attention to this paper (Bi et al., 2019), which we had missed. He makes a good point and we were not attempting to single out any particular device. In fact, since this time yet another instrument has also emerged (Brunner and Kanji, 2020), we reformulate to include both new references:

  "Although we are currently far from the best-case scenario of a (near) continuous automated global network of INP measurements, there are promising new developments (e.g. Bi et al., 2019; Brunner and Kanji, 2020; Möhler et al., 2020) that may provide a vital step towards long-term (semi-)automated measurements of immersion mode INPs in the near future."

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Long-term deposition/condensation INP measurements from four stations across the globe

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Abstract.

Ice particle activation and evolution have important atmospheric implications for cloud formation, initiation of precipitation and radiative interactions. The initial formation of atmospheric ice by heterogeneous ice nucleation requires the presence of a nucleating seed, an ice nucleating particle (INP), to facilitate its first emergence. Unfortunately, only a few long-term measurements of INPs exist and as a result, knowledge about geographic and seasonal variations of INP concentrations is sparse. Here we present data from nearly two years of INP measurements from four stations in different regions of the world: the Amazon (Brazil), the Caribbean (Martinique), Central Europe (Germany) and the Arctic (Svalbard). The sites feature diverse geographical climates and ecosystems that are associated with dissimilar transport patterns, aerosol characteristics and levels of anthropogenic impact (ranging from near pristine to mostly rural). Interestingly, observed INP concentrations, which represent measurements in the deposition and condensation freezing modes, do not differ greatly from site to site, but usually fall well within the same order of magnitude. Moreover, short-term variability overwhelms all long-term trends and/or seasonality in the INP concentration at all locations. An analysis of the frequency distributions of INP concentrations suggests that INPs tend to be well-mixed and reflective of large-scale air mass movements. No universal physical or chemical parameter could be identified to be a causal link driving INP climatology, highlighting the complex nature of the ice nucleation process. Amazonian INP concentrations were mostly unaffected by the biomass burning season, even though aerosol concentrations increase by a factor of 10 from the wet to dry season. Caribbean INPs were positively correlated to parameters related to transported mineral dust, which is known to increase during the northern hemispheric summer. A wind sector analysis revealed the absence of an anthropogenic impact on average INP concentrations at the Central European site. Likewise, no Arctic Haze influence was observed on INPs at the Arctic site, where low concentrations were generally measured. We consider the

collected data to be a unique resource for the community that illustrates some of the challenges and knowledge gaps of the field in general, while specifically highlighting the need for more long-term observations of INPs worldwide.

1 Introduction

Ice nucleating particles (INPs) are a crucial element in cloud formation and precipitation processes (DeMott et al., 2010; Lohmann, 2015). INPs are a rare subclass of aerosol particles with special physicochemical properties that enable the first emergence of ice crystals by reducing the critical energy barrier for spontaneous nucleation (Vali et al., 2015). ~~Depending on ambient temperature and supersaturation, INPs serve as a kind of cold temperature equivalent to cloud condensation nuclei (CCN) in the atmosphere.~~ Known species of INPs include mineral dust, soil dust, primary biological aerosol particles ~~and marine (biological) aerosol~~of terrestrial and marine origin, as well as organics and glassy aerosols (Kanji et al., 2017). In a supercooled and supersaturated cloud regime INPs may activate to ice crystals, which will then grow and possibly form secondary ice by splintering or other multiplication processes. Once grown to critical size, crystals may initiate precipitation. This is especially important for mixed-phase clouds that consist of both supercooled water droplets and ice crystals. In the presence of ice crystals water droplets will evaporate, feeding the crystals with more water vapor, a phenomenon known as the Wegener-Bergeron-Findeisen process. It is well established that the majority of global precipitation is formed through this pathway, especially over continental regions and the mid-latitude oceans (e.g. Mülmenstädt et al., 2015). INPs also influence local and global radiation budgets and related aerosol cloud interactions by affecting the phase of clouds (Lohmann, 2015).

Ice nucleation research first received some scientific attention in the 1950s and '60s, and since then interest has intensified, especially during the last one or two decades (DeMott et al., 2011). However, due to several difficulties in quantifying and characterizing INPs in the atmosphere, there are still large knowledge gaps concerning geographic and vertical distributions, seasonal and/or interannual variations, chemical composition and sources of INPs. Although there have been significant advances in identifying ~~globally relevant INP species~~ some of the INP species of global relevance (e.g. Atkinson et al., 2013; O'Sullivan et al., 2015; Wilson et al., 2015; Hiranuma et al., 2019), understanding microscopic freezing processes (e.g. Marcolli, 2014; Kiselev et al., 2017; David et al., 2019), parameterizing INP concentrations (e.g. DeMott et al., 2010; Niemand et al., 2012; DeMott et al., 2015), intercomparing INP instrumentation in standardized procedures (Hiranuma et al., 2015; DeMott et al., 2018; Hiranuma et al., 2019) and designing and characterizing new measurement techniques ~~(e.g. Garimella et al., 2016; Schrod et al., 2016; ?)~~(e.g. Garimella et al., 2016; Schrod et al., 2016; Möhler et al., 2020) , we are still far from having a complete picture. A major shortcoming is the lack of global coverage and continuous longer-term observations of INPs. Large regions of the Earth (including whole continents and oceans) are underrepresented or even completely missed by INP measurements. For those regions where observations exist, measurements primarily cover periods of a few days or weeks. Very few published INP measurements qualify as long-term observations that cover multiple seasons or year-to-year variations. A further obstacle to INP monitoring ~~is~~ was that many instruments ~~are currently~~ were previously not suited for sustained, long-term monitoring tasks due to their complex and labor intensive operating principles. However, recent

developments in INP instrumentation and a shift in sampling focus may lead to more long-term INP measurements becoming publicly available now and/or in the near future (e.g. Schneider et al., 2020).

It is noteworthy ~~, however,~~ that several projects in the early years of ice nucleation research actually succeeded in acquiring longer-term records of INP abundance. Although changes in instrumentation and sampling techniques sometimes make it difficult to utilize these decades old results in an absolute sense, the trends and relative results are quite informative. For example, Soulage (1966) coordinated a regional network of nine European stations that synchronously collected samples during the summer of 1964. In that study INP samples were analyzed using mixing chambers at $-21\,^{\circ}\mathrm{C}$. In the resulting publication the author speculated that some positive anomalies in the record of INPs were associated with episodes of advected Saharan dust and/or might have been affected by industrial particles. From 1959 to 1962 Kline (1963) measured INPs for the U.S. National Weather Service at 15 sites using an expansion-type chamber that operated from $-20\,^{\circ}\mathrm{C}$ to $-24\,^{\circ}\mathrm{C}$. The measurements present evidence that terrestrial aerosol particles dominate the INP budget of the lower atmosphere. The geographic site-to-site variability was about an order of magnitude, while day-to-day fluctuations of up to several orders of magnitude were recorded at single sites. Bigg collected INPs on membrane filters across Eastern Australia and New Zealand during several months of 1962 – 1964 (Bigg and Miles, 1964). Later he continued sampling in the marine boundary layer over large parts of the remote Southern Ocean around Australia from 1969 to 1972 (Bigg, 1973). Samples were analyzed in a thermal vapor diffusion chamber. Bigg's most striking results were (i) the similarity of INP abundances in the continental atmosphere and in the marine boundary layer, and (ii) the occurrence of high concentrations of INPs in remote areas far west and east of the Australian continent. In another multi-year study from 1964 to 1968 the Austrian Meteorological Service (Zentralanstalt für Meteorologie und Geodynamik) measured the abundance of INPs at $-21\,^{\circ}\mathrm{C}$ using the method of Soulage (1965) at three sites, three times per day (Müller, 1969). That data also displays a relatively high day-to-day variability of INP abundance. The sparseness of these few historic measurement efforts highlights the need for more long-term INP observations.

Measurements of cloud-active aerosols in remote and/or near pristine environments are particularly rare and therefore inherently valuable. Such regions may be studied to gain insight into aerosol conditions in environments that are only marginally perturbed by humans. This information is needed to estimate the reference baseline of pre-industrial aerosol (Carslaw et al., 2017). Such a baseline is vital to the accurate evaluation of anthropogenic climate effects, as it is integral to the assessment of the anthropogenic contribution to present day radiative forcing. All estimates of anthropogenic aerosol effects are highly sensitive to the assumed pre-industrial baseline, including the degree to which cooling aerosol effects have compensated for the radiative forcing by greenhouse gases in the past and present (Andreae et al., 2005; Andreae, 2007; Carslaw et al., 2013; Gordon et al., 2016, 2017). Moreover, the largest uncertainty with respect to global radiative forcing emerges from knowledge gaps related to interactions between aerosols and clouds, as highlighted within IPCC assessment reports (IPCC, 2014). Although some recent studies indicate that urban pollution aerosol do not make efficient INPs (e.g. Chen et al., 2018), the overall anthropogenic impact on the INP concentration is still rather inconclusive (see also Schrod et al., 2020). Given the poor understanding of INP climatology and life cycles, it is not surprising that the magnitude and effects of a potential anthropogenic INP perturbation cannot yet be assessed (Boucher et al., 2013, IPCC AR5, chapter 7). Similarly, in a review of the state of knowledge on pre-industrial aerosols Carslaw et al. (2017) were unable to comprehensively discuss the matter due to a lack of

thorough understanding regarding which aerosol components dominate the INP spectra. They argue that the concentrations of INPs, which tend to be large particles, likely have not changed as much as those of smaller particles, which have been found to be significantly altered since the pre-industrial era (Hamilton, 2015; Gordon et al., 2017). Nonetheless, Carslaw et al. (2017) acknowledge that potential anthropogenic modifications to INP concentrations or compositions and related impacts on cloud formation, radiation interactions and precipitation processes since the industrialization remain unquantified.

Here we present long-term measurement data of INPs from a small but unique network of stations spanning over 80° in latitude. Observational sites were located within vastly contrasting climates and ecosystems, featuring continental tropical, marine subtropical, continental mid-latitude and Arctic mountaintop locations. The sites are exposed to varying and seasonally different degrees of anthropogenic influence; yet all can be classified as rural, remote and/or pristine environments for at least parts of the year. However, truly pristine regions, which still resemble their pre-industrial state in all facets, may be hard to find on an increasingly polluted planet (Hamilton et al., 2014). For this study, INPs were sampled at the Amazon Tall Tower Observatory (Brazil, 2.144° S, 59.000° W, Fig. S1), the Volcanological and Seismological Observatory of Martinique (Caribbean Sea, 14.735° N, 61.147° W, Fig. S2), the Taunus Observatory (Germany, 50.221° N, 8.446° E, Fig. S3) and the Zeppelin Observatory (Norwegian Arctic, 78.908° N, 11.881° E, Fig. S4).

Between May 2015 and January 2017 a total of 1212 aerosol samples (7704 data points) were collected and analyzed for INPs in the deposition and condensation freezing modes (Fig. 1). Aerosol samples were collected using electrostatic precipitation onto silicon substrates in a semi-automated routine. Samples were shipped to our laboratory in Frankfurt and were subsequently analyzed for ice nucleation activity using the FRIDGE isothermal vacuum diffusion chamber (Schrod et al., 2016, 2017). Each sample was analyzed at multiple combinations of temperature ($-20\,^{\circ}\mathrm{C}$, $-25\,^{\circ}\mathrm{C}$ and $-30\,^{\circ}\mathrm{C}$) and relative humidity (95%, 97%, 99%, 101% w.r.t. water).

The main objectives of this study were to (1) observe the long-term concentrations and variability of INPs, (2) investigate potential trends and/or seasonalities, (3) compare the INP concentrations of diverse geographic locations, (4) estimate the anthropogenic impact on INPs at semi-pristine sites and (5) try to identify what factors control ice nucleation in the atmosphere.

2 Methods

2.1 FRIDGE operational modes

The FRIDGE instrument was originally introduced by Bundke et al. (2008) and Klein et al. (2010), but was fundamentally reevaluated and updated by Schrod et al. (2016). Since this effort FRIDGE has participated in laboratory intercomparisons (Hiranuma et al., 2015; DeMott et al., 2018; Hiranuma et al., 2019) and field campaigns (Schrod et al., 2017; Thomson et al., 2018; Gute e
. In its original design FRIDGE serves as an isothermal static diffusion chamber for offline analysis of ice nucleation. In this standard operation mode FRIDGE analyzes deposition and condensation freezing INPs on substrates that had been laden with atmospheric aerosol particles by electrostatic precipitation. To avoid confusion, we point out that the FRIDGE instrument can in fact be modified to serve as a cold stage for droplet freezing assay measurements as well, which was, however, not done for the results presented here.

2.2 Aerosol sampling

In all locations aerosol samples were collected using the Programmable Electrostatic Aerosol Collector (PEAC7, Schrod et al., 2016). PEAC7 precipitates aerosol particles, which have been charged by collision with corona-discharge electrons, electrostatically onto a semi-conducting grounded sample substrate made from commercially available silicon wafers. The 45 mm diameter substrates have three laser-engraved crosses used to generate a coordinate system that allows ice crystals and thus particles to be located in the INP counter FRIDGE (Sec. 2.3). Electrostatic precipitation is advantageous compared to simple impaction, as particles are distributed more homogeneously across the surface. Thereby, FRIDGE is able to activate and count up to about 1000 separate ice crystals simultaneously on one sample substrate. The PEAC7 collection efficiency has been found to be about 60 %, independent of particle size (Schrod et al., 2016). Accordingly, a correction factor of 0.6 has been applied to the data. No inlet size-cutoffs were used for the results presented here, and thus we expect to sample the complete particle spectrum, except for the usual particle losses that may occur for large particle sizes. ~~This is of some advantage compared to in-situ INP counters with optical detection that need to distinguish unactivated large aerosol particles from activated INP (i.e. ice crystals) by eliminating large particle intake (> 1.5 or 2.5). Since ice nucleation tends to increase with particle size/surface area (DeMott et al., 2010), this may bias results.~~ The exact aerosol inlet configuration differed substantially between sites and was mainly predetermined by the local observatory facilities. Unfortunately, these inconsistencies may lead to some aerosol sampling artifacts with respect to the absolute particle losses. The individual sampling configurations are described in section 2.4 and Tab. 1.

PEAC7 utilizes a step motor powered rotary disc with seven sample substrate slots for programmed sampling. When connected to a PC with an internet connection, PEAC7 can be programmed either directly or remotely to start and stop sampling at prescribed times. This configuration enables daily sampling for one week with minimal service and maintenance. Combined with the ease of operation, this makes PEAC7 a well-suited instrument ~~for use within an INP monitoring network~~to collect aerosol particles at multiple field sites for subsequent offline INP analysis.

A PEAC7 unit was first installed in 2012 at the Mt. Kleiner Feldberg Observatory of the Goethe University of Frankfurt. PEAC7 units were deployed at the other three sites during the summer and fall of 2014. The local staff of each observatory conducted the regular measurements and maintenance after being trained in the handling of the instrument. Concurrent sampling began in May 2015 and continued (with some interruptions) until January 2017 for the three overseas stations. The measurements at Taunus Observatory began earlier and continued longer, but here we focus on the concurrent sampling effort conducted within the framework of the EU FP7 BACCHUS project (Fig. 1). Due to the failure of the complementary aerosol instrumentation at the Caribbean site, sampling was interrupted between December 2015 and May 2016. Furthermore, the exchange of sampling substrates with the Amazonian site was logistically challenging. Thus, the Amazon data set is represented by several shorter periods of continuous measurements. ~~Difficulties in obtaining sufficiently clean new substrates also prevented measurements below~~ Between October 2015 and February 2016 some unexplained contamination in the process of wafer cleaning prevented to clean substrates to below the desired background level of INP at the lowest temperature. As a consequence no data below −25 °C ~~between October 2015 and February 2016 in some cases~~are available for this period.

Typically, aerosol samples were collected with PEAC7 daily or once every two days at local noon. Sampling time was prescribed to 50 minutes with a 2 L min^{-1} flow rate. The sampled aerosol particles resulting from this 100 L of air were found to usually generate well-resolved ice crystal numbers ~~for a broad spectrum of temperatures~~ in the investigated temperature regime using the FRIDGE analysis system. ~~Samples were~~ However, the level of representativeness of the deployed sampling strategy is difficult to assess (see discussion). Yet, the pursued sampling protocol ensured a consistent data base. Samples were then stored in PetriSlide containers after collection until they were shipped unfrozen in packages of 25 – 50 to our laboratory in Frankfurt (transport time was usually less than a week). As a result, several weeks often passed between sample collection and analysis, which may introduce an aging effect. However, in a previous study no effect of storage time on ice nucleation activity was observed within the investigated temperature regime (Schrod et al., 2016). Since a frozen storage and transport could not be logistically guaranteed for all sites and for all times, samples were stored and transported at ambient temperatures, which may have affected the warm end of (biological) INPs.

2.3 Analysis of ice nucleation samples

~~FRIDGE is an isothermal static diffusion chamber for offline analysis of ice nucleation. In its standard operation mode FRIDGE analyzes deposition and condensation mode INPs on substrates that had been laden with atmospheric aerosol particles by electrostatic precipitation. FRIDGE was originally introduced by Bundke et al. (2008) and Klein et al. (2010), but was fundamentally reevaluated and updated by Schrod et al. (2016). Since this effort FRIDGE has participated in meaningful laboratory intercomparisons (Hiranuma et al., 2015; DeMott et al., 2018; Hiranuma et al., 2019) and field campaigns (Schrod et al., 2017; . In this context FRIDGE has been validated as a reliable method for INP measurements and can be regarded as a valuable addition to the widely used online continuous flow diffusion chambers and offline droplet freezing assays. To avoid confusion, we like to point out that the FRIDGE instrument can in fact be modified to serve as a cold stage for droplet freezing assay measurements as well, which was, however, not done for the results presented here.~~

~~During measurements~~

During a FRIDGE measurement the sample substrate is placed on the cold table inside a sealed measurement cell. The temperature of the substrate is controlled by a Peltier element and monitored by a PT-1000 sensor at the wafer surface. The measurement cell is connected by a valve to a water vapor source. The vapor source vessel is evacuated, except for water vapor from a thin ice film coating the inner walls, which are temperature-controlled by a cryostat (Huber Petit Fleur). Thus, the temperature of ice film defines the water vapor pressure (Clausius-Clapeyron equation), which is measured by an Edwards Barocel capacitance manometer. The measurement cell is kept at near vacuum conditions, until a controlled amount of water vapor is introduced as a measurement begins by opening the valve to the vapor source. Ice crystals activate rapidly on the surface of INPs and grow to macroscopic sizes within some tens of seconds. The ice crystals are counted automatically by a CCD camera viewing the measurement from above. After a measurement is completed, the valve to the water vapor source is closed and the valve to the vacuum pump is opened. Subsequently, ice crystals evaporate and a new combination of temperature and ice supersaturation can be selected (Tab. 2). Typical measurement uncertainties are summarized in the caption of Tab. 4. A complete description of the method can be found in Schrod et al. (2016).

One of the main strengths of FRIDGE is the direct visual observation of the ice crystal formation on the surface of the sample substrate. No complicated data analysis is required to establish the number of INPs. Furthermore, knowing the exact location of a specific ice crystal, allows for a subsequent electron microscopy analysis to determine the chemical composition and morphology of individual INPs. We refer to our previous study for methodological details about coupling FRIDGE to an scanning electron microscope (Schrod et al., 2017).

2.3.1 Freezing modes

It should be noted that we cannot predict how our deposition/condensation freezing measurements would translate to the immersion freezing mode in a situation given in the atmosphere. Some conclusions may however be drawn from previous parallel measurements (unpublished) with the FRIDGE diffusion chamber and the FRIDGE droplet freezing assay in different environments during the FIN-03 (Storm Peak Laboratory, SPL, USA, 2015), GLACE (Jungfraujoch, JFJ, Switzerland, 2017) and PICNIC (Puy de Dome, PDD, France, 2018) campaigns. Daily average INP concentrations (i.e. one day sample and one night sample) covered three orders of magnitude at $-25\,^{\circ}\mathrm{C}$. When transforming the INP concentrations to log-space, we find that the two operational modes are well-correlated (R = 0.81, N = 44), with the immersion freezing INPs being on average a factor of 10 higher than deposition/condensation INPs. In fact, the INP concentrations measured in the droplet freezing assay were always higher. One may speculate that both species simply covary for the reason of having the same sources and sinks, or that deposition INPs may represent just a subset of immersion INPs, when observed by FRIDGE, or both. We will present the results of this comparison in more detail in a forthcoming publication, in which we will further investigate how exactly the nucleation modes of both methods are connected to each other.

Except when noted otherwise, the discussion presented in section 3 will focus on the highest ice supersaturation(s) RH_{ice} at each of the three examined activation temperatures (Tab. 2). At these highest saturation conditions, at or slightly above water saturation, we observe the highest INP concentrations. We expect the nucleation mechanism to be a mixture of deposition nucleation and condensation freezing. At lower supersaturations we qualitatively observe trends and variability in INPs that are similar, but at lower absolute concentration levels.

2.4 Measurement Sites

2.4.1 Amazon Tall Tower Observatory – AZ

The Amazon Tall Tower Observatory (ATTO, 2.144° S, 59.000° W, 130 m AMSL) was established to investigate atmosphere-biosphere interactions and for observing long-term changes in the Amazonian environment. The ATTO site is located about 150 km northeast of Manaus, Brazil. Atmospheric measurements have been conducted here since 2012, when two 80 m towers were constructed. The main ATTO tower (325 m) was finished in 2015.

The Amazon basin contains the largest rainforest in the world and thus has great importance for global and regional carbon- and water cycles and biodiversity. Although the “green ocean” is unparalleled in size, distinct changes in the water- and energy budgets of the Amazon basin are becoming apparent due to anthropogenic impacts such as agricultural expansion, deforesta-

tion and climate change (Davidson et al., 2012). According to Davidson et al. (2012) the Amazon basin is already in transition and it is therefore important to monitor changes and their related effects on the biosphere and the atmosphere. Andreae et al. (2015) present a detailed description of the site characteristics and provide an overview of the vast array of ecological, meteorological, trace gas and aerosol measurements at ATTO. Pöhlker et al. (2019) expanded upon the general site characterization by presenting a comprehensive analysis of the backward trajectory footprint region for the ATTO site and included an in-depth discussion about land cover transformations. Back trajectories differ significantly between the wet season (February to May: northeast) and the dry season (August to November: southeast). There is also a distinct seasonality in pollution markers measured at the site (Saturno et al., 2018; Holanda et al., 2020). During the dry season biomass burning heavily influences the site, resulting in an order of magnitude increase in aerosol number concentration. Pöhlker et al. (2016) conducted size segregated CCN measurements that provide near continuous coverage of a complete seasonal cycle. They found a pronounced CCN seasonality that covaries with both aerosol number concentration and pollution markers. However, during the wet season aerosol conditions remain largely unaffected by pollution and are considered to be comparatively clean. According to Pöhlker et al. (2018) there are typically 10 to 40 days from March to May, which can be considered as pristine. During both dry and wet season (and especially in February and March) plumes of long-range transported aerosol are relatively frequent. These aerosols include Saharan dust (mainly wet season), particles from biomass burning in Africa and sea salt from the Atlantic Ocean. During such episodes of long-range transport, coarse mode particle concentrations may rise above $100\,\mu g\,m^{-3}$, altering the aerosol size spectrum and composition substantially (Moran-Zuloaga et al., 2018). Except for these singular events, coarse mode particle concentrations remain fairly constant throughout the year, showing only a weak seasonality. In the absence of long-range transport, primary biological aerosol particles (PBAP) dominate the coarse mode population. It is important to note here, however, that PBAPs peak during the night time in Amazonia. At local noon, when the samples were collected, concentrations of PBAPs are typically a factor of 2 – 5 lower (Huffman et al., 2012).

The INP sampling device PEAC7 was installed inside a container at the base of one of the smaller 80 m towers. Ambient air was introduced to PEAC7 through a 25 mm stainless steel line, connected to a total suspended particle inlet at 60 m AGL (i.e. 30 m above canopy height). Moran-Zuloaga et al. (2018) show that losses of particles < 2 µm at realistic particle densities are usually well below 10% for this setup and the transmission efficiency only drops below 50% for particles larger than 6 µm and a high particle density of $2\,g\,cm^{-3}$. An extensive inlet characterization can be found in the supplementary information of Moran-Zuloaga et al. (2018).

INP measurements from this site are labeled with the abbreviation AZ.

2.4.2 Volcanological and Seismological Observatory of Martinique – MQ

The Volcanological and Seismological Observatory of Martinique (OVSM, 14.735° N, 61.147° W, 487 m AMSL) is located on the Morne des Cadets mountaintop in northwestern Martinique, which is an island in the Lesser Antilles in the Caribbean Sea. The observatory, in its current form, was built in 1937 after scientific interest increased following a devastating volcanic eruption of the close-by Mt. Pelée in 1902 and a second period of activity from 1929 to 1932. The observatory is operated by the Institut de Physique du Globe de Paris and closely monitors the local volcanic and regional seismic activity.

About two thirds of Martinique is protected by regional natural parks to preserve the island's environment. A regional park completely surrounds the observatory and encompasses the majority of northwestern Martinique, which contains large areas that are labeled as natural zones of major interest (PNRM). The observatory is about 15 km north of the capital Fort-de-France and about 20 km northwest of the island's airport. Eastern trade winds are dominant and air masses reaching the site are primarily of maritime origin. Thus, we find it unlikely that our measurements of INPs are significantly influenced by local pollution.

Similar to the Amazonian site, the Caribbean site is also subject to a seasonality in precipitation and atmospheric transport patterns due to the migration of the Intertropical Convergence Zone (ITCZ). The dry season begins in December and ends in May, the wet season lasts from June to November.

Stevens et al. (2016) analyzed two years of daily 10-day back trajectories arriving at 3 km over Barbados. Qualitatively, this analysis should also be representative of the large scale transport pattern to Martinique, which is only 200 km northwest of Barbados. It was found that the majority of air masses originated north of 10° N and east of 55° W. Approximately half of the air masses traveled from this direction during the dry season and about two-thirds during the wet season, respectively. During the dry season 8% of these air masses are influenced by the European or African continent(s), and 55% during the wet season. Accordingly, seasonal wind shifts regulate the amount of long-range transported aerosol arriving in the Caribbean. The maximum contribution of Saharan mineral dust over the Lesser Antilles is found in the Northern Hemisphere (NH) summer. Yet, the interactions between dust and precipitation introduce considerable variability in aerosol optical depth (AOD) during the wet season (Stevens et al., 2016). Some "clean periods" with AOD below 0.01 were observed, despite the generally heavy dust load during the wet season. In the dry season the amount of dust reaching the Caribbean is reduced considerably. The long-term trends, variation and seasonality of mineral dust transported to the Caribbean have been monitored almost continuously since 1965 (Prospero and Lamb, 2003). The Lesser Antilles' location at the end of the transatlantic trade wind flow and the well characterized dust fraction make it an excellent place to investigate the influence of mineral dust on cloud formation.

Sea salt makes up most of the remaining mass fraction of Caribbean aerosol. The mass concentration of sea salt is typically of the same order of magnitude as mineral dust, yet its seasonality is different (Stevens et al., 2016). Due to higher wet scavenging and slower wind speeds from June to November, the sea salt contribution is at a minimum during the wet season and a maximum during the dry season.

To date few investigations of atmospheric aerosol and cloud formation have been conducted in the Lesser Antilles and none at OVSM. In 2011 the extensive field campaign DOMEX-2011, which focused on the formation of orographic clouds and related precipitation events, was based from Dominica, the island just to the north of Martinique (Smith et al., 2012). The DOMEX campaign, which included several research flights, found that the clouds and precipitation were strongly sensitive to trade wind speeds and therefore local dynamics and convection. In that campaign INPs were not considered as an important variable or driver of clouds and precipitation.

Prior to the initiation of the PEAC7 sampling in September 2014, OVSM was not equipped with aerosol instrumentation. Therefore, a TSI OPS 3330 (optical particle diameter: 0.3 – 10 µm) was installed to compliment the PEAC7 measurements. Both instruments were connected to a 2 m stainless steel line, mounted on the north side of the building. The inlet was open

to freely circulating air coming from west, north and the east (main wind direction) and was protected from precipitation and spray water by a custom made lid.

INP measurements from this site are labeled with the abbreviation MQ.

2.4.3 Taunus Observatory – TO

The Taunus Observatory (TO, 50.221° N, 8.446° E) is located on top of the Mt. Kleiner Feldberg (825 m AMSL) within the Taunus highlands of central Germany. There are several mountain peaks of similar height in the immediate vicinity (e.g. Mt. Großer Feldberg at 878 m AMSL and Mt. Altkönig at 798 m AMSL). The Taunus mountains are nearly completely forested, predominantly with coniferous trees. Sobanski et al. (2016) described the land cover of the area surrounding the Kleiner Feldberg, and found that about 80% of the area within 5 km is covered by forest. Within 50 km about one third of the area is forested, while agriculture makes up another 40% and urban areas about 10%. The Taunus mountain range extends about 70 km from the Rhine river to the northeast and serves as a natural barrier to the Rhine-Main metropolitan region, with its center located to the south of the range. The Rhine-Main metropolitan region is heavily industrialized and densely populated, with about 2.2 million people living in and around the city of Frankfurt. The city lies about 20 km southeast of the Taunus Observatory. At the southwestern end of Frankfurt is the industrial area Höchst, which is one of the largest chemical and pharmaceutical industrial sites in Europe. The Frankfurt Airport is also roughly 20 km to the south of the observatory. The cities of Wiesbaden and Mainz are also located 20 – 30 km to the southwest. In contrast, the northern sector is sparsely populated and predominantly devoid of industrial influence for 50 to 100 km.

Pollutant data, measured routinely by the Hessian Agency for Nature Conservation, Environment and Geology (HLNUG) using a Horiba APNA 370 (NO and NO_2), a Horiba APOA 370 (O_3) and Digitel DHA-80 (PM_{10}), has been analyzed for TO for the years 2015 to 2017, in order to quantify the predominant ~~wind direction at TO and~~ direction of the anthropogenic influence. Thirty-minute mean concentrations of pollutants have been divided into wind sectors and are presented in ~~Table~~Tab. 3. As expected, pollutant concentrations are significantly higher when originating from the metropolitan sector, compared to air coming from other directions. However, as can be seen in ~~Table~~Tab. 3 the site is rarely downwind from the highest pollution sources. In fact, the main wind direction is west. Thus generally, the site may be categorized as primarily rural with anthropogenic impacts.

Samples were collected from the upper level of Atmospheric Physics Laboratory at the hilltop. The aerosol inlet was at 11 m above ground. A main flow of ambient air was pumped through a HORIBA ASS-370 type inlet (ÖNORM, 2007) with a 40 mm I.D. x 7 m length stainless steel tube into the laboratory. The PEAC7 collected aerosol isokinetically at 2 $L\,min^{-1}$ from the main flow through a nozzle of 2.2 mm diameter.

INP measurements from this site are labeled with the abbreviation TO.

2.4.4 Zeppelin Observatory – SB

The Zeppelin Observatory, operated by the Norwegian Polar Institute, is located on Zeppelin Mountain close to Ny-Ålesund in Svalbard (78.908° N, 11.881° E, 474 m AMSL). Svalbard, and Ny-Ålesund in particular, is a well-established site for Arctic

and atmospheric research. The scientific focus of the observatory is to characterize the Arctic atmosphere and identify relevant atmospheric processes in a changing Arctic climate. The mountain top Zeppelin Observatory was chosen for its elevated position, which ~~limits~~ likely limited the effects of ~~local pollution and direct influence of sea salt aerosol~~locally produced pollution and of sea spray from the surf zone. However, the observatory largely remains within the planetary boundary layer (Tunved et al., 2013). The station is representative of the remote Arctic, making it a unique location to study atmospheric aerosol. A variety of trace gases, greenhouse gases, aerosol particles, heavy metals and other compounds are monitored continuously at Zeppelin. A whole air inlet was used for aerosol particle sampling according to the ACTRIS guideline for stations that are often embedded in clouds. The flow through the inlet was kept constant to ensure near isokinetic sampling conditions. A short description about the inlet characteristics of the Zeppelin Observatory can be found in Karlsson et al. (2020).

Tunved et al. (2013) calculated a monthly climatology of air masses arriving at Mt. Zeppelin between 2000 and 2010. They observed two primary transport patterns: For most of the year trajectories predominantly originated from Siberia and Eurasia. These air masses are mainly transported over the Arctic Ocean before arriving at Svalbard. During the summer months Atlantic air masses arriving from the southwest are most frequent. Although the Arctic is generally associated with clean atmospheric conditions, there are times of the year when contaminants are transported to the Arctic, leading to a significant decrease of air quality. This so-called Arctic Haze phenomenon has been long known and is well-studied. The Arctic Haze occurs during late winter and spring when air is transported from industrialized source regions in Eurasia and North America. Tunved et al. (2013) observed the aerosol mass concentration over a period of 10 years at Zeppelin Observatory and confirmed an annually repeating Arctic Haze signal with a maximum in spring. Long-term black carbon measurements at Zeppelin show virtually the same seasonal pattern (Eleftheriadis et al., 2009). Cruise ships have been identified as an additional important local source at Zeppelin (Eckhardt et al., 2013). In a generally clean environment this might be of importance to INPs, as ship emissions have previously been observed to amplify INPs (Thomson et al., 2018). Weinbruch et al. (2012) analyzed over 50,000 individual particles in 27 aerosol samples collected between summer 2007 and winter 2008 at Mt. Zeppelin by electron microscopy. Potential INP-related particles, i.e. particles with a diameter larger than 0.5 µm, were mainly categorized as sea salt, aged sea salt, silicates or mixed particles (i.e. mixtures of sea salt, silicates and calcium sulphates). Mineral dust particles were found to follow a seasonal pattern with a summer minimum.

INP measurements from this site are labeled with the abbreviation SB.

3 Results and Discussion

3.1 Concentrations, variations, trends and seasonality of INPs

~~Except when noted otherwise, the following discussion will focus on the highest ice supersaturation(s) RH_{ice} at each of the three examined activation temperatures (Tab. 2). These are highlighted, because pure deposition nucleation is considered to be relatively unimportant to ice nucleation at the observed temperatures of most mixed phase clouds (e.g. **?**). At these highest saturation conditions, at or slightly above water saturation, we expect the nucleation mechanism to be a mixture of deposition~~

~~nucleation and (incomplete) condensation freezing. At lower supersaturations we qualitatively observe trends and variability in INPs that are similar to what we present here, but at lower absolute concentration levels.~~

~~In Figs. 2, 3 and 4 the~~ The INP concentrations from May 2015 to January 2017 at the four stations at $-20\,^{\circ}\mathrm{C}$, $-25\,^{\circ}\mathrm{C}$ and $-30\,^{\circ}\mathrm{C}$ are presented ~~.~~ in Figs. 2, 3 and 4. Key statistical parameters of the data set are summarized in Tab. 4. The most striking result from the time series is that the deposition/condensation freezing INP concentrations do not fundamentally differ from station to station. We find that average INP concentrations at the examined temperatures are of the same order of magnitude for all sites. This observation is somewhat surprising, since the sites represent drastically different environments. It seems that the climate and ecosystem defining characteristics, like the geography of maritime versus continental locations, Arctic versus temperate versus tropical systems, and the altitude within the planetary boundary layer, are not overly critical to INP abundance. Instead, it appears as though these differences are mostly lost in the large variability of the INP concentrations. Figure 5 shows the day-to-day variability of the time series. The magnitude of the short-term variability is often almost as high as the total variability of the complete data set, which is represented as the standard deviation in the figure. Overall, short-term variability far outweighed any long-term trend or seasonality at any location or temperature. In fact, mean INP concentrations remained remarkably constant throughout the investigated time period, which is apparent from the 10 point moving averages in Figs. 2, 3 and 4. Moreover, the lack of well-defined peak INP concentrations is evident (on the logarithmic scale). These findings are remarkable considering that the climatic and geographical features of the sites are accompanied by vastly dissimilar air mass transport patterns, aerosol source locations and levels of anthropogenic impact. However, it should be noted here that the collected data represents single 50 minute sampling intervals at local noon with a frequency of 0.5 to 1 sample per day. The level to which the sampling strategy may implicitly result in the observed high short-term variability is uncertain and should be carefully explored. Comparisons with other recently published data sets suggest that long-term trends may be better captured using different sampling strategies ~~(?).~~ (Schneider et al., 2020). The authors of that study observe a clear seasonal cycle of (biological) immersion INPs in a boreal forest using 24 – 144 h filter sampling at 11 $\mathrm{L\,min^{-1}}$, which is a much longer sampling period than has been used here. Thus it remains an open challenge for the INP community to establish robust measurement protocols for monitoring efforts. Moreover, we cannot entirely exclude the possibility that storage effects may have dampened the trends of the INP concentrations to some degree. Furthermore, differences between the inlet configurations of the individual sites may have influenced the particle sampling process (see section 2.2).

On average, INP concentrations were lowest at SB, which is what can be expected for an Arctic environment. Yet, mean INP concentrations at the other stations were only higher by a factor of 2 – 4 at $-30\,^{\circ}\mathrm{C}$, with those at MQ being the greatest. Especially during the summer of 2015 MQ concentrations were relatively high. However, at the warmest temperature ($-20\,^{\circ}\mathrm{C}$), the highest INP concentrations are measured at TO. In addition, there are fewer samples below the detection limit or the significance level at $-20\,^{\circ}\mathrm{C}$ at TO. ~~As~~ Because the site is surrounded by forests, this might point to a local source of biological INPs, which are known to activate at warmer temperatures. For example, O'Sullivan et al. (2018) found that immersion INP concentrations at $-20\,^{\circ}\mathrm{C}$ at a northwestern European site were reduced by more than a factor of 2 in 59% of the cases when samples were heated to 100 $^{\circ}\mathrm{C}$. For warmer temperatures the reduction was found to be significantly higher.

Decreasing the nucleation temperature by 5 °C enhances average INP concentrations by a factor of 2.4 to 5.6. However, as seen in Figs. 6 and ~~S1~~S4, average INP concentrations depend predominantly on ice supersaturation. Decreasing temperature alone does not significantly enhance INP concentrations in the addressed nucleation mode. Rather, decreasing the temperature by 5 °C implicitly leads to an increase in RH_{ice} by approximately 6% for our ascribed conditions (Tab. 2). Thus, if there were any temperature dependence of note in our data, it would appear as a discontinuity in these plots. Figure 6a shows the median INP concentrations for all measured conditions at each site as a function of supersaturation. The figure implies strong exponential correlations between the INP concentrations and the ice supersaturation (R^2 between 0.95 and 0.98). Once more, we see that at TO more active INP are found at lower supersaturation, i.e. warmest temperature (−20 °C). At intermediate ice supersaturations INP concentrations at TO, MQ and AZ are all similar. At the highest RH_{ice} (−30 °C) AZ and MQ INP concentrations are the greatest. The concentrations at SB are lowest throughout the full RH spectrum, the reason likely being that the site is farthest away from substantial INP sources. Interestingly, the slopes fitted to the measurements from the European TO and SB stations are nearly identical, as are the slopes of data from the tropical MQ and AZ stations (Figs. 6a and 6b). The differences in the activation spectra may result from different contributions of certain species of INPs at the respective sites. MQ and AZ samples possibly entail a larger fraction of mineral dust compared to TO and SB samples, which may have led to the steeper increase of concentrations. Our view of a generally higher abundance of mineral dust at the low latitude sites MQ and AZ as compared to the high latitudes of SB and TO is supported by dust observations from surface stations (Prospero, 1996), remote sensing (Kaufman et al., 2005) and models (Zender et al., 2003; Lee et al., 2009). Moreover, median INP concentrations at TO are a factor of approximately 2 higher than SB throughout the spectrum. An increase of 2 % in RH_{ice} results in 1.5 (SB and TO) to 1.7 (MQ and AZ) times higher INP concentrations. Increasing RH_{ice} by 10 % yields 7.4-fold (SB), 7.6-fold (TO), 12.8-fold (MQ) or 14.7-fold (AZ) changes in INP concentrations. Supplementary Fig. ~~S1~~ S5 expands upon Fig. 6 by adding more statistical information, such as the arithmetic mean, the interquartile range and the 5–95 % range. The findings complement those presented in Fig. 6. Overall, the variability of relative abundance with temperature suggests that the dominant species of INPs do change temporally and between locations. The extent to which changes can be attributed to local versus more remote INP sources is an interesting question that should be a focus in future studies.

Figure 7 shows the relative frequency distributions of INP concentrations at −20 °C (a), −25 °C (b) and −30 °C (c). For the purposes of Fig. 7, samples below the detection limit (or with zero active INPs) or, in a few cases, overloaded samples are excluded. As a result, the distribution tails may be somewhat truncated, because the highest and lowest values are not adequately represented. Such an effect is likely more important at −20 °C, because relatively more samples are below the background detection limit at this temperature. Scaled Gaussian fits in log space are added to emphasize the log-normal nature of the binned frequency distributions that emerge. Welti et al. (2018) analyzed INP data from the subtropical maritime boundary layer and various other marine environments (Welti et al., 2020) in a similar fashion and argued that the observed log-normal nature of the distributions can be explained in an analogous manner to the distributions of pollutant species suggested by Ott (1990). The assertion is that for any species of interest (i.e. INPs), many consecutive random dilutions of an air mass containing that species will result in a log-normal distribution of species concentration. Such dilutions will naturally occur during transportation through the atmosphere from the sources to the measurement sites. Variations in source strength are

associated with systematic shifts of the whole concentration distribution. For example, when a measurement site is close to a local source, a more left-skewed distribution is to be expected, as a higher proportion of air masses with fewer dilutions will occur. ~~That said~~However, the picture that we construct from the INP measurements made at a single point of arrival are convoluted, because there is not necessarily one singular source of INPs.

Considering the vastly different geographical locations and environments of the four measurement sites, as well as the inherent variance of atmospheric transportation patterns over time, we do not expect to find simple answers by inspection of the frequency distributions. A few interesting features are, however, apparent and the log-normal fitting agrees very well with the shape of the INP frequency distributions, which means that the dilution effect may be of importance here. The log-normal shape of the $-25\,^{\circ}\mathrm{C}$ and $-30\,^{\circ}\mathrm{C}$ distributions is especially evident (R^2 ranges from 0.92 to 0.97). Here we observe unimodal and regular bell shapes at all four sites. At $-20\,^{\circ}\mathrm{C}$ the fits are not as good (R^2 ranges from 0.74 to 0.91) and some distributions appear to be potentially bimodal ~~.~~(e.g. SB). However, the strength of the fit may also be related to the fact that at $-20\,^{\circ}\mathrm{C}$ few ice crystals activate on each sample substrate, introducing a relatively high uncertainty in the INP concentration. Consequently, the incrementation is not ideal for $-20\,^{\circ}\mathrm{C}$, because measured concentrations are often near the limit of detection and have a poor resolution. This explanation is self-consistent with the observed minimum R^2 found for SB, where the distribution is heavily skewed to the right. In addition to reflecting the generally low INP concentration of the Arctic environment, this may point to reduced biological activity over much of the year. Interestingly, the shape of the distribution at TO seems to indicate a slight shift towards higher concentrations, pointing to a potential local source of INPs. However, at lower temperatures we do not find this feature. This could mean that, in addition to whatever long-range transported aerosols contribute to INPs at TO, there might be a biological source from the surrounding forest. However, there is no strong evidence for such a signal in our data overall~~.~~, possibly due to the comparably low sampling volume. As a result the temperature range of our measurements overlaps only very little with the regime where biological particles nucleate. Remarkably, such a feature seems to be entirely absent from the Amazonian rainforest site, where one would more readily expect to find a local source of primary biological particles that may be potential INPs. On the other hand, surface temperatures never drop below $0\,^{\circ}\mathrm{C}$ in the Amazon. Therefore, local species of plants or bacteria may be less likely to have evolved traits that induce freezing~~in order to~~. It has previously been posited that some microbiology (e.g. bacteria like *Pseudomonas syringae*) gain an evolutionary ~~benefit as is believed to be the case for certain bacteria such as *Pseudomonas syringae*~~ advantage by being able to induce freezing (Morris et al., 2014).

At $-25\,^{\circ}\mathrm{C}$ we find relatively minor differences between the four sites. SB concentrations are slightly shifted to lower concentrations and the spectrum at MQ concentrations is slightly broader. Differences are more apparent at $-30\,^{\circ}\mathrm{C}$. Here we find distinctly dissimilar shapes of INP concentration frequency distributions. SB and AZ exhibit narrow peaks relative to the more broad shapes of TO and MQ. The curves are also more distinctly separated in concentration space, with the maximum of the distribution at a minimum concentration for SB, followed by TO, MQ and AZ.

Supplementary Fig. ~~S2~~ S6 visualizes the information presented in Fig. 7 as function of the relative humidity. The occurrence frequency is color-coded, with cool colors indicating a low and warm colors a high likelihood of this INP concentration at a given saturation condition. Thus Fig. ~~S2~~ S6 can be understood as follows: a single column (e.g. the rightmost column) gives the full frequency distribution of a single measurement condition (e.g. 135 % RH_{ice}, corresponds to Fig. 7c). Fewer warm

colors appear in a column, when the distribution of INP concentrations is broad at that condition. Conversely, fewer cool tones indicate a narrow distribution. The respective median INP concentration will be close to the maximum of the relative frequency at each condition. Consequently, following the maxima yields information about the steepness of the INP spectra, similar to what is depicted in Fig. 6.

Overall, Figs. 7 and ~~S2~~ S6 suggest that the INP concentrations measured in the investigated temperature regime at these stations are largely defined by background air masses, and that local sources are only of secondary importance. More discussion of the site specific local sources and characteristic features is provided in the following section.

3.2 Site specific INP characteristics

At each measurement station a diverse array of supplementary meteorological, aerosol and gas data from the stations were collected in parallel to the INP sampling. Unfortunately, the parameters, instrumentation and time coverage vary considerably between the four sites. Observations include typical meteorological parameters such as temperature, relative humidity, precipitation, etc., as well as the total aerosol particle number and mass concentrations, aerosol size distributions, black carbon concentrations, aerosol optical thickness, gaseous pollutant markers and greenhouse gases. However, despite a rigorous effort including correlation analysis, factor analysis and trajectory sector analysis, we were ultimately unable to identify a single parameter or a set of parameters that account for the total observed variation of INPs. This highlights the complex nature of the ice nucleation process and the particles involved. Whereas similar but somewhat larger-scale long-term measurements of CCN are able to largely explain the corresponding variability and provide closure studies (Schmale et al., 2018), unfortunately, the same cannot yet be said for INPs.

Although a common, definitive driver of INP climatology was not identified in our study, we will point out a few key findings specific to the respective measurement sites.

3.2.1 AZ

The Amazonian site is characterized by a distinct seasonality of pollutants that follow the biomass burning season. During the dry season (August to November) the aerosol concentration and other pollution markers rise by about one order of magnitude compared to the cleaner wet season (February to May) – a change which is largely attributable to human activities. Notably, an effect of the strong anthropogenic biomass burning is absent in the INP signal. In fact, the number of INPs normalized by the total number of aerosol particles (TSI OPS 3330) in a volume of air (i.e. the activated fraction AF) is anti-correlated to parameters related to ~~biomass burning~~ the abundance of biomass burning products (Fig. 8). The AF can be understood as a simple metric that indicates the ice nucleating efficiency of particles within a specific aerosol sample. The observed anti-correlation ~~suggests~~ seems to suggest that aerosol particles from ~~fire sources~~ fires are relatively poor ice nuclei~~,~~; an observation that agrees with previously published findings (Kanji et al., 2017, 2020). ~~The~~ Considering the recent literature consensus regarding biomass burning INPs, these results are not unexpected. Biomass burning INPs have been studied in the laboratory investigating both surrogate and real combustion particles (Petters et al., 2009; Levin et al., 2016; Kanji et al., 2020), and in the field (Prenni et al., 2012; McCluskey et al., 2014; Schill et al., 2020). Although at least a regional impact of biomass burning

on INP abundance is reported, the nucleation temperatures are usually close to the homogeneous freezing limit. Some of these studies suggest that water supersaturation is a requirement for biomass burning aerosol to act as INPs (e.g. Petters et al., 2009; Schill et al., 2 . In this regard, our data may demonstrate the limits of what is explorable with FRIDGE. Either biomass burning aerosol is in fact a poor source for Amazonian INPs in the investigated temperature regime or the method simply cannot represent the freezing behavior of these particles accurately.

Furthermore, the significance of low AFs resulting from biomass burning in this study is difficult to assess, as the seasonality of the AF is largely dominated by the seasonal changes in aerosol concentration for the AZ site. Vegetation fires therefore seem to emit disproportionally more (non ice-active) aerosol particles than INPs. Another way to interpret the anti-correlation of AF and ~~markers of biomass burning~~ biomass burning markers is by coupling the metric to precipitation rates. There are several intricate interactions of note here. On ~~the~~ one hand more precipitation leads to ~~a higher removal of aerosol particles (and INPs)~~ higher aerosol particle (and INP) removal by wet deposition. Moreover, ~~the~~ enhanced precipitation during the wet season ~~largely prevents~~ can largely prevent wild fires and the accompanied particle emissions in the first place. On the other hand, it has been postulated previously that precipitation may be ~~another driver of INP abundance~~a driver of biological INPs (Huffman et al., 2013), and large tropical rainforests like the Amazon have been highlighted in that regard (Morris et al., 2014). ~~Huffman et al. (2013) suggested a connection between precipitation in a semi-arid pine forest and an increase in primary biological particle production, which subsequently might act as INPs. The~~ However, the processes responsible for the release of the biological particles have not yet been deciphered in detail. ~~Huffman et al. (2013) hypothesized that a) mechanical agitation by rain causes fungal spores and bacteria to be released into the air and/or b) mechanisms that stimulate bio-particle emissions (fungal spores, pollen fragments) are activated by a longer phase of high humidity and leaf moisture. Although~~

Moreover, although the AZ measurements are somewhat more sparse than those of other stations, our observations do not support significant differences in absolute INP concentrations between dry and wet seasons.

Overall, the INP concentrations of our study compare reasonably well to the measurements of Prenni et al. (2009), who observed average INP concentrations of about $1\,L^{-1}$ at $-20\,^{\circ}C$, $4\,L^{-1}$ at $-25\,^{\circ}C$ and $10\,L^{-1}$ at $-30\,^{\circ}C$ using a continuous flow diffusion chamber (CFDC) to study condensation and immersion mode ice nucleation during a field campaign in February/-March 2008 in a region close to the present location of the ATTO site. However, our observed concentrations are clustered at the low end of ~~Prenni et al. (2009)~~those presented by Prenni et al. (2009) (i.e. a factor of 5 lower on average at $-30\,^{\circ}C$), which is ~~likely~~ presumably due to the different nucleation modes addressed. During that short campaign Prenni et al. (2009) identified mineral dust and carbonaceous aerosol (mostly biological particles) to be the main contributors to atmospheric INPs in the Amazon using transmission electron microscopy and energy-dispersive X-ray spectroscopy.

Within our sampling period, Moran-Zuloaga et al. (2018) identified several long-range transport (LRT) events at the site with markedly increased concentrations of mineral dust during the wet season of 2015/2016 (Dec./Jan.). INP concentrations of these LRT samples were positively correlated with the aerosol number concentration measured with an optical particle counter (TSI OPS 3330, $R = 0.80$, $N = 9$, $p < 0.01$). However, mineral dust may be a relevant INP in this region even in the absence of distinct LRT events~~.~~: An analysis of the average composition of INPs ~~for~~ of six samples (4 in April 2016, 2 in December 2016) using scanning electron microscopy (SEM, Figure 9), identified that nearly half of the particles that activated to ice crystals

in FRDIGE were mineral dust. ~~Most of the characterized INPs~~ This finding suggests that there seems to be a well-mixed and diluted background concentration of mineral dust INPs at all times present at AZ. The diameter of most of the INPs investigated by SEM in this study ~~were measured to be between 1~~ was between one and a couple of micrometers ~~in diameter~~ (Figure 9b). Note however, that the contribution to the larger size bins might be potentially underrepresented due to particle losses from the inlet configuration. The second half of identified INPs had a strong carbonaceous fraction and consisted of biological particles and biomass burning products. Furthermore, it is possible that some PBAP activity was missed due to the chosen sampling strategy, given local noon is a daily minimum for PBAPs. Qualitatively, these findings agree very well to those of Prenni et al. (2009).

3.2.2 MQ

Of the results presented here, the average INP concentration of the Caribbean site was the highest, but only by a small margin. There is some evidence that summertime INP concentrations are higher on average than those during winter, although there is no clear seasonality. However, the possible seasonal ice nucleation effects are difficult to assess due to the large interruption of measurements between December 2015 to May 2016. Although we consider it rather speculative, a trend of higher concentrations during summer does stand to reason, as it would reflect the annual cycle of the mineral dust transport, which is driven by the movement of the ITCZ. The seasonality of mineral dust is well reflected by the PM_{10} concentration, which is monitored routinely in Martinique by the local agency for air quality (MadininAir). The seasonality of dust motivates a deeper investigation with respect to INPs. In general, we observe a significant correlation between the INP concentration at OVSM and the PM_{10} concentration at an air quality station close to the observatory (Schoelcher, 14 km distance), as well as between INPs and the OPS aerosol number concentration at the observatory. The correlations improve for colder temperatures and higher ice supersaturations. At $-30\,^{\circ}\mathrm{C}$ and 135 % RH_{ice} the Pearson correlation coefficients between INP and aerosols are $R = 0.46$ ($N = 124$, $p \ll 0.01$) for PM_{10} (Fig. ~~S3~~S7) and $R = 0.50$ ($N = 69$, $p \ll 0.01$) for the OPS concentration, respectively. We conclude that the MQ INP concentration at the investigated temperatures is likely dominated by natural processes such as the long-range transport of Saharan mineral dust. However, there is still a large variability in the INP signal, which cannot be fully explained ~~only considering~~ by considering only the seasonal dust transport.

We observe significantly lower INP concentrations for all conditions after the large interruption in measurements. For example, the average INP concentration at $-30\,^{\circ}\mathrm{C}$ and 135 % RH_{ice} in 2015 was $7.47 \pm 6.42\,\mathrm{L}^{-1}$ ($N = 58$) and only $1.37 \pm 1.39\,\mathrm{L}^{-1}$ ($N = 72$) in 2016. This observation does, however, correspond to measured PM_{10} concentrations, which also show a significantly lower average in 2016 ($25\,\mu\mathrm{g\,m}^{-3}$, $N = 8225$) than 2015 ($35\,\mu\mathrm{g\,m}^{-3}$, $N = 8636$). Although, the observed 2015 to 2016 factor of 5 decrease in INP concentrations is large compared to the $\approx 30\%$ difference in PM_{10}, the cubic scaling implicit in the number to mass translation needs to be considered.

DeMott et al. (2016) presented results from offline immersion freezing experiments and characterized INP concentrations from research flights from St. Croix in the US Virgin Islands, and ground sampling from Puerto Rico, which were collected during the ICE-T campaign in July 2011. The focus was on marine INPs and determining representative marine background concentrations and only samples collected within the marine boundary layer were presented. They measured INP concentra-

tions of 0.06 L^{-1} at $-20\,^{\circ}C$ and 0.3 L^{-1} at $-24\,^{\circ}C$, which ~~are only~~ agrees within a factor of ~~3 to 4 lower than our average~~ two to our median INP concentrations at $-20\,^{\circ}C$ and $-25\,^{\circ}C$~~, respectively. Considering that marine INPs are typically thought to represent a minor fraction of the total INP population (except for certain regions like the Southern Ocean), the comparison seems to be reasonable.~~ .

3.2.3 TO

During the time frame of the global sampling effort (about 640 days) 400 PEAC7 samples were collected and analyzed from TO (i.e. 1 sample every 1.6 days). The sampling frequency of valid INP concentrations (i.e. above the detection limit) remains as good as 1 sample every 2 days for measurements at $-20\,^{\circ}C$ and $-25\,^{\circ}C$. This is by far the best data coverage of the four stations.

We found a moderate but significant correlation between the PM_{10} concentrations and INPs throughout the spectrum of T and RH conditions. The Pearson correlation coefficient is as high as R = ~~0.28~~ 0.27 (N = ~~293~~304, $p \ll 0.01$) at $-25\,^{\circ}C$, where we have the best data coverage. Although the particulate matter was significantly enhanced, when wind was coming from the heavily populated and industrialized Rhine-Main metropolitan region (Tab. 3), the average INP concentration was not found to differ significantly from other times, when air masses were arriving from other directions (Fig. 10). Therefore, a strong anthropogenic impact on INPs at TO is unlikely.

3.2.4 SB

~~Given~~ Due to its remoteness and relatively clean atmosphere, the Arctic may be particularly sensitive to small changes in aerosol particulate. Furthermore, within the Arctic climate system there are well known feedbacks that can amplify small changes in significant ways (Serreze and Francis, 2006; Boy et al., 2019). Historically, this has motivated quite a few research studies targeting ice nucleation in the Arctic environment. For example, clay was identified in the center of Greenlandic snow crystals by Kumai and Francis (1962) as early as 1960. Past studies generally agree that INP concentrations in the Arctic tend to be on the lower side of the spectrum. Yet, individual findings and conclusions vary considerably (e.g. see Tab. 2 in Thomson et al., 2018). New ice core records may illuminate long-term trends of Arctic INPs by estimating historic (pre-industrial) concentrations from droplet freezing experiments of ice core melt water (Hartmann et al., 2019; Schrod et al., 2020).

In two recent studies immersion mode ice nucleation in the Arctic was investigated by Tobo et al. (2019) and Wex et al. (2019). Tobo et al. (2019) focused on two field campaigns held in Ny-Ålesund (Zeppelin) in July 2016 (6 samples) and March 2017 (7 samples). Wex et al. (2019) report INP concentrations from four pan-Arctic locations (Canada, Alaska, Ny-Ålesund and Greenland) that cover observations ranging from 10 weeks to a full year of mostly weekly sampling. Both studies observed enhanced INP concentrations during summer months. Tobo et al. (2019) report INP concentrations at $-20\,^{\circ}C$ of about 0.01 L^{-1} in March 2017 and about 0.1 L^{-1} in July 2016. At $-25\,^{\circ}C$ INP concentrations were on the order of 0.1 L^{-1} and 0.5 L^{-1} for the March and July field campaigns, respectively. Wex et al. (2019) distinguished between samples that were collected in Ny-Ålesund from March to May 2012 (5 samples) and those from June to September 2012 (7 samples). During spring, INP concentrations at $-20\,^{\circ}C$ were consistently found to be about 0.01 L^{-1}. Most summertime samples were completely frozen

before reaching −20 °C, and thus seem to to suggest that concentrations were up to one order of magnitude higher in summer. Very recent measurements from Greenland during March/April 2018 qualitatively agree very well to these concentration levels (Hartmann et al., 2020). However, a recent study by Rinaldi et al. (2020) did not observe a distinct seasonal signal in their INP measurements between −15 °C and −22 °C in the spring and summer of 2018 in Ny-Ålesund. Rinaldi et al. (2020) present INP concentrations from two separate methods, one of which is fairly similar to FRIDGE, addressing the condensation freezing (DFPC) and immersion freezing (WT-CRAFT) modes.

Further, Wex et al. (2019) report correlation coefficients with complementary measurements that are mostly insignificant including PM_{10}. Exceptions include significant correlations between INPs and sulphate (R = −0.6) and potassium (R = −0.57), pointing to complex factors determining the Arctic INP population. Moreover, Tobo et al. (2019) present evidence that mineral dust (possibly with organic inclusions) from Arctic glacial outwash plains influence the INP activity in Ny-Ålesund. They conclude that these glacial sediments may be a large-scale source of mineral dust in the Arctic. Rinaldi et al. (2020) present evidence that Arctic INP concentrations are influenced by sources of marine biological INPs by providing a spatio-temporal correlation analysis between Chlorophyll-a fields from satellite data and a trajectory model.

We present a significantly larger data set with respect to temporal coverage and our INP concentrations agree well with these previous studies from Ny-Ålesund. At −20 °C we find concentrations of about 0.1 L^{-1}. At −25 °C the average INP concentration increases to about 0.3 L^{-1}. However, the ~~consistently~~ frequently reported finding of summertime INP enhancement, does not emerge from our analysis. Furthermore, we did not observe any seasonal changes in the INP signal with regards to the anthropogenic Arctic Haze phenomenon. Moreover, we did not observe significant correlations between INPs and available aerosol parameters. The concerning lack of meaningful correlations and/or seasonal trends may be in part related to a relatively poor signal-to-noise ratio ~~for the~~ in our SB measurements. INP concentrations were often at or close to the limit of detection or the significance level, respectively. In retrospect, we now would increase the sampling volume for SB measurements to be able to resolve lower concentrations more accurately.

4 Conclusions

The data from our small but unique measurement network can be considered particularly valuable, and we hope lessons can be ~~taken~~ learned from this effort that will help to guide future INP monitoring efforts. Significant infrastructural and logistical investments are represented by the INP measurements that cover an observational period of 21 months in total. Well above 1000 samples were collected, retrieved and analyzed in this project at a large array of temperature and supersaturation conditions, characterizing the INP concentrations in the deposition and condensation freezing modes. The investigated sites represent diverse climatic regions and ecosystems that experience varying degrees of anthropogenic influence.

In spite of the great differences in basically all characteristics that are expected to define the aerosol concentration, composition and source apportionment, we observed fairly similar INP concentrations for all four stations ~~. Recently, Welti et al. (2020) reported a qualitatively similar finding: ship-based measurements of marine INPs in the Arctic, Atlantic, Pacific and Southern Ocean showed surprisingly little differences in the INP concentration despite their distant geographic locations.~~ for the methods

and sampling strategy applied. In our study, average concentrations differed between sites by less than a factor of 5. Short-term variability dominated most of the total variability at all locations. Trends, annual cycles and well-defined peak concentrations were prominently absent from the time series. Still, the range of observed INP concentrations do compare reasonably well with previously published literature, where available. Importantly, the relative frequencies of observed INP concentrations are generally well-represented by log-normal distributions, a finding that suggests distributed INP sources that result from INPs being well-mixed within sampled air masses. These findings emphasize the important contribution of INPs from background air masses. Moreover, no physical or chemical parameter was identified to continuously co-vary with INPs at all sites, and therefore a comprehensive causal link to INP concentrations remains lacking.

Overall, we did not detect much evidence for a strong anthropogenic impact on the concentrations of ice nucleating particles. At AZ the INP concentrations appear unrelated to human induced biomass burning, which otherwise leads to a tenfold increase in aerosol particle number concentrations during the dry season. The INP concentrations at MQ were well correlated with aerosol characteristics that are driven by natural processes, like long-range transport of Saharan mineral dust and marine aerosol production. Average TO INP concentrations showed no significant difference between wind sectors that can be separated into anthropogenically dominated areas and rural environments. Likewise, no significant changes in the INP concentration were observed at SB during the Arctic Haze period.

Considering these findings, the approach of estimating order-of-magnitude pre-industrial INP concentrations from present-day measurements in near-pristine locations does seem to both be viable and yields reasonable results, which merit further investigation. In this sense, we consider the lower concentration end of our measurements likely to be the most realistic assessment of pre-industrial atmospheric INP concentrations. However, ~~we strongly advise cautious use of~~ when using the presented data ~~, as there are substantial limitations and uncertainties in conceptional aspects of the approach, as well as to the measurements themselves.~~

~~It should be noted here that we cannot predict with certainty how these measurements would translate to the immersion freezing mode in the atmosphere. Measurements by the FRIDGE diffusion chamber and FRIDGE droplet freezing assay of previous campaigns were usually well-correlated, but the INP concentration in the standard mode is often lower by a factor in the order of a few up to one magnitude~~one should be aware of the substantial limitations of the conceptual aspect of the approach and the uncertainties that are inherent in the aerosol sampling and INP measurements themselves.

5 Outlook

This study clearly highlights that there is a strong need for increased continuous observations of INPs worldwide. Several important ~~open~~ questions need to be addressed by the community, when considering how to best implement a systematic long-term monitoring strategy:

1) What are the best time resolution(s) and sampling frequencies? Obviously, the answer to this depends on the scientific question that a group is trying to address and the requirements and capabilities of the specific INP counter. Furthermore, bearing in mind that INP measurements are primarily of interest for illuminating cloud and precipitation processes it may be

important to recognize that cloud processes are geographically different, and thus the answers to these questions may also differ. For example, for areas where tropical and sub-tropical deep convection dominates cloud formation, sampling priorities may differ from the mid-latitudes where synoptic scale weather systems are predominant. Judging from the results we have presented, it could be argued that longer sampling times (several hours to days) are advantageous for elucidating longer-term trends. Longer sampling ~~effectively acts~~ may effectively act as a low-pass filter and ~~would~~ thereby reduce the considerable short-term variability in INPs that is observed everywhere. Naturally, ideal monitoring could be done with short but densely spaced sampling times. This would enable averaging to be done at the data analysis level and thus both short- and long-term variation could be reasonably captured. However, such an instrument and/or technique ~~is currently not available~~ has not been available in the past and will likely present both technological and human resource challenges. In the meantime, we suggest that long-term measurements are initiated with some weeks of intensive measurements to establish baseline information with regard to INP concentration and variability.

2) What supporting instrumentation/measurements should accompany the INP monitoring? Naturally, it is good to have as much information about aerosol concentration, size distribution and chemical composition as possible. However, a thorough aerosol characterization does not guarantee robust correlations with INPs or even a fully explained total INP variability. To-date the community has had limited success in using co-located measurements to establish causal links with INPs. Initiating further long-term measurements at highly equipped research stations may be a pathway towards learning what additional tools best compliment INP studies.

3) What measurement conditions and nucleation modes should be addressed? Again, this depends on the both the researchers scientific focus and the capabilities of the respective INP instrument. However, the literature consensus firmly suggests that immersion freezing is the most atmospherically relevant nucleation mechanism.

From the experience built in this study, we recommend future studies, especially those that include remote sampling locations, to plan conservatively for the required logistics and workload, with respect to sampling frequency, analysis conditions, sampling consistency, etc. We emphasize the importance of a well-conceived sampling strategy and well laid out logistics. Instrument malfunctions, maintenance and various other difficulties and interruptions are to be expected. All of these may be easily addressed separately, but amount to a significant challenge, when a long-distance network is to be kept running across a hemisphere. Nonetheless, we encourage other groups and collaborations to more strongly emphasize long-time observations in addition to the common standard of campaign-based measurements. Although we are currently far from the best case scenario of ~~an~~ a (near) continuous automated global network of INP measurements, there are promising new ~~instruments (e.g. PINE, ?)~~ developements (e.g. Bi et al., 2019; Brunner and Kanji, 2020; Möhler et al., 2020) that may provide a vital ~~intermediate~~ step towards long-term ~~semi-automated~~ (semi-)automated measurements of immersion mode INPs in the near future.

In addition to the goal of establishing more long-term global observations of continuous INP concentrations there are certainly other important areas for future research to address. For example, as most measurements are conducted at ground level, we believe there is a need to systematically study the vertical distribution of INPs – for example at heights where INPs are transported over long-ranges and/or where cloud formation occurs. Moreover, more extensive data sets from long-term INP monitoring might shed light on what mechanisms result in the observed log-normal INP frequency distributions (and

departures from ideality etc.) as presented here and, for example, by Welti et al. (2018). Murray et al. (2020) has recently enumerated many crucial areas into which future INP research should delve. First and foremost, the authors emphasize the need to accurately implement ice nucleation related cloud-phase interactions in climate models in order to predict future climate scenarios correctly. We gladly refer the interested reader to Murray et al. (2020) for a more extensive list of future ice nucleation related research questions, as is presented in this study.

Data availability. The INP data will be made available using the Data Publisher for Earth & Environmental Science PANGAEA (https://www.pangaea.de/).

Author contributions. JS, JK and DW performed the INP measurements. JS compiled and analyzed the INP data with support of JK and HB. JS created the figures. Particle measurements at ATTO were performed by CP, JoS and FD. ME performed the SEM measurements. All authors took part in the discussion of the results. JS wrote the manuscript together with HB and ET, receiving valuable input from the other co-authors.

Competing interests. The authors declare no competing interests.

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Table 1. Main characteristics of the geographic sampling location and inlet configuration at the sites.

	AZ	MQ	TO	SB
Geograph. coordinates	2.144° S, 59.000° W	14.735° N, 61.147° W	50.221° N, 8.446° E	78.908° N, 11.881° E
Altitude [m AMSL]	130	487	825	474
Climate	tropical	(sub-)tropical	temperate	Arctic
Continental / marine	continental	marine	continental	marine
Mountain site	no	yes	yes	yes
Predominant vegetation	tropical rainforest	diverse (i.e. ranging from alpine to tropical rainforest)	coniferous forest	low-growing tundra (summer) / snow-covered (winter)
Anthropogenic impact	near pristine to polluted	remote to polluted	rural to polluted	near pristine to polluted
Inlet type	Total Suspended Particulate (Moran-Zuloaga et al., 2018)	1/4" tube, rain shield (no characterized inlet)	HORIBA ASS-370 type (ÖNORM, 2007)	Whole-air (Karlsson et al., 2020)
Inlet height [m AGL]	60	2	11	7.5
Isokinetic flow splitter	yes	no	yes	yes
Length of tubings to PEAC7 [m]	1.5	2	1	2

~~Thermodynamic conditions for INP analysis in FRIDGE. Conditions were selected in order to steadily progress from lower to higher RH_{ice} with the respective highest and lowest supersaturations overlapping at each temperature increment. T C RH_{water} $\%RH_{\text{ice}}$ %95 115.6 97 118.0 99 120.4 101 122.9 95 121.3 97 123.9 99 126.4 101 129.0 95 127.4 97 130.1 99 132.7 101 135.4~~

Table 2. Thermodynamic conditions for INP analysis in FRIDGE. Conditions were selected in order to steadily progress from lower to higher RH_{ice} with the respective highest and lowest supersaturations overlapping at each temperature increment.

T [°C]	RH_{water} [%]	RH_{ice} [%]
-20	95	115.6
	97	118.0
	99	120.4
	101	122.9
-25	95	121.3
	97	123.9
	99	126.4
	101	129.0
-30	95	127.4
	97	130.1
	99	132.7
	101	135.4

Table 3. Air quality data at Taunus Observatory as function of local wind direction: average values of major pollutants measured between 2015 and 2017 (HLNUG).

Region	Wind sector [°]	Relative frequency	NO [µg m^{-3}]	NO_2 [µg m^{-3}]	O_3 [µg m^{-3}]	PM_{10} [µg m^{-3}]
Frankfurt	110 – 140	6%	0.73	8.17	78.30	12.36
Airport / Autobahn interchange	150 – 170	3%	1.08	11.67	78.64	11.23
Wiesbaden / Mainz	200 – 230	12%	0.68	8.06	67.44	8.02
Total Rhine-Main area	110 – 230	29%	0.78	9.26	72.79	9.87
Not Rhine-Main (rural)	0 – 110; 230 – 359	71%	0.61	6.42	67.35	8.93
All sectors	0 – 359	100%	0.66	7.25	68.96	9.21

Table 4. Statistical parameters extracted from the INP concentrations measured at the four sites. N_{sig} is the number of samples that had concentrations above the significance level, which was set to twice the background INP concentration. N_{valid} is the number of valid measurements at this condition, i.e. measurements were non-zero and above the detection limit. Such measurements typically have an uncertainty of RH $\pm$ 2 %. Repeated measurements revealed typical uncertainties in the INP concentration on the order of $\pm$ 30 %.

	−20 °C, 101 %				−25 °C, 101 %				−30 °C, 101 %			
	SB	TO	MQ	AZ	SB	TO	MQ	AZ	SB	TO	MQ	AZ
Median [L^{-1}]	0.06	0.17	0.11	0.10	0.19	0.39	0.44	0.31	0.69	1.09	1.80	2.06
Arith. Mean [L^{-1}]	0.12	0.22	0.20	0.17	0.29	0.55	0.86	0.55	1.15	2.01	4.09	3.07
Geo. Mean [L^{-1}]	0.07	0.14	0.11	0.10	0.17	0.32	0.38	0.30	0.64	0.99	1.79	2.03
Std. Dev. [L^{-1}]	0.20	0.20	0.23	0.19	0.34	0.52	1.22	0.78	1.27	2.39	5.35	3.01
N_{valid}	186	342	184	110	182	307	164	120	115	194	130	107
N_{sig} / N_{valid} [%]	60	86	77	75	73	83	82	84	78	84	88	97
N_{valid} / N_{total} [%]	54	86	65	60	53	77	58	66	33	49	46	59

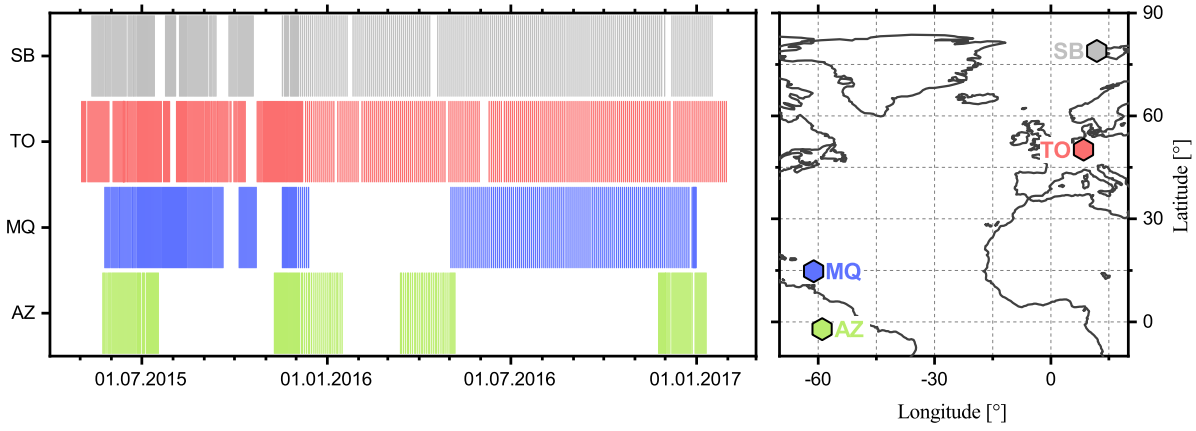

Figure 1. Sampling days at the four stations (left) and their corresponding geographic location (right). Line thickness indicates the sampling frequency (thick connected lines: daily; thin non-connected lines: 1 sample every two days).

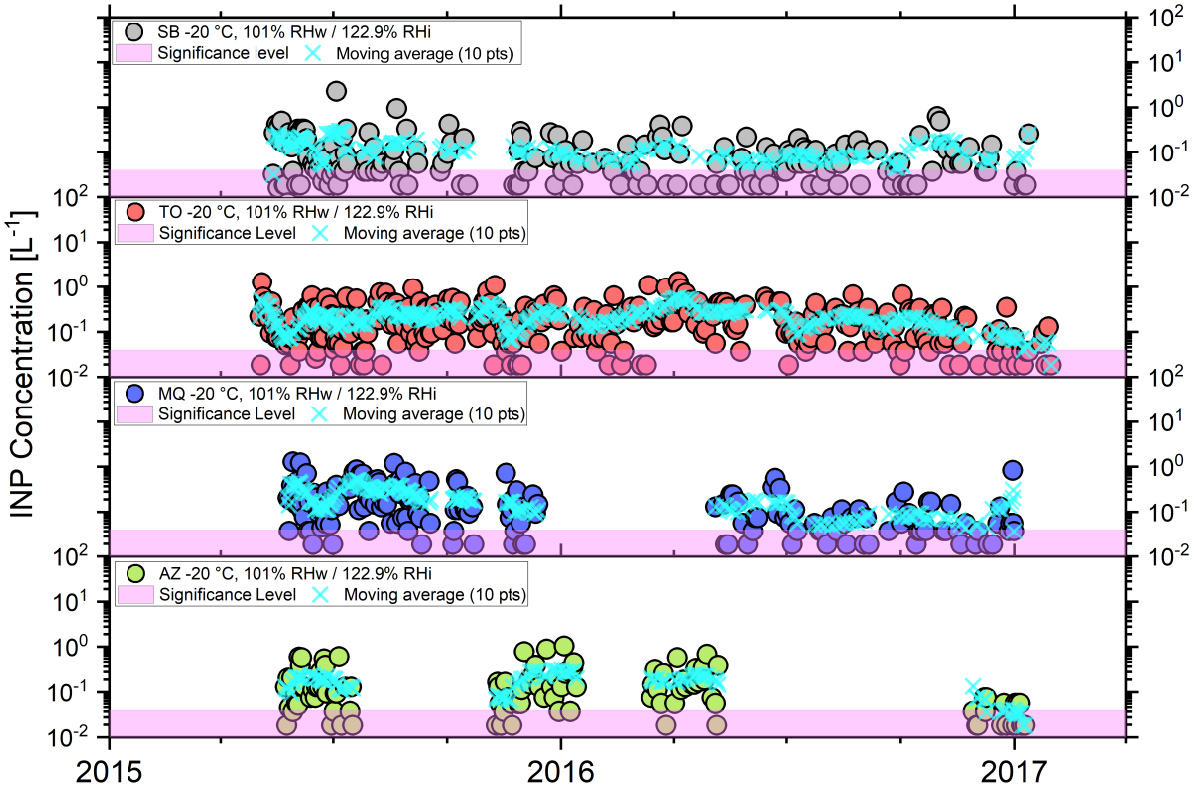

Figure 2. INP concentration at $T = -20\,^{\circ}\mathrm{C}$ and $RH_{water} = 101\,\%$, which is $RH_{ice} = 122.9\,\%$. The significance level is indicated in pink shading. Cyan crosses are the result of a 10 point moving average for INP concentrations. X-axis ticks are shown for January 1st, April 1st, July 1st and October 1st.

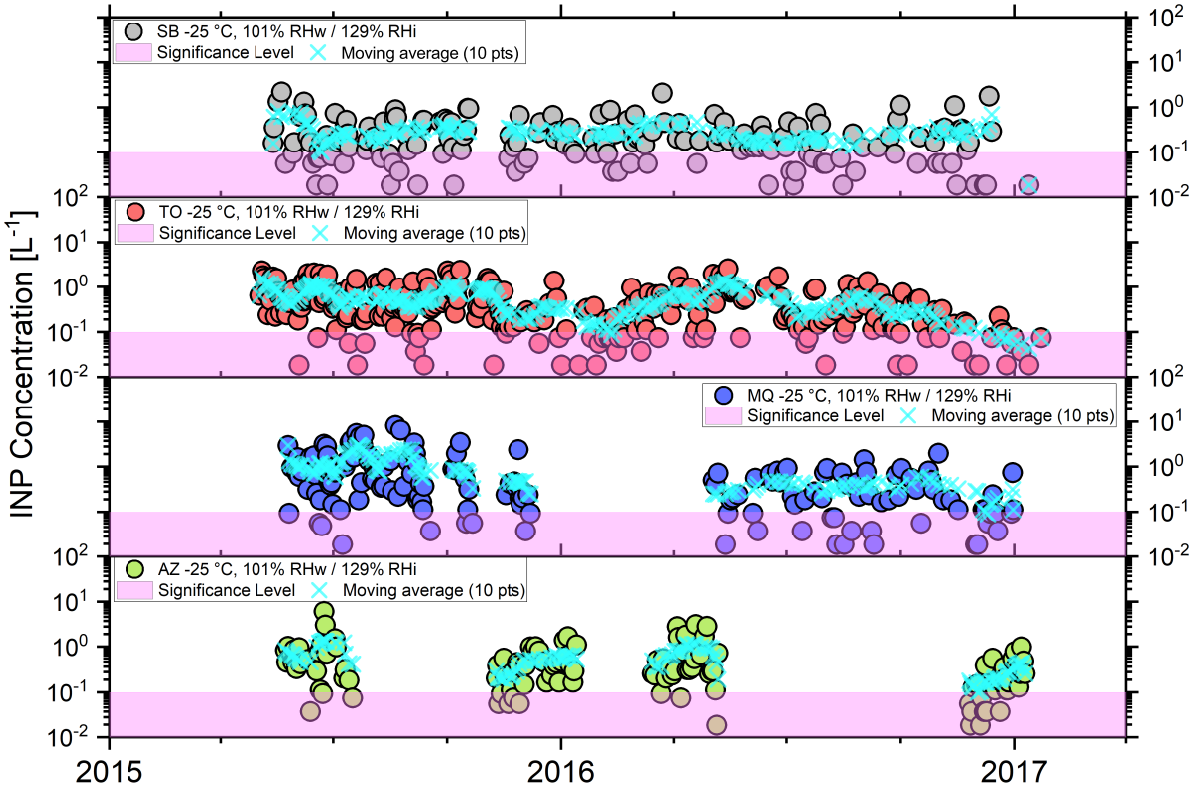

Figure 3. INP concentration at $T = -25\,^{\circ}\mathrm{C}$ and $RH_{water} = 101\,\%$, which is $RH_{ice} = 129\,\%$. The significance level is indicated in pink shading. Cyan crosses are the result of a 10 point moving average for INP concentrations. X-axis ticks are shown for January 1st, April 1st, July 1st and October 1st.

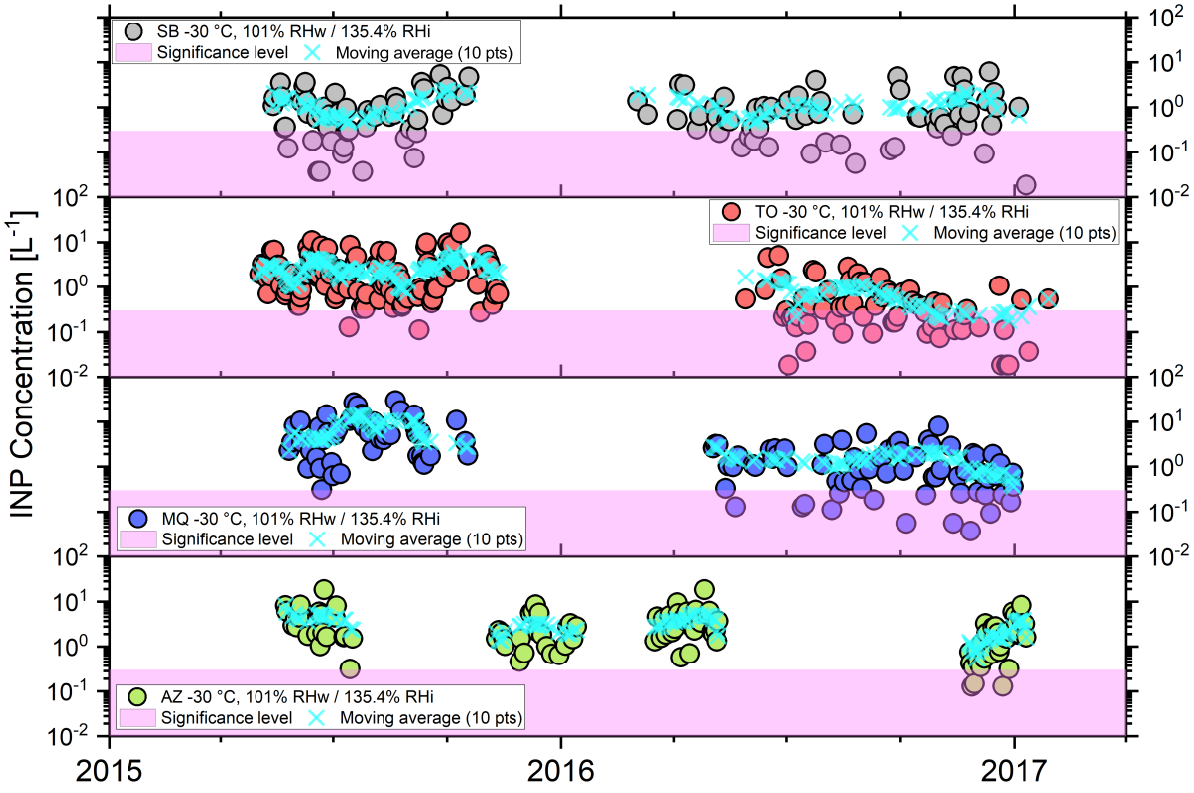

Figure 4. INP concentration at $T = -30\,^{\circ}\mathrm{C}$ and $RH_{water} = 101\,\%$, which is $RH_{ice} = 135.4\,\%$. The significance level is indicated in pink shading. Cyan crosses are the result of a 10 point moving average for INP concentrations. X-axis ticks are shown for January 1st, April 1st, July 1st and October 1st.

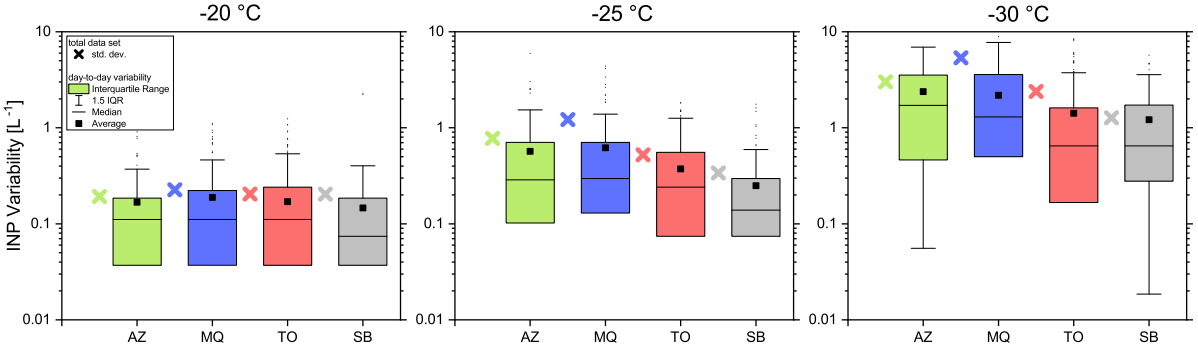

Figure 5. INP variability for $T = -20\,^{\circ}\mathrm{C}$ (left), $T = -25\,^{\circ}\mathrm{C}$ (middle) and $T = -30\,^{\circ}\mathrm{C}$ (right) at $RH_{water} = 101\,\%$. Crosses show the standard deviation of the total data set for each site. Box-plots show the distribution of sample-to-sample differences in the INP concentration of consecutive samples (i.e. day-to-day or every other day). Lower whiskers are not shown when the lower 1.5 IQR is at zero.

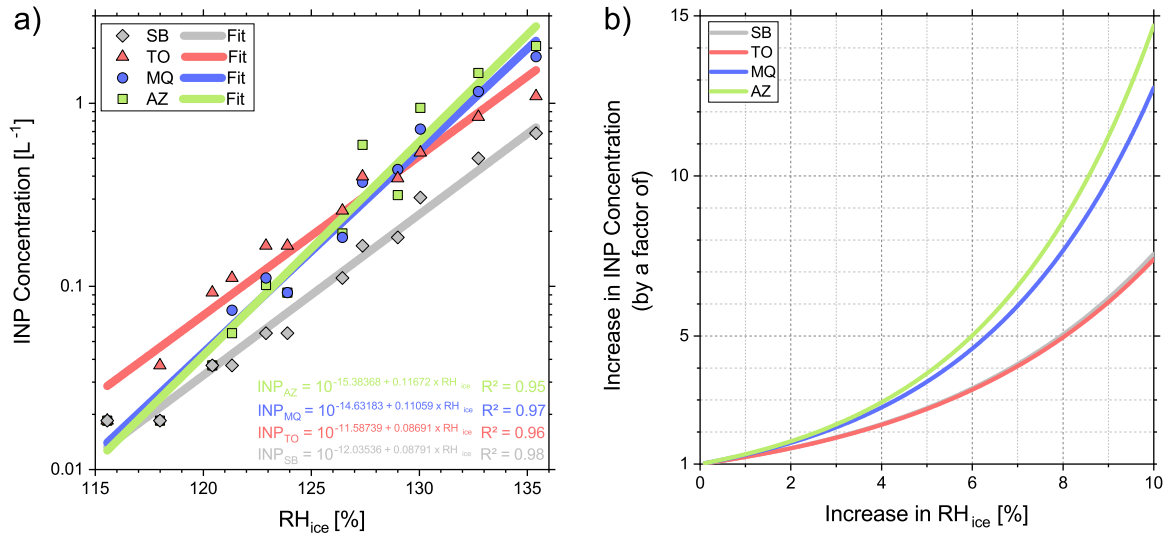

Figure 6. a) Median INP concentrations at the four sites measured at T= $-20\,^{\circ}\mathrm{C}$, $-25\,^{\circ}\mathrm{C}$ and $-30\,^{\circ}\mathrm{C}$ plotted as a function of RH_{ice} according to Table 2. b) The sensitivity of INP concentrations to increasing ice supersaturation based on the fits shown in a). Please note that the gray SB curve is largely superimposed by the red curve.

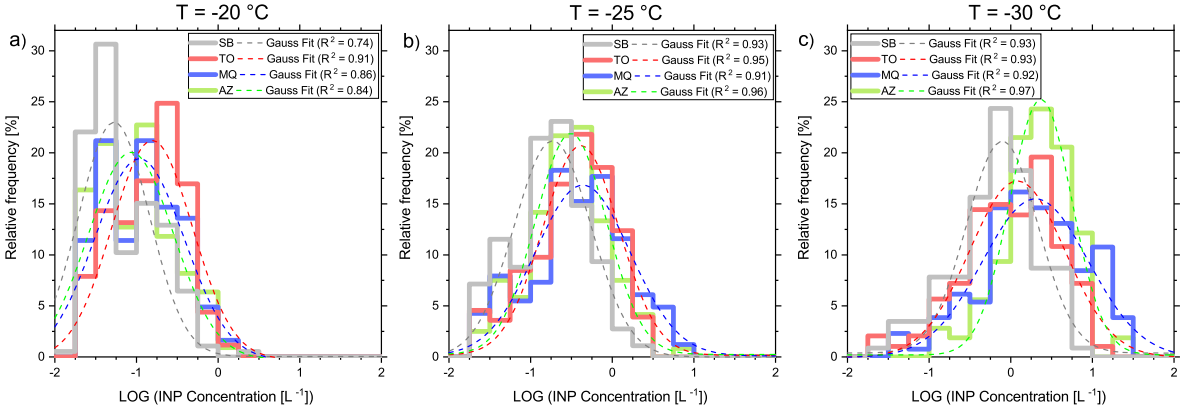

Figure 7. Probability density distribution plots of the INP concentrations at $RH_{water} = 101\,\%$ and $-20\,^{\circ}\mathrm{C}$ (a), $-25\,^{\circ}\mathrm{C}$ (b) and $-30\,^{\circ}\mathrm{C}$ (c).

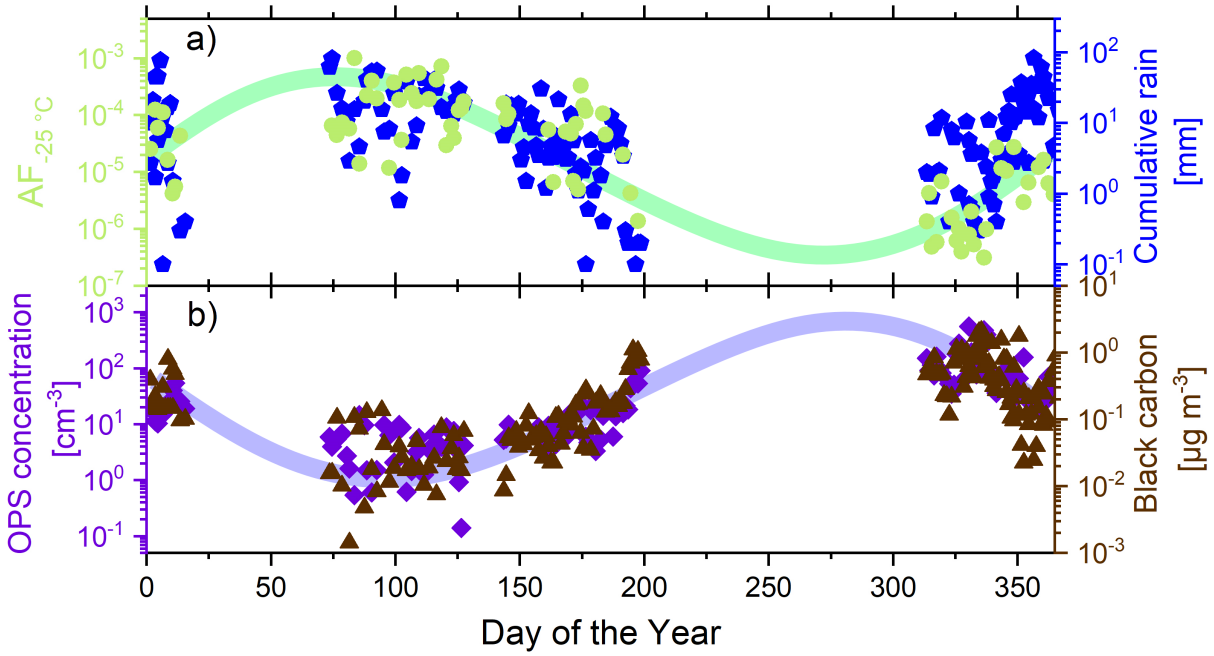

Figure 8. Seasonal variation of the activated fraction at $T = -25\,^{\circ}\mathrm{C}$ and $RH_{water} = 101\,\%$ at AZ and the cumulative precipitation along the trajectory reaching the site at the time of sampling (both a). Aerosol number concentration retrieved from a co-located OPC and the black carbon mass concentration (both b) at AZ. Lines are added to guide the eye.

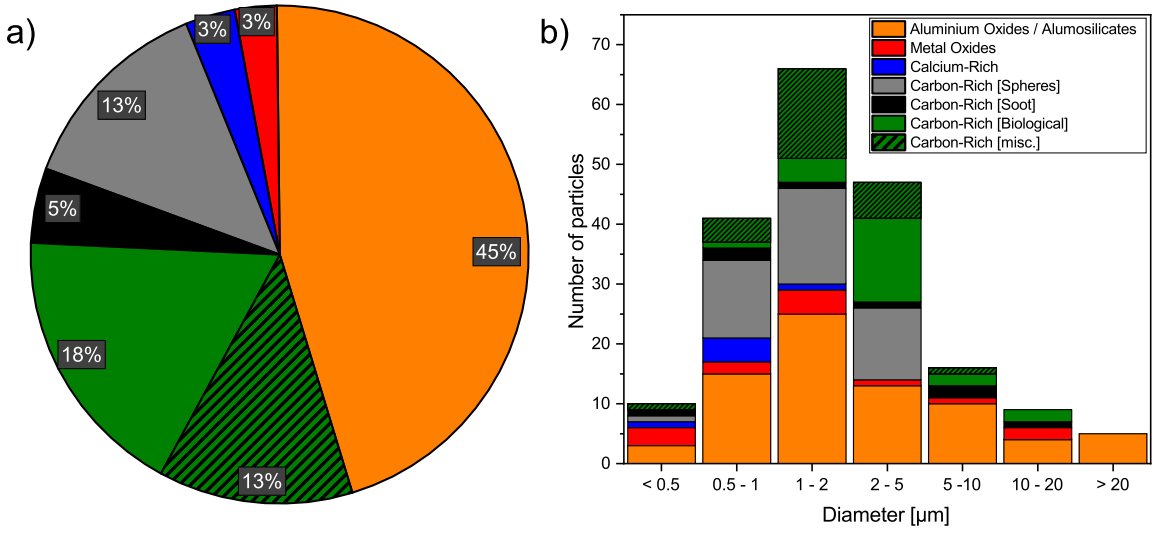

Figure 9. a) Average INP composition of six equally weighted AZ samples measured by electron microscopy (N = 196). b) Size distribution of identified INPs. Particles labeled as Carbon-Rich [Spheres] show distinct features of tar balls and are likely products from biomass burning.

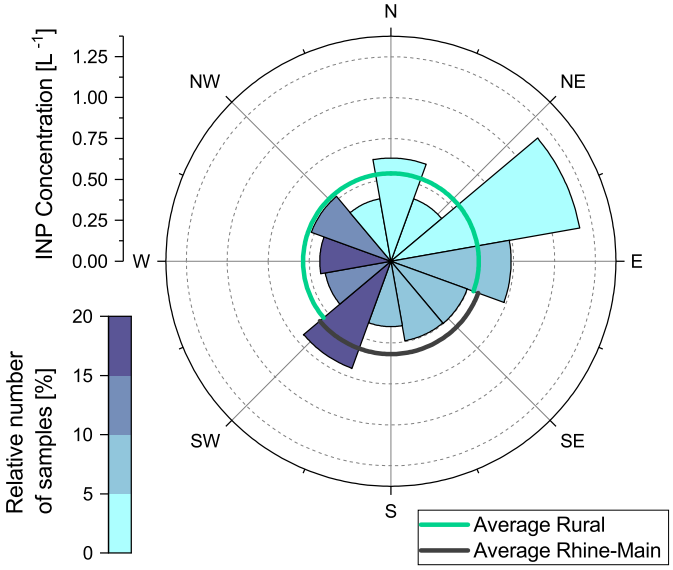

Figure 10. Average INP concentration at $T = -25\,^{\circ}\mathrm{C}$ and $RH_{water} = 101\,\%$ at TO depending on local wind direction. Note that the wind rose is divided into sectors to match the distinction between the sectors of the metropolitan (black line average) and rural (green line average) area according to Tab. 3. The relative frequency of local wind directions during sampling is indicated by the color-coding.