

**We would like to thank Reviewer #1 for his/her constructive suggestions, which helped us to improve the manuscript. Specific answers are given in blue text and manuscript modifications related to the Reviewer's comments are given in green text. Line numbers below correspond to the clean revised manuscript.**

**Anonymous Referee #1:**

The paper reports on a one-week measurement campaign collecting samples at two locations in the north and south of Mexico City, 16 km apart. Size-segregated samples were analysed for ice nucleating particle (INP) concentration, and aerosol chemical composition, bioaerosol concentration, concentrations of several gases, and meteorological parameters were monitored. The INP concentration was found to differ between the sites on at least one day of sampling, and a connection to aerosol chemistry is explored. The paper requires major revisions, in particular because of a temporal misalignment problem in the correlation analysis.

A/ Thank you for pointing out the temporal misalignment between the different measurements. We hope that the revised version covers all your concerns.

**Specific comments:**

Line 29: Specify which criteria pollutants (PM<sub>2.5</sub>, SO<sub>2</sub>, NO<sub>x</sub>, CO, O<sub>3</sub>) were measured. Not all readers may be familiar with the term.

A: The text was corrected as follows. **Lines 28-30:** "We found differences in the chemical composition, criteria pollutants (PM<sub>2.5</sub>, O<sub>3</sub>, CO, NO<sub>x</sub>, and SO<sub>2</sub>), and biological content between northern and southern MCMA, separated by 16 km."

Lines 33, 34, 126, 259, 326, 421, 426, 429, 455, 524, 537, 544, 549, 567 and throughout the manuscript: Replace INP "efficiency", "ability", "activity", and "behaviour" with "INP concentration". This change is necessary because the study measures INP concentration, not the ice nucleation efficiency of a known substance with a defined surface area.

A: We thank the reviewer for this suggestion. The revised manuscript was modified accordingly.

Line 36f: Clarify how the role of aerosol in cloud formation was evaluated.

A: The sentence was modified as follows. **Lines 35-37:** "Although the urban aerosol's physicochemical properties, biological content, and its sources were found to differ at both sites, it did not strongly impact the INP concentrations, with the exception of the largest measured particles"

Lines 38, 353, 396: The concept of microclimates, including their definition and identification criteria, needs to be explained in the introduction. According to Met Office factsheet 14 (Microclimates), microclimate criteria apply on climatic timescales that cannot be determined based on one week of data. Please clarify which factors are assumed to create a microclimate within the MCMA.

A: The following text was added to clarify the concept of microclimates. **Lines 72-78:** "A microclimate can be referred as a relative small-scale area with a distinctive climate over it as a whole (Met Office Factsheet 14). Thanks to its large area, and the clear variability of land use (e.g., industrial, rural, residential, commerce, and ecological preservation), the northern and southern MCMA present significant differences in temperature (heat islands), rainfall, wind patterns, humidity, aerosol and gas emissions, indicating the presence of a

clear microclimate differentiation (Met Office Factsheet 14; Molina and Molina, 2004; Amador-Muñoz et al., 2013; Castro Romero et al., 2024)”.

Lines 39f, 81: The discussion of how aerosol–cloud interactions impact extreme precipitation events is limited to one sentence in the introduction. If this is a main motivation for the study, it could be summarized in more detail.

A: The following text was added to the revised manuscript. **Lines 103-112:** “Aerosol particles have the potential to influence the development of deep convective clouds those of which are typically associated with extreme rainfall events (Burrows et al., 2022). Efficient INPs can promote specific processes as the seeder-feeder mechanism (Ohneiser et al., 2025) triggering primary ice particle formation as well as ice multiplication, increasing the ice water content in MPC (Purdy et al., 2005). These ice particles can grow at expenses of the surrounding water droplets, via the Wegner-Bergeron-Findeisen process, enhancing precipitation rates (Heymsfield et al., 2020; Ohneiser et al., 2025). Toll et al. (2024) showed that the presence of anthropogenic particles hot spots can modify cloud microphysics, leading to cloud glaciation and precipitation events under stratiform non-convective clouds.”

Line 69f: Related to the previous comment, elaborate on what is meant by microclimate theory and provide a supporting reference. Molina and Molina (2004) do not discuss microclimate theory.

A: The following text was added to clarify the concept of microclimates. **Lines 72-78:** “A microclimate can be referred as a relative small-scale area with a distinctive climate over it as a whole (Met Office Factsheet 14). Thanks to its large area, and the clear variability of land use (e.g., industrial, rural, residential, commerce, and ecological preservation), the northern and southern MCMA present significant differences in temperature (heat islands), rainfall, wind patterns, humidity, aerosol and gas emissions, indicating the presence of a clear microclimate differentiation (Met Office Factsheet 14; Molina and Molina, 2004; Amador-Muñoz et al., 2013; Castro Romero et al., 2024)”

Line 74: Elaborate on why microclimatic effects are considered highly important for local precipitation events in the MCMA and provide references. It would be expected that synoptic-scale moisture supply and dynamical forcing are at least equally important.

A: The following text, added to the revised manuscript, reinforced this idea. **Lines 80-85:** “This is of high importance to understand the microclimates along the MCMA and their relationship with local precipitation events. Zhu et al. (2024) evaluated precipitation events across China, finding that precipitation characteristics could differ across climatic zones. Additionally, Li et al. (2019) showed that atmospheric circulation changes driven by warming modulated the intensification of extreme precipitation events across North America.”

Line 81: Extend the discussion on how INPs affect extreme precipitation, for example through their influence on deep convective clouds associated with extreme rainfall.

A: The following text was added to the revised manuscript. **Lines 103-112:** “Aerosol particles have the potential to influence the development of deep convective clouds those of which are typically associated with extreme rainfall events (Burrows et al., 2022). Efficient INPs can promote specific processes as the seeder-feeder mechanism (Ohneiser et al., 2025) triggering primary ice particle formation as well as ice multiplication, increasing the ice water content in MPC (Purdy et al., 2005). These ice particles can grow at expenses of the surrounding water droplets, via the Wegner-Bergeron-Findeisen process, enhancing

precipitation rates (Heymnsfield et al., 2020; Ohneiser et al., 2025). Toll et al. (2024) showed that the presence of anthropogenic particles hot spots can modify cloud microphysics, leading to cloud glaciation and precipitation events under stratiform non-convective clouds.”

Table 1: Provide the sample volume in an additional column.

A: Table 1 was updated as suggested.

Line 180: In comparison, the inlet cut-size of 2.5  $\mu\text{m}$  of the MiniVol excludes particle sizes collected on the two upper and partially the third of the four MOUDI stages used to obtain INP concentrations. As the four MOUDI stages contribute equally to the INP concentration (no size dependence observed), this indicates that over 60% of INPs are excluded from the MiniVol samples. This is the first reason why the correlation analysis between INP concentration and MiniVol-derived parameters can be misleading.

A: We agree with the reviewer and we have included in the revised manuscript the data corresponding to stage 6 (0.56  $\mu\text{m}$  to 1.0  $\mu\text{m}$ ). Note that the inclusion of additional stages, i.e., stage 7 (0.32  $\mu\text{m}$  to 0.56  $\mu\text{m}$ ) and stage 8 (0.18  $\mu\text{m}$  to 0.32  $\mu\text{m}$ ) is not possible as the large particle concentration at these stages represent a technical limitation, as a large particle loading on the stages inhibits individual droplet formation. Also, it is important to note that submicron particles on stages 6 to 8 typically represent a small fraction (~10%) of the overall INP population at temperatures above  $-25^{\circ}\text{C}$  (Ladino et al., in preparation).

Section 2.2: The MOUDI flow rate and sample substrate (line 263) could be included in this section to consolidate information on sampling procedures. It would be helpful to report sampling flow rates, time of day of collection, and time resolution for all samplers.

A: Thank you for this suggestion. Section 2.2 was modified and the following text was added.

Lines 216-230: “The simultaneous sampling was performed using, per site, a MiniVol TAS (Tactical Air Sampler; Airmetrics) with a 2.5  $\mu\text{m}$  cut-size inlet operated at  $5 \text{ L min}^{-1}$ , an eight stage micro-orifice uniform deposit impactor (MOUDI 100R; MSP) operated at a  $30 \text{ L min}^{-1}$  flow rate to separate particles as a function of their aerodynamic diameter (cut sizes of 0.18  $\mu\text{m}$ , 0.32  $\mu\text{m}$ , 0.56  $\mu\text{m}$ , 1.0  $\mu\text{m}$ , 1.8  $\mu\text{m}$ , 3.2  $\mu\text{m}$ , 5.6  $\mu\text{m}$  and 10  $\mu\text{m}$ ), and a single-stage BioStage Quick Take 30 cascade impactor for viable particles (SKC Inc. USA) operated at a  $28.3 \text{ L min}^{-1}$  flow rate. The MOUDI samples, used to evaluate the INP concentrations, were collected one time a day from May 16<sup>th</sup> to May 20<sup>th</sup>, 2022, with the sampling times shown in Table 1 (more details are provided in section 2.2.6). The MiniVol samples were collected daily for 24 h on May 12<sup>th</sup>, May 13<sup>th</sup>, May 16<sup>th</sup>, May 17<sup>th</sup>, May 18<sup>th</sup>, May 19<sup>th</sup> and May 20<sup>th</sup>, 2022, on 47 mm Teflon filters (Pall Science), and were used for the ionic and elemental composition analysis. The BioStage impactor samples with a 10  $\mu\text{m}$  cut-size inlet were used for culturable bacteria and fungi identification. They were collected once a day (at 10:00 am for 5 mins) on the same dates as the MiniVol samples (more details are described in section 2.2.5). The general description of the sampling campaign is shown in Table 1.”

Line 243: At what time of day were the samples collected, and how many samples were collected per day?

A: This information is now included in Section 2.2.

Line 294: Do you mean the area on which aerosol is deposited? Is aerosol deposited exclusively on the coverslip and not over the entire impaction stage?  $A_{\text{deposit}}$  is defined as the coverslip area also in Manson et al. (2016); however, their Fig. 7 shows that the coverslip

covers only about one third of the impaction stage. For normalization of the sampled volume, the entire area over which aerosol is deposited should be used. Please include a photo of a loaded sample stage in the reply to this comment for clarification.

A: Yes, you are right. We use  $A_{\text{deposit}}$  as the area of the coverslip on which the aerosol is deposited. Therefore, we incorporate correction factors to account for not using the complete stage as described and discussed in Mason et al. (2015). Although there could be additional corrections, these are the most important ones that allow us to report a confident INP concentration. As shown in Lacher et al. (2024), the INP concentrations delivered by the UNAM-MOUDI-DFT are comparable with those reported by other six different ice nucleation setups from Europe and the US.

Lacher, L. et al.: The Puy de Dôme ICe Nucleation Intercomparison Campaign (PICNIC): comparison between online and offline methods in ambient air, *Atmos. Chem. Phys.*, 24, 2651–2678, <https://doi.org/10.5194/acp-24-2651-2024>, 2024.

Section 3.1: Figures S4, 2, and 3 show only one sample per day, while Table 1 indicates that two samples were taken on both 17 and 18 May. Please include these samples to show diurnal variability in INP concentration and add a corresponding discussion.

A: We are sorry for this confusion. We accidentally included two samples in Table 1; however, this information is not available. Table 1 was corrected accordingly. We agree that it would be valuable to evaluate the INP concentration diurnal variability; however, this was not an objective from the present study, and hence, we don't have data to address this point.

Line 320: Selecting a restricted size range is not necessary. Using all eight MOUDI stages allows investigation of ~100% rather than 70% of INPs. There are two additional reasons to include the lower stages: (1) these stages are better represented by the MiniVol samples with a 2.5  $\mu\text{m}$  cut-off (see previous comment), and (2) the main finding of no size dependence in INP concentration could be further supported. There is a potential contradiction between “no size dependence” and “70% of INPs are super-micron” that could be resolved. The analysis could clarify whether the lack of size dependence applies only to super-micron particles or across a broader size range.

A: We agree with the reviewer that it would be ideal to use all MOUDI stages; however, as mentioned above, the high particle loading on the lower stages inhibits the proper formation of individual spherical droplets. We have now included the stage 6 data (0.56  $\mu\text{m}$  to 1.0  $\mu\text{m}$ ). Below, Figure A1 from Mason et al. (2016) shows the INP concentration for the 8-stages at six different locations (most of them remote places). From the Figure it is concluded that the INP concentrations on stages 7 and 8 are extremely small compared to the other stages.

We forgot to specify that the stage-based data discrimination was applied to Figs. 5 and S4 only (this is now corrected in the supplementary material). The rest of the figures, except the performed correlations, were plotted using all available data (i.e., stages 2 to 6). For the correlation heatmap we only use the three final stages of the MOUDI in order that the cut-sizes of the used instruments match between them.

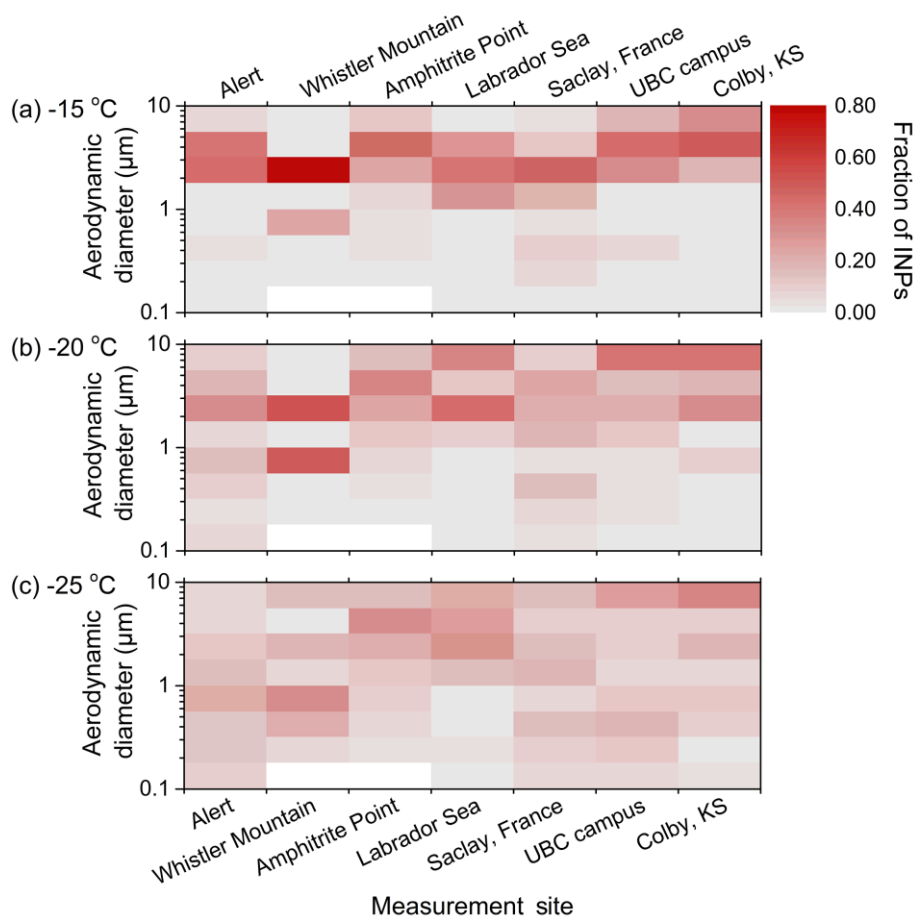


Figure A1. Fractional INP concentrations as a function of aerosol particle size, location, and activation temperature: (a) -15 °C; (b) -20 °C; and (c) -25 °C. The color bar indicates the fraction of INPs measured in each particle size bin. Aerosol particle sizes correspond to the 50% cutoff aerodynamic diameters of the MOUDI stages (Marple et al., 1991). Missing sizes for the Whistler Mountain and Amphitrite Point sites are uncolored.

Mason, R. H., Si, M., Chou, C., Irish, V. E., Dickie, R., Elizondo, P., Wong, R., Brintnell, M., Elsasser, M., Lassar, W. M., Pierce, K. M., Leaitch, W. R., MacDonald, A. M., Platt, A., Toom-Sauntry, D., Sarda-Estève, R., Schiller, C. L., Suski, K. J., Hill, T. C. J., Abbatt, J. P. D., Huffman, J. A., DeMott, P. J., and Bertram, A. K.: Size-resolved measurements of ice-nucleating particles at six locations in North America and one in Europe, *Atmos. Chem. Phys.*, 16, 1637–1651, 2016.

Line 324: Describe how the homogeneous freezing line was determined and how it compares with published measurements, for example those in Shardt et al. (2022) for 100 μm droplets.

A: To clarify this, the following text was added to the revised manuscript. **Lines 364-369:** “The homogeneous freezing line was determined using the same procedure described in section 2.2.6 with a brand-new substrate (i.e., without aerosol particles impacted on them). The average onset freezing temperature ( $T_0$ ) of the homogeneous freezing experiments (i.e., -34.3 °C) is comparable with other data for supercooled liquid drops such as the 100 μm (-34.2 °C) and  $89 \pm 7$  μm (-35.5 to -36.7 °C) liquid water drops reported by Shardt et al. (2022) and Tarn et al. (2021), respectively.”

Line 327: Explain how the averages and error bars in Fig. 2 were calculated. In particular, clarify how freezing curves from different MOUDI stages were combined and how differences in droplet numbers between experiments were accounted for.

A: The average was calculated as the mean of the  $T_0$  and  $T_{50}$  values for each MOUDI stage freezing curve. To clarify this, Figure 2 was replaced with a box plot. Regarding the droplet number differentiation, this was assessed using the "correction for non-uniformity aerosol deposit" (Mason et al., 2015, section 3.4) to estimate INP concentration; however, for the frozen fraction, we report normalized data as a function of droplet number.

Line 332f: Please quantify and analyse the causes of the differences in  $T_{50}$  and  $T_0$  compared to literature. For example, the introduction notes that Knopf et al. (2010) reported ice nucleation at cirrus conditions, whereas the present study measures freezing of droplets in the MPC regime.

A: The sentences in Lines 332 (original manuscript) simply wanted to let the readers know that we found warmer temperatures than previous studies. The observed differences in  $T_{50}$  and  $T_0$  between previous studies and the present study could come from different sources such as different equipment, different time of the year, different pollution levels, different specific sampling location, and different meteorological patterns during sampling, etc. Therefore, it is very difficult to identify the main cause of these differences, a task that it is out of the scope of this study.

Knopf et al. (2010) reported onsets for northern Mexico City via immersion freezing and deposition nucleation relevant to mixed-phase and cirrus clouds, respectively. The introduction was slightly updated to indicate that Knopf et al. (2010) includes data from both types of clouds. Therefore, in Line 332 (original manuscript) we compared our data with the immersion freezing experiments from Knopf et al. (2010).

Line 342, Fig. 3: The error bars of South-20220520 overlap with those of North-20220520. Please clarify what is meant by statistically significant INP concentrations. What do the error bars represent, and how are they calculated? For South-20220520, why are the error bars smaller at  $-13$  and  $-14$  °C than at  $-12$  and  $-15$  °C? Consider using the method of Agresti and Coull (1998) to calculate 95% confidence intervals.

A: We have updated Figure 3 to improve its readability. Error bars were calculated using the same method described by Mason et al. (2015), which accounts for the experimental uncertainty carried through all corrections applied to INP concentration calculation. We decided to rearrange Fig. 3 to show the May 20<sup>th</sup> data only. In this case, we can see a visually significant difference (no overlap of error bars) between the northern and southern samples between  $-22$  °C and  $-19$  °C. Additionally, we use the Agresti and Coull (1998) method as recommend. We obtain significance difference (Group 1 (North) Adjusted Proportion: 0.875, Group 2 (South) Adjusted Proportion: 1.400, Difference ( $p_1 - p_2$ ): -0.525, 95% Confidence Interval: [-0.525, -0.525], Result: Significant difference found) between both group of data for May 20<sup>th</sup> (we use  $n = 5$ , which represent all MOUDI stages we have for May 20<sup>th</sup>).

The following text was added to the revised manuscript. **Lines 398-403** "The total INP concentrations (i.e., the accumulated INP concentration, represented by the sum of each MOUDI stage INP concentration for each sample) at both sites are shown in Fig. 3a. Although the INP concentrations measured at both sites were comparable, the exemption was the May 20<sup>th</sup> sample (Fig. 3a), where higher and statistically significant differences in INP concentrations were measured in the southern site between  $-19$  °C and  $-22$  °C (considering the Agresti and Coull (1998) method to calculate 95 % confidence intervals)."

Line 345, Figure 3: Explain why Beijing is an appropriate city for comparison of INP concentrations. Consider adding data from Rodríguez-Gómez (2021) and Pereira (2021) to Fig. 3 (see comment on Fig. 4).

A: Although Beijing is not a tropical city, it is a megacity like Mexico City with high pollution levels. Therefore, we consider that the comparison with the Chen et al. (2024) data is appropriate. While we did not include the data from Pereira et al. (2021) in Fig. 3 because the units are not comparable, as they reported  $L^{-1}$  in water, the data from Rodríguez-Gómez (2021) was added to Figure 3.

The following text was added to the revised manuscript.

Lines 403-406: “Figure 3a also indicates that the INP concentrations from the present study agree well with those reported by Cabrera-Segoviano et al. (2022) for Mexico City and by Chen et al. (2024) for Beijing (between  $-19\text{ }^{\circ}\text{C}$  and  $-22\text{ }^{\circ}\text{C}$ ), a polluted megacity such as the MCMA”.

Lines 425-427: “As shown in Fig. 3b, the INP concentrations measured in the present study agree with those reported for southeastern (Rodríguez-Gómez, 2021) and southern sites (Cabrera-Segoviano et al., 2022) of the MCMA.”

Line 353: Specify how the average accumulated INP concentration is calculated, which data are averaged, and what the error bars in Fig. 4 represent.

A: The text was modified as follows. Lines 418-421: “To better assess the differences in the INP concentration across the two microclimates within the MCMA, the average INP concentrations (represented by the average of all samples’ total INP concentration) for both sites at four different temperatures ( $-15\text{ }^{\circ}\text{C}$ ,  $-20\text{ }^{\circ}\text{C}$ ,  $-25\text{ }^{\circ}\text{C}$ , and  $-30\text{ }^{\circ}\text{C}$ ) were calculated, as shown in Fig. 3b.”

Line 357: The difference between the north and south samples at  $-15\text{ }^{\circ}\text{C}$  is not clearly evident in Fig. 4, given the overlapping concentration ranges.

A: The sentence was modified as follows. Lines 422-425: “Although at  $-15\text{ }^{\circ}\text{C}$ , a clear difference close to one order of magnitude can be observed between both sites (C5 ( $0.04 \pm 0.04\text{ L}^{-1}$ ) and CU ( $0.38 \pm 0.31\text{ L}^{-1}$ )), the difference is not statistically significant (Agresti and Coull, 1998).”

Figure 4: The figure does not provide substantial information beyond what is already shown in Fig. 3. It could be removed, with the reference data added to Fig. 3 instead. In addition, the yellow data symbol is difficult to see; a darker colour would improve visibility.

A: Thank you for pointing this out. Figure 3 and Figure 4 were merged in the revised manuscript.

Line 371ff: It is correct that particle size and surface area affect the ice nucleation efficiency of particles with the same composition. When multiple particles of different compositions are present in a droplet, the combined abundance of ice-active sites at a given temperature determines ice formation. The amount and composition of particles on different MOUDI stages likely differs but is unknown. It is also unknown how the amount and composition of particles changes from day to day and between the sampling locations. Because only INP concentration per stage is known, interpretations involving coatings or physicochemical heterogeneities require supporting evidence or should be omitted.

A: The reviewer is right; we cannot hypothesize without a robust evidence. The text was modified as follows. Lines 429-437: “The impact of particle size on the frozen fraction at both

sampling sites does not show a clear trend (Fig. S4). Likewise, Fig. 4 shows that the mean INP concentration (which represents the average of all samples for each MOUDI stage) measured on urban particles from the MCMA is not clearly size-dependent. In theory, particle size and INP efficiency are related. This relationship is attributed to surface active sites, as larger particles contain a higher concentration of active sites (Vali, 1996; Hoose and Möhler, 2012; Kanji et al., 2017); however, as urban ambient particles are a complex mixture of particles with different compositions, the relationship between particle size and INP is not straightforward as it requires deeper chemical analysis to understand the heterogeneity in particles chemical composition on each MOUDI stage.”

Figure 5: Consider avoiding “dynamite stick” plots. Showing individual data points would be more informative. In general, bar plots on a logarithmic scale can be misleading because bar area has no physical meaning.

A: Thank you for this suggestion. Figure 5 (now Figure 4) was modified accordingly.

Line 399ff: It may be useful to note that NO<sub>x</sub> and measured radiation are higher at the northern site; thus, elevated O<sub>3</sub> concentrations at the southern site could reflect higher VOC levels, which were not measured. Any impact on INP concentration remains speculative. Wang et al. (2012) measured naphthalene, an anthropogenic VOC associated with combustion rather than biogenic SOA, and investigated ice nucleation at cirrus conditions, outside the experimental range of the present study. Moreover, typical SOA particle sizes are below 1 μm, whereas super-micron particles were used for the INP analysis.

A: Although we are confident that the VOC concentrations are higher at the southern site (this is well known along the MCMA), the reviewer is correct that they were not measured in the present study, and therefore, we cannot draw any conclusion about VOC vs. INPs.

The Wang et al. (2012) sentence was deleted and the text was modified as follows. **Lines 469-473:** “It is well known that VOCs may participate in O<sub>3</sub> production by photochemistry and lead to higher concentrations (Pinto et al., 2010; Amador-Muñoz et al., 2016). Therefore, the southern site is likely enriched in biogenic secondary organic aerosols (SOA) compared to the northern site (Aiken et al., 2009; Cooke et al., 2024), with unknown implication in the INP population.”

Line 414: Describe how these measurements were processed and averaged to match the INP sample collection periods.

A: The text was modified as follows. **Lines 479-492:** “Figure 5 shows the calculated Pearson correlation coefficients between the measured criteria pollutants with T<sub>0</sub>, T<sub>50</sub> and INP concentration at -20 °C, -25 °C, and -30 °C for both sampling sites (for particles ranging between 0.56 μm and 3.2 μm). Mean criteria pollutant concentrations between 08:00 h and 13:00 h local time were used to match the INP sampling periods. Figure 5 shows high correlations between PM<sub>2.5</sub>, O<sub>3</sub>, and the INP parameters at the southern site, implying that both pollutants can impact the physicochemical properties of the INP population at this site. On the other hand, no significant correlations were found at the northern site. As the INP sizes in both sites are identical, the observed differences are likely linked with differences in the PM<sub>2.5</sub> composition. As shown in Figs. 6 and S5, the PM<sub>2.5</sub> elemental and ionic composition in the northern and southern sites have important differences. As the composition is clearly different, the interaction between the fine particles, and hence INPs with O<sub>3</sub> is expected to differ in both sites as well. As the PM<sub>2.5</sub> sampling time was much larger

(24 h) than the 4 h INP sampling, a direct correlation between the elemental and ionic composition with the INP concentrations was not assessed.”

Line 425: Provide an explanation of how different compounds may influence INP concentration and why these effects could differ between sites. Clarify why INP parameters correlate with chemical parameters at one site but not the other. The small number of data points ( $n = 5$ ) makes the correlation analysis sensitive to outliers. Inspecting scatterplots could help identify non-linear relationships or outliers. In addition, explain how high correlations with  $T_{50}$  can occur without corresponding correlations in INP concentrations at  $-20$  or  $-25$  °C, the temperature range where  $T_{50}$  is located. Please assess how robust the correlations are at  $\pm 1$  °C from the chosen temperatures. The possibility of spurious correlations due to limited sample size (second reason why the correlation analysis may be misleading) should be addressed by presenting scatterplots.

A: The correlation between the elemental and ionic composition with the ice nucleation parameters was removed in the revised manuscript because of the large differences in the sampling times. The following text was added to the revised manuscript. Lines 489-492: “As the composition is clearly different, the interaction between fine particles, and hence INPs, with  $O_3$  is expected to differ in both sites as well. As the  $PM_{2.5}$  sampling time was much larger (24 h) than the 4 h INP sampling, a direct correlation between the elemental and ionic composition with the INP concentrations was not assessed.”

Figure 6: Indicate the confidence level associated with values marked by an asterisk.

A: The following text was added to the former Figure 6 (now Figure 5). “The statistically significant coefficients (with 95 % confidence level) are marked with an asterisk.”

Line 432ff: INP samples were collected during a 4-hour morning period, whereas filter samples were collected over 24 hours. As shown in Fig. S6, air mass origin changed during the 24-hour period, indicating that different aerosol populations were analysed for composition and INP concentration. For correlation analysis, sampling intervals must be temporally consistent. Correlating temporally misaligned samples constitutes a methodological issue. This is the third reason why the correlation analysis involving MiniVol data can be misleading. I recommend removing this part of the analysis and the associated discussion.

A: We agree with the reviewer that the differences in the MOUDI and Minivol sampling times could bring us to unintentional misleading conclusions. Unfortunately, the MOUDI is not an automatic instrument and we did not have the possibility to have two online aerosol composition spectrometers such as the ACSM.

In the revised manuscript the bulk aerosol composition was used to show the differences in the aerosol composition in both sampling sites, but the direct correlations with the INP concentrations were removed.

Line 454: In Fig. 6, the correlation with INP concentration at  $-20$  °C is shown as not significant.

A: This part was removed in the revised manuscript.

Line 466ff: This appears to contradict the discussion of O<sub>3</sub> concentrations in lines 399–407. If VOC concentrations are higher in the north, higher O<sub>3</sub> concentrations would also be expected there.

A: The sentence was deleted.

Lines 470–473: This discussion repeats points made in lines 452–456.

A: The sentence was deleted.

Line 475: Provide the altitude of the trajectories. Overlaying Figs. S7 and S6 could clarify which trajectories are influenced by biomass burning and why this effect is more pronounced at the southern site. Potassium, a tracer for biomass burning, is higher at C5 than at CU on most days (Fig. 7).

A: The figures were overlaid considering the HYSPLIT backward trajectories for the sampling period only (May 12<sup>th</sup> to May 20<sup>th</sup>, 2022), and the text was modified as follows.

Lines 544-549: “Figure S6 shows that the HYSPLIT backward trajectories at 250 m AGL at both MCMA sites overlaid on the NASA FIRMS real-time active fire locations for the sampling period (i.e., May 12<sup>th</sup> to May 20<sup>th</sup>, 2022). Even though not all backward trajectories pass through active fires, the overlap between some back-trajectories and active fires suggests that the local and regional transport of BB particles could contribute to the observed differences in the chemical composition, as shown elsewhere (e.g., Carabali et al., 2021).”

Line 481ff: The interpretation of the three clusters requires further explanation. For example, why are Pb, Cl<sup>-</sup>, Mn, and Ca assigned to the soil cluster in the north but to the anthropogenic cluster in the south? Briefly explain the clustering method and how to interpret the dendrogram produced using Ward’s method with Pearson correlation coefficients. Clarify how clustering leads to source identification and whether these sources relate to observed INP concentrations.

A: The sentence was added as follows. Lines 555-561: “Hierarchical clustering was conducted using Ward’s method, with Pearson correlation coefficients employed as the similarity measure. This technique groups variables by minimizing increases in within-cluster variance, leading to clusters of species with similar temporal patterns. The resulting dendrogram illustrates the level of similarity among variables, where shorter linkage distances represent stronger relationships. Principal cluster components can be linked to a potential source as shown in previous literature analysis of similar samples (Reynoso-Cruces et al., 2023).”

Line 510: Explain how the finding that 57% of bacteria are Gram-positive affects the analysis, given that ice-nucleation-active bacteria are predominantly Gram-negative.

A: In this paragraph we did not performed any correlation between bacteria and INPs. This is an introductory paragraph where we compare our measured bacteria concentrations with literature data.

Figure 8: INP concentrations were measured between 16–20 May. Why is a longer time series of bacteria and fungi shown? What additional insight is provided by comparison with PM<sub>2.5</sub>?

A: Thank you for pointing this out. The figure was adjusted to the same time period of the INP concentrations, and PM<sub>2.5</sub> data was removed.

Line 530: Pseudomonas, Pantoea, Alternaria, and Fusarium from other locations have been reported to nucleate ice above  $-10\text{ }^{\circ}\text{C}$ . Are local strains not producing ice-nucleation proteins?

A: The following text was added to the revised manuscript. **Lines 609-611:** “Although some of the identified bacteria and fungi genera and species have been reported to act as INPs at warm temperatures (Tables S5 and S6), it is completely unknown if the MCMA microorganisms contained the INA protein.”

Line 533: Clarify why cross-correlation analysis was performed in the context of this study.

A: We performed Pearson correlation instead on cross-correlation analysis in the original manuscript. This was corrected on Tables S7 and S8 as well in **Lines 614-618:** “The behavior of bacterial and fungal concentration between the northern and southern sites were evaluated by the Pearson correlation analysis shown in Tables S7 and S8. As expected, mixed values of Pearson coefficients reflect that not all bacteria and fungi found at the southern site (closed to vegetated areas) are present in the northern site.”

Line 550: Explain why correlations with these parameters imply compositional effects rather than simply reflecting aerosol amount (e.g.,  $\text{PM}_{2.5}$ ).

A: The following text was added to the revised manuscript. **Lines 636-639:** “The present results clearly demonstrated the existence of microclimates within the MCMA. The INP parameters of the MCMA urban particles correlated with  $\text{PM}_{2.5}$  and  $\text{O}_3$ , at the southern site, corroborating that particle mass concentration and ozone concentration are very important for the southern MCMA microclimate”

Lines 552–556: Clarify the connection between these particle types and INP concentration.

A: The following text was added to the revised manuscript. **Lines 639-641:** “Nevertheless, urban aerosol particles show similar INP concentrations across both sites, suggesting that INP activity does not depend on a specific aerosol type, but rather on the bulk complex mixture of aerosol particles”.

Line 559: Specify which atmospheric processes are referred to and how particle formation is linked to INP concentration.

A: The following text was added to the revised manuscript. **Lines 648-650:** “aerosol sources and atmospheric processes linked to particle formation and aerosol aging (e.g., gas-to-particle conversion, organic coatings, and photochemistry) are quite different”.

Lines 560ff, 543: Explain why INP concentrations are compared with those from Beijing. Similar concentrations might suggest that, contrary to the conclusions, urban INP concentrations are not strongly linked to the listed factors.

A: Please see our answer above (Line 345, Figure 3)

Line 566: Specify what concrete information was obtained.

A: The following text was added to the revised manuscript. **Lines 662-665:** “Although the present work shows that air pollutants such as  $\text{PM}_{2.5}$  and ozone can be linked with the ice nucleating abilities of urban aerosol particles, it is important to understand the role and the origin of the super-micron particles as they are a large contributor to the MCMA INP population.

Table S6: Consider adding a column indicating Gram-positive or Gram-negative classification and another listing temperature ranges over which species are reported to act as INPs, based on literature data.

A: The requested information was added to Tables S5 and S6.

Figure S1: Fig. S6 suggests predominantly westerly winds at midday, whereas these wind roses show mainly easterly winds. Restricting the wind analysis to the MOUDI sampling periods could be informative.

A: Thank you for the suggestions. Figure S1 was modified accordingly.

#### Technical corrections:

Line 80: something is missing in this long sentence. Do you mean "... information on *the interplay ...*"?

A: Corrected.

Line 118: Delete the "B" before *proteobacteria*.

A: Corrected.

Figure 6: Br is missing from panel (a) but appears in Fig. S8. CO is missing from panel (b) but is shown in Fig. S2.

A: The correlation between the INP concentrations and the chemical composition was removed in the revised manuscript.

Figure 7: Replot the figure including zero on each ordinate rather than overlapping y-axes.

A: Corrected on new Figure 6.

Figure 8: Red stars without connecting lines are filled symbols in the plot but shown as open symbols in the legend.

A: Corrected on new Figure 7.

Figure S3: "*Adapted*" implies modifications. "Reprint of Fig. 3 from Córdoba et al. (2021)" would be accurate.

A: Corrected on Figure S3.

Figure S5: The y-axis labels of individual subfigures seem irregular. Replot including zero on each ordinate.

A: Corrected on new Figure S6.

Figures S8 and S9: Blue lines below the green cluster are difficult to see. Consider using different colours for clusters in Fig. S9, as they do not correspond to the same sources as in Fig. S8.

A: Corrected on new Figures S8 and S9.

#### References:

Agresti, A. and Coull, B. A.: Approximate is better than "exact" for interval estimation of binomial proportions, *Am. Stat.*, 52, 119, <https://doi.org/10.2307/2685469>, 1998.

MetOffice factsheet 14,

[https://www.metoffice.gov.uk/binaries/content/assets/metofficegovuk/pdf/research/library-and-archive/library/publications/factsheets/factsheet\\_14-microclimates\\_2023.pdf](https://www.metoffice.gov.uk/binaries/content/assets/metofficegovuk/pdf/research/library-and-archive/library/publications/factsheets/factsheet_14-microclimates_2023.pdf)

Shardt, N. et al.: Homogeneous freezing of water droplets for different volumes and cooling rates, *Phys. Chem. Chem. Phys.*, 24, 28213-28221, <https://doi.org/10.1039/D2CP03896J>, 2022.

**We would like to thank Reviewer #2 for his/her constructive suggestions, which helped us to improve the manuscript. Specific answers are given in blue text and manuscript modifications related to the Reviewer's comments are given in green text. Line numbers below correspond to the clean revised manuscript.**

**Anonymous Referee #2:**

The manuscript describes measurements of atmospheric aerosol particles done on a few days (5 to 7, depending on sample) at two different sites (16 km apart) in Mexico city. Measurements include a variety of parameters from three types of samples: a MiniVol Tactical Air Sampler (Airmetrics) with a 2.5  $\mu\text{m}$  cut-size inlet for chemical analysis; an eight stage micro-orifice uniform deposit impactor (MOUDI) for INP (ice-nucleating particle) analysis with an upper sampling size of 10 mm; and a BioStage cascade impactor (cut-off size not given, likely total suspended particles) for the analysis of viable bacteria and fungi. All sample types not only had different cut-off sizes, but also different sampling durations (24h, ~ 4h and 5 min, respectively) but also a different amount of collection days, and it did not become clear which data from which days were used for comparisons.

**A:** We thank the reviewer for pointing this out. We agree that having all three sensors with the same high temporal resolution is ideal; however, this is not feasible. Considering the recommendations from both reviewers we have modified the manuscript. We hope that the revised version covers all your concerns.

Conclusions drawn by the authors oftentimes seem to include some wishful thinking, as I will elaborate on in more detail below. Due to this, but also due to the data as such and of what they show, I strongly suggest to the editor to consider if this should rather be published as a measurement report. But in any case, I can recommend publication of this study only after the data interpretation will have been adapted to what the data really show and after the text will have been thoroughly and accordingly revised.

**A:** A large part of the discussions and conclusions were adjusted in the revised manuscript. We are open to move the manuscript from "Article" to "Measurement report" if the Editor and reviewers consider it appropriate.

My main points of criticism (all of them equally important) are the following:

**1)** The above-mentioned different cut-off sizes for the different samples, their different collection durations and the different days of sample collection make a comparison of the (bulk) results for the different particle characteristics difficult or even meaningless.

**A:** As stated below we have removed the direct comparison of the chemical composition with the INP parameters.

INP data from the two study sites differ particularly in the larger size bins (> 5.6 mm for 4 of 5 samples, 3.2 – 5.6 mm for two and 1.8 – 3.2 mm for one sample). This is an interesting result, which, however, is not discussed at all. Unfortunately, for these larger sizes, there is no information on the chemical composition.

**A:** We agree with the reviewer and we have strengthened this part in the revised manuscript (see below).

On the other hand, for the presented correlation between INP data and chemical composition (Fig. 6 and related text) it was not described for which INP data (all MOUDI size bins or only the ones for smaller particles?) this was done. Hence the presented correlation may or may not be meaningless in general. From the text I assume that the fully summed up INP concentrations (over all MOUDI stages) were used for the comparison. It would make sense to sum up the two MOUDI-stages with the smallest INPs on them and compare the resulting INP concentrations with results from the PM<sub>2.5</sub> chemical analysis. Then, it can also be described which fraction of all INPs is in these two smallest MOUDI-stages. However, sub-micron particles will still be missed in the INP analysis, making the correlation still less than optimal.

A: we have removed the direct comparison of the chemical composition with the INP parameters and now report the MOUDI stages used when performing the correlation with PM<sub>2.5</sub>.

2) As I understand, sampling duration for INP samples cannot be much larger as particles need to be separated enough to allow for droplet formation in your offline measurement technique (the UNAM-MOUDI-DFT) in such a way that droplets do not touch (I deduce this from your remark in lines 274-275). With this, the lowest INP concentration limit that can be measured in this study was roughly 0.2 1/L. And as can be seen from your INP spectra, you mostly only observe INPs that are ice active at temperatures below -15°. INPs of biological origin are typically present at higher temperatures, and typically with lowering concentrations towards increasing temperatures. With the presented measurements you simply cannot detect most of these biological INPs (if they were there). Hence a comparison with results on biological particles cannot really be done.

A: This is plausible; however, using the exact same method, we have been able to measure INP concentrations above -15°C under the influence of marine aerosol particles and cold fronts (Ladino et al., 2019) and biomass burning particles (Cabrera-Segoviano et al., 2022). Therefore, we are convinced that efficient biological INPs were absent in the collected samples.

Ladino, L.A., G.B. Raga, H. Alvarez-Ospina, M.A. Andino-Enriquez, I. Rosas, L. Martinez, E. Salinas, J. Miranda, Z. Ramirez-Diaz, B. Figueroa, C. Chou, A.K. Bertram, E.T. Quintana, L.A. Maldonado, A. Garcia-Reynoso, M. Si, and V.E. Irish (2019): Ice Nucleating Particles in a Coastal Tropical Site. *Atmos. Chem. Phys.*, 19, 6147–6165, doi: 10.5194/acp-19-6147-2019

Cabrera-Segoviano, D., Pereira, D. L., Rodriguez, C., Raga, G. B., Miranda, J., Alvarez-Ospina, H., and Ladino, L. A.: Inter-annual variability of ice nucleating particles in Mexico City, *Atmos. Environ.*, 273, 118964, <https://doi.org/10.1016/j.atmosenv.2022.118964>, 2022.

3) Figure 3 shows (as far as this is visible), that on four of your five sampling days, the overall INP concentrations at your two measurements sites were mostly very similar. You even (correctly) describe this in lines 340-343. “Although the INP concentrations measured at both sites were comparable, the exemption was the May 20th sample, where notable higher and statistically significant INP concentrations were measured in the southern site between -12 °C and -22 °C.” So: Only INP concentrations measured at the southern site on May 20 were elevated, compared to the others. But then you calculate average INP concentrations for the northern site and for the southern site. It is not described how the averaging was done, but it is quite clear that the mean was used (instead of the median). This increases the average for the southern site, due to this one sample on May 20. Then, for the remainder of

the text, the southern site is suddenly discussed as being elevated in concentration in general. The latter does not fit to your measurements, and hence also all conclusions drawn from that (biased) observation are invalid.

A: We agree with the reviewer and as described below, we have adjusted and corrected this important point in the revised manuscript.

**4)** A possible influence of biomass burning (BB) to INPs is discussed. Backward trajectories are shown in Fig. S6 and a fire map with fires from the sampling period in Fig. S7. Overlaying the fire map with the backward trajectories (which I took the liberty to do for this review), it can be seen that the region in the south of the fire map, which showed pronounced fires, is not the region where air masses at the sampling sites came from. The remaining few spots showing active fires on the fire maps in the regions crossed by the backward trajectories are so scarce and small that it is difficult to follow the argument about the importance of BB for INPs.

A: Following your comment and Reviewer #1 suggestions, we have merged the data into new Figure S6 (see more details below).

Also, concerning “regional transport”, the text states: “Figure S6 also suggests that the air masses arriving at the northern site at noon and midnight, at 250 m and 500 m AGL, were not transported over the southern site, and vice versa.” However, when overlaying the backward trajectories for both sides onto the fire map, it becomes obvious that the air masses arriving at both sides often came from the same directions. While the above statement is correct, it does give a wrong impression, as it suggests different air masses were observed at the two sites.

A: Thank you for pointing this out. We have modified the text to clarify this point (see below).

**5)** A general remark about some of the values that were used in this manuscript to characterize ice activity of INPs, namely the temperature at which the first freezing is observed ( $T_0$ ) and the temperature at which half of all examined droplets are frozen ( $T_{50}$ ):

$T_0$  and  $T_{50}$  can only be used to compare data that were collected and evaluated under the same conditions concerning sampling flow, sampling duration and evaluation conditions. This can be seen when looking at equation (2), in which there is “V” in the denominator (“V is the volume of air through the MOUDI (L)”). The sampled air volume determines the INP concentration range one will get. And that determines the temperature range in which data will be obtained. And that determines  $T_0$  and  $T_{50}$ . This makes a comparison of  $T_0$  and  $T_{50}$  obtained here with data obtained in other studies (as done in e.g. lines 332-334) meaningless, unless these literature data were obtained under the same conditions.

But anyway, the passage in which  $T_0$  and  $T_{50}$  are described (lines 326 – 334 and Fig. 2) does not add anything above what again is discussed below for concentrations. Therefore, this part could be deleted.

A: We think that  $T_0$  is still valid as this refers to the temperature at which the first freezing event was detected. On the other hand, we agree with the reviewer that  $T_{50}$  is not a fair comparison and hence we have removed the  $T_{50}$  comparison with literature data.

In the following, abovementioned concerns will come up again, together with additional comments. Parts of the text that are concerned by abovementioned concerns that are not explicitly mentioned below nevertheless need to be revised.

A/ We thank again the reviewer for pointing out these important points.

### Major comments:

Abstract, lines 29: What are “criteria pollutants”? Maybe delete these two words?

A: The text was corrected as follows. **Lines 28-30**: “We found differences in the chemical composition, criteria pollutants (PM<sub>2.5</sub>, O<sub>3</sub>, CO, NO<sub>x</sub>, and SO<sub>2</sub>), and biological content between northern and southern MCMA, separated by 16 km”

Abstract, lines 30-31: Did the INPs you found really originate from the Mexico City region, or was it long-range transport? This cannot be said, based on your data. All you can say for sure was, that aerosol particles collected at the two sites in the MCMA were found to act as INPs.

A: The sentence was modified as follows. **Lines 32-34**: “Although the measured INP concentrations were similar in both sites, the southern samples showed a higher INP concentration for larger aerosol particles (i.e., particles between 5.6-10 μm).”

Abstract, lines 32-33: Samples "are" not INPs, samples "contain" INPs.

A: The text was modified as follows. **Lines 32-34**: “Although the measured INP concentrations were similar in both sites, the southern samples showed a higher INP concentration for larger aerosol particles (i.e., particles between 5.6-10 μm).”

Abstract, lines 33-34: There is only a weak positive correlation. Revise.

A: The sentence was deleted in the revised manuscript.

Abstract, lines 34-35: See my comments on biological particles. Revise accordingly.

A: The sentence was deleted in the revised manuscript.

Abstract, line 37: The difference was only found for one of five sample collection days.

A: The sentence was modified as follows. **Lines 32-34**: “Although the measured INP concentrations were similar in both sites, the southern samples showed a higher INP concentration for larger aerosol particles (i.e., particles between 5.6-10 μm).”

Abstract, lines 37-39: While there may be different microclimates at the two sites, you do not show this clearly for the INPs, and you do not show the reasons for the higher INP concentrations on May 20. Also, you do not show any connection to conditions higher up in the atmosphere. Any connection to aerosol-cloud interactions cannot be derived from your data. Revise.

A: The idea was modified as follows. **Lines 35-37**: “Although the urban aerosol’s physicochemical properties, biological content, and its sources were found to differ at both sites, it did not strongly impact the INP concentrations, with the exception of the largest measured particles.”

Line 99: The sequence in the introduction is strange: You talked about the MCMA before, then added some general text on mixed phase clouds and now come back to the MCMA. There should be a stronger common thread.

A: Given that the Introduction suffered several changes, we hope that the revised version does not look strange to the reviewer.

Lines 102-105: This sentence is only important for cirrus clouds. However, you are not touching cirrus clouds or cirrus cloud conditions at all in your study. I suggest to delete it.

A: Given that the Knopf et al. (2010) was relevant to cirrus and MPC, the text was modified as follows. Lines 130-134: “The first ice nucleation study in the MCMA was conducted by Knopf et al. (2010) as part of the MILAGRO project. The authors reported that the particles in the northern part of the City are dominated by organics, and can efficiently act as INP under cirrus and MPC conditions, i.e., relative humidity with respect to ice ( $RH_{ice}$ ) of ~105 % to 150 % and temperatures of 205 K to 255 K.”

Line 124-125: You are characterizing the atmospheric aerosol on ground. And although this also includes INPs, which potentially may play a role in clouds in their lifetime, you are not looking into aerosol-cloud interactions in general, let alone for different microclimates in the city. It remains fully open how much mixing would happen from the ground up to a potential cloud level, and how differences in these sites that are 16 km apart would influence this. This is misleading. Revise.

A: The sentence was modified as follows. Lines 152-154: “Therefore, there is a poor understanding of how urban aerosol particles could influence cloud formation across the different MCMA’s microclimates”.

The following remarks down to the one concerning line 243 are about the presentation of your measurements, which was not done in a straight forward way. Generally, information on the three samplers is scattered in Section 2. It would help to have one table including all three methods, their cut-offs, sampling durations and sampling dates.

A: Thank you for this suggestion. Table 1 was modified accordingly.

Line 170: Here you give the impression that culturable microorganisms’ identification is done on samples collected for 24 hours. In 2.2.5, you write that the sampling duration on the BioStage impactor was set to 5 min. What is correct?

A: The text was modified as follows. Lines 203-204: “Culturable microorganisms were obtained through different microbiological analysis described in section 2.2.5, on 5 min collected samples”.

Line 172-176: You mention “the 24-hour samples” here, but from the text above it is not clear which samples you are referring to. This is confusing. I assume in the following, that you refer to the MiniVol TAS samples which you describe below. This is part of the flow in this chapter that needs to be improved.

A: The text was modified as follows. Lines 201-203: “The ionic composition and elemental composition were obtained using ion chromatography and X-ray fluorescence, respectively, on the 24-hour collected samples”

Also, in Table 1 below, the sampling duration is ~ 4 h for the INP samples, which is different from the 24 hours you had for the PM<sub>2.5</sub> samples. This is confusing and could be presented

more clearly (e.g., in one table for all sampling methods as suggested above). Also: Discuss somewhere in your text: How do you expect different sampling durations to influence correlations between data from different samples?

A: Thank you for this suggestion. Table 1 was modified accordingly and the direct correlations between the bulk composition and INP concentrations were removed in the revised manuscript.

Then you mention 24 h samples for May 12 and 13 in the text, but on these days, no INP samples were collected. Were these samples from May 12 and 13 used in the analysis, anyway? If yes, how does that influence correlations between data on chemical composition and INPs?

A: The direct correlations between the bulk composition and INP concentrations were removed in the revised manuscript. The bulk composition was only used to demonstrate the differences in the aerosol composition in both sites.

Line 175, Table 1: You show 7 filter samples in this table, but only 5 in the SI, Fig. S4. Where does this discrepancy come from? If you only discuss 5 samples in this manuscript, adjust Table 1 accordingly.

A: Thank you for pointing this out. Table 1 was modified accordingly. The source of the discrepancy was an unintentional mistake in the original manuscript.

Lines 242-243: The sampling duration of the BioStage impactor was very short compared to the sampling duration for the other samples. That can be problematic. Comment on that. Also, give the cut-off size for the BioStage impactor.

A: The text was modified as follows to add the requested information.

Lines 226-229: “The BioStage impactor samples with a 10 µm cut-size inlet were used for culturable bacteria and fungi identification. They were collected once a day (at 10:00 am for 5 mins) on the same dates as the MiniVol samples (more details are described in section 2.2.5).”

We agree with the reviewer that the short sampling time of the biological samples could have impacted the correlations with the INP concentrations. Similar to the chemical bulk composition, the biological analysis was mainly performed to demonstrate the differences between sites. However, given that we do not expect to have huge changes in the biological content during the INP sampling, we performed the correlations, knowing in advance that biological particles did not play a key role in the measured INP concentrations due to the absence of ice nucleation above -10°C.

Lines 328-329: Here you give a misleading impression by describing “the highest T<sub>0</sub> difference”. Only in the next paragraph you, quite correctly, state that there was a statistically significant difference between INP concentrations at both measurement sites only on one of the five sampling days. Revise.

A: The sentence was modified as follows. Lines 373-374: “Overall, the average T<sub>0</sub> and T<sub>50</sub> values were similar between northern and southern MCMA samples”

Line 354 and Fig. 4: Usually when authors decide to show data at only a few temperatures, this is done to allow for a clearer presentation. Bar charts can be used for that. However, here only INP spectra are shown (again), apart from the fact that now average data are

shown and the temperature spacing is larger. This could be presented in a better way. But: as discussed above, using the mean for averaging distorts your results. And even then, the average INP concentrations from the two sites are really only (almost) different at  $-15^{\circ}\text{C}$  – generally, as far as I can see, they agree within error bars.

(A further remark: If you show INP spectra in figures, please put your own data on top.)

A: Thank you for this suggestion. Figure 3 and 4 (now Figure 3) were modified and merged.

Line 356: The fact that the southern samples are higher in Fig. 4 only originates in one high sample collected on May 20, and in you using the mean to obtain the average. (Which, by the way, should be mentioned.) This gives the wrong impression.

An example: If data are averaged that span a broad range of values, using the median is better. Imagine you have e.g. values of 1,2,3,4,5,6,7,8,9,10,10000. The median is 6. The mean is 914. What you are doing is similar to interpreting the value of 914 as something representing the whole range of values.

A: The idea was modified as follows. Lines 418-422: “To better assess the differences in the INP concentration across the two microclimates within the MCMA, the average INP concentrations (represented by the average of all samples’ total INP concentration) for both sites at four different temperatures ( $-15^{\circ}\text{C}$ ,  $-20^{\circ}\text{C}$ ,  $-25^{\circ}\text{C}$ , and  $-30^{\circ}\text{C}$ ) were calculated, as shown in Fig. 3b. INP concentrations at both sampling sites are comparable at all temperatures (i.e.,  $-15^{\circ}\text{C}$ ,  $-20^{\circ}\text{C}$ ,  $-25^{\circ}\text{C}$ , and  $-30^{\circ}\text{C}$ ).”

Please note that Figure 2 was also modified considering your comment.

Lines 371-372: Yes, in theory, particle size and INP efficiency ARE related, IF you look at particles of different sizes from the SAME substance. It is not valid in general, when comparing different types of INPs. In your samples, you likely have different particles acting as INPs in the different size classes, and therefore they cannot be compared like that!

You can see this nicely in the possibility to use a parameter as the surface site density. This parameter is valid for INPs from one particle type which shows that indeed particle size and INP efficiency are related. BUT it is different between different particle types. An example can be seen in Fig. 3 in Ullrich et al. (2017).

A: We agree that  $n_s$  could be a more reliable parameter to compare different datasets; however, even in  $n_s$  most of the time the composition of the particles is a rough approximation, especially when working with the highly complex mixtures of urban particles. Although this is a huge limitation when working with ambient samples, several studies have shown a relationship between particle size and INP efficiency in ambient samples (e.g., Mason et al., 2016; Creamean et al., 2018; Gong et al., 2019; Gong et al., 2020; Córdoba et al., 2021), especially when a distinction between sub-micron and super-micron is assessed. This is because the composition of the particles is size-dependent.

The text was modified as follows. Lines 432-437: “In theory, particle size and INP efficiency are related. This relationship is attributed to surface active sites, as larger particles contain a higher concentration of active sites (Vali, 1996; Hoose and Möhler, 2012; Kanji et al., 2017); however, as urban ambient samples are a complex mixture of particles with different compositions, the relationship between particle size and INP is not straightforward as it

requires deeper chemical analysis to understand the heterogeneity in particles chemical composition on each MOUDI stage.”

Mason, R. H., Si, M., Chou, C., Irish, V. E., Dickie, R., Elizondo, P., Wong, R., Brintnell, M., Elsassner, M., Lassar, W. M., Pierce, K. M., Leaitch, W. R., MacDonald, A. M., Platt, A., Toom-Saunty, D., Sarda-Estève, R., Schiller, C. L., Suski, K. J., Hill, T. C. J., Abbatt, J. P. D., Huffman, J. A., DeMott, P. J., and Bertram, A. K.: Size-resolved measurements of ice-nucleating particles at six locations in North America and one in Europe, *Atmospheric Chem. Phys.*, 16, 1637–1651, <https://doi.org/10.5194/acp-16-1637-2016>, 2016.

Creamean, J. M., Kirpes, R. M., Pratt, K. A., Spada, N. J., Maahn, M., de Boer, G., Schnell, R. C., and China, S.: Marine and terrestrial influences on ice nucleating particles during continuous springtime measurements in an Arctic oilfield location, *Atmos. Chem. Phys.*, 18, 18023–18042, <https://doi.org/10.5194/acp-18-18023-2018>, 2018.

Gong, X., Wex, H., Müller, T., Wiedensohler, A., Höhler, K., Kandler, K., Ma, N., Dietel, B., Schiebel, T., Möhler, O., and Stratmann, F.: Characterization of aerosol properties at Cyprus, focusing on cloud condensation nuclei and ice-nucleating particles, *Atmos. Chem. Phys.*, 19, 10883–10900, <https://doi.org/10.5194/acp-19-10883-2019>, 2019.

Gong, X., Wex, H., van Pinxteren, M., Triesch, N., Fomba, K. W., Lubitz, J., Stolle, C., Robinson, T.-B., Müller, T., Herrmann, H., and Stratmann, F.: Characterization of aerosol particles at Cabo Verde close to sea level and at the cloud level –Part 2: Ice-nucleating particles in air, cloud and seawater, *Atmos. Chem. Phys.*, 20, 1451–1468, <https://doi.org/10.5194/acp-20-1451-2020>, 2020.

Córdoba, F., Ramírez-Romero, C., Cabrera, D., Raga, G. B., Miranda, J., Alvarez-Ospina, H., Rosas, D., Figueroa, B., Kim, J. S., Yakobi-Hancock, J., Amador, T., Gutierrez, W., García, M., Bertram, A. K., Baumgardner, D., and Ladino, L. A.: Measurement report: Ice nucleating abilities of biomass burning, African dust, and sea spray aerosol particles over the Yucatán Peninsula, *Atmospheric Chem. Phys.*, 21, 4453–4470, <https://doi.org/10.5194/acp-21-4453-2021>, 2021.

Lines 375-379: All of this gives a wrong impression – see the comment directly above.  
Revise text accordingly.

A: We agree with the reviewer and the text was deleted in the revised manuscript.

And more general, a difference between the two sites is mainly seen for larger diameters (Fig. S4 and main criticism 1), and from looking at Fig. 4 it may be deduced that this is also what explains the difference in INP concentrations on May 20. Therefore, atmospheric processing is a less likely mechanism to explain the difference you observe. A larger contribution from larger (biogenic?) particles at the southern site may explain your observations.

A: Thank you for this suggestion. The text was modified as follows. **Lines 439-446:** “Even though the particle size did not show a trend, a clear difference is observed at larger particle sizes (i.e., particles between 5.6-10  $\mu\text{m}$ ) between the two sampling sites. Fig. 2b shows that four of the five samples from stage 2 (i.e., particles between 5.6-10  $\mu\text{m}$ ) from the southern site present warmer  $T_{50}$  than the same samples for the northern site. Additionally, the INP average concentrations at -20 °C shows the same behavior as shown in Fig. 4. The contribution from larger particles to the INP concentrations was found to be greater in the south of the MCMA. Although there is no chemical composition information available for these large particles, we encourage future studies to help understating the importance of  $\text{PM}_{10}$  particles.”

Line 405-407: In the here cited paper by Wang et al. (2012), amorphous SOA particles are examined. These amorphous particles do not form at the temperatures and atmospheric conditions you are looking at - it takes much lower temperatures (as said in the cited publication). Remove this citation and the reasoning about a possible SOA contribution to INPs for your southern site, as it is highly misleading!

A: The Wang et al. (2012) sentence was deleted and the text was modified as follows. **Lines 469-473:** “It is well known that VOCs may participate in O<sub>3</sub> production by photochemistry and lead to higher concentrations (Pinto et al., 2010; Amador-Muñoz et al., 2016). Therefore, the southern site is likely enriched in biogenic secondary organic aerosols (SOA) compared to the northern site (Aiken et al., 2009; Cooke et al., 2024), with unknown implication in the INP population.”

Lines 413 ff and Fig. 6: For which of the INP data is this correlation done? Only for those INP samples on the smaller MOUDI stages, or for all? I assume the latter, which makes the correlations meaningless.

A: The correlation analysis was performed using MOUDI stages inside the 0.56-3.2 μm range, so we replot Fig. 6 (now Fig. 5) with correct data. Additionally, we decided to put out chemical composition data of Fig. 5 because of the MiniVol sampling time.

The text was modified as follows. **Lines 479-483:** “Figure 5 shows the calculated Pearson correlation coefficients between the measured criteria pollutants with T<sub>0</sub>, T<sub>50</sub> and INP concentration at -20 °C, -25 °C, and -30 °C for both sampling sites (for particles ranging between 0.56 μm and 3.2 μm). Mean criteria pollutant concentrations between 08:00 h and 13:00 h local time were used to match the INP sampling periods.”

Line 425-426: You again stress “the importance of the different criteria pollutants on the ice nucleating abilities of the urban particles” and how they differ with microclimate. However, from your data, there is no consistent picture, likely because there is no correlation. And, as described above, the two sites do not really differ much, besides for one day on which most notably the largest INPs occurred in higher concentrations at the southern site. These additional INPs were particles > 3.2 μm, which means they were in the size range in which you do not have any chemical information (due to sampling PM<sub>2.5</sub>).

You yourself mentioned another study (Cabrera-Segoviano et al., 2022) which looked at high pollution. But in that other study, INP concentrations were very similar to yours. To me, this rather indicates that pollution does not add INPs.

Generally, sources for INPs differ from pollution sources. INPs often come from mineral dust or from biogenic sources. So, if you really look at what your data show, your study just repeats what many other studies in other parts of the world also found, and what is easy to explain: No correlation of INP concentrations with pollution! (More citations on that could be added to what you already added in your introduction in lines 96-97.)

In summary: It does not make sense to assume that the two sites at which you measured are different in the sense you suggest with this sentence. Delete!!!

A: The text was modified as follows: **Lines 483-499:** “Figure 5 shows high correlations between PM<sub>2.5</sub>, O<sub>3</sub>, and the INP parameters at the southern site, implying that both pollutants can impact the physicochemical properties of the INP population at this site. On the other hand, no significant correlations were found at the northern site. As the INP sizes in both sites are identical, the observed differences are likely linked with differences in the PM<sub>2.5</sub> composition. As shown in Figs. 6 and S5, the PM<sub>2.5</sub> elemental and ionic composition in the northern and southern sites have important differences. As the composition is clearly different, the interaction between fine particles, and hence INPs, with O<sub>3</sub> is expected to differ in both sites as well. As the PM<sub>2.5</sub> sampling time was much larger (24 h) than the 4 h INP sampling, a direct

correlation between the elemental and ionic composition with the INP concentrations was not assessed.

This suggest that different sources of particles could be present at both MCMA sites, but no correlation was found that anthropogenic pollution could modify INP concentration. The relationship between PM<sub>2.5</sub> and INP concentrations has been previously evaluated (Chen et al., 2018; Bi et al., 2019; Córdoba et al., 2021; Cabrera-Segoviano et al., 2022), with highly contrasting results, but showing that urban particle concentrations alone do not affect INP concentration.”

Lines 451-453: The rise in S and K on May 20 is much stronger for the northern site, which, however, did not show elevated INP concentrations. Take that into account in your arguments throughout the text. Also, could K be related to K-feldspar?

There are studies showing that biomass burning (BB) does not increase INP concentrations (e.g. Tarn et al., 2018).

A: The sentence was deleted in the revised manuscript.

Lines 474-477: I overlaid the fire map with the backward trajectories, and it does NOT seem as if there were many fires along the trajectories. Revise!

A: Thank you for this suggestion. Figure S6 was replotted accordingly, and the text was modified as follows. Lines 544-549: “Figure S6 shows that the HYSPLIT backward trajectories at 250 m AGL at both MCMA sites overlaid on the NASA FIRMS real-time active fire locations for the sampling period (i.e., May 12<sup>th</sup> to May 20<sup>th</sup>, 2022). Even though not all backward trajectories pass through active fires, the overlap between some back-trajectories and active fires suggests that the local and regional transport of BB particles could contribute to the observed differences in the chemical composition, as shown elsewhere (e.g., Carabali et al., 2021).”

Lines 477-479: Similarly, yes, the backward trajectories for one site did not cross the other, but air-masses came from very similar directions (particularly those from the north-east at midnight). Revise!

A: The sentence was modified as follows. Lines 549-551: “Additionally, Fig. S6 shows that air-masses in both sampling sites came from very similar directions during the sampling period, so particle transport between two sites cannot be despised at all.”

Lines 481-492: What do you want to show with these dendrograms? They are merely shown but not really discussed. The last sentence just gives a very general statement, reflecting what earlier studies found before.

I expect that these dendrograms were done based on results from the PM<sub>2.5</sub> samples? Therefore, while it is fine to corroborate earlier results, it however cannot be connected to the other samples (INP and bio-particles). Make this clear!

A: The text was modified as follows. Lines 569-571: “This cluster analysis highlights the effects of land use and BB on the chemical composition of the urban particles across these two microclimates of the MCMA and denotes sample complexity.”

Line 494 ff (Chapter 3.3) and related text elsewhere in the manuscript: Particles for biological analysis were only sampled for 5 minutes, compared to ~ 4 h for the INP samples. At what

time of the day were the bio-samples taken? Also, likely the inlet cut-off differed between the MOUDI and the bio-sampler (which I assume to have a total air inlet). So while the data on bio-particles stand for themselves, a correlation with INP data and all other data obtained for PM<sub>2.5</sub> cannot easily be made. Mention this caveat in the text.

A: The text was modified as follows. **Lines 602-607**: “Although the northern site showed relative higher, but not significant, correlations between microorganisms’ concentration with INP parameters (Fig. 5), the low T<sub>0</sub> measured values, compared to other biological INPs, indicate that the identified culturable microorganisms did not play a primary role in the measured INP concentration of the MCMA samples. Additionally, differences between the biological and INP analysis sampling methods (i.e., differences in cut-off and total sampling time) inhibits quantitative correlations.”

Lines 517-519: Your lower detection limit seems to be too high (i.e., the sampling duration too short) to detect the ice activity of bioparticles. They are rarer than your lowest detection limit, so you cannot say anything about them. Also, the above comment on T<sub>0</sub> applies here. Revise this sentence and also the whole paragraph.

A: We do not think that our lower detection limit is too high to detect the impact of biological particles in the INP concentrations. Using the exact same method, we have been able to measure INP concentrations above -15°C under the influence of marine aerosol particles and cold fronts (Ladino et al., 2019) and biomass burning particles (Cabrera-Segoviano et al., 2022). Therefore, we are convinced that efficient biological INPs were absent in the collected samples.

Ladino, L.A., G.B. Raga, H. Alvarez-Ospina, M.A. Andino-Enriquez, I. Rosas, L. Martinez, E. Salinas, J. Miranda, Z. Ramirez-Diaz, B. Figueroa, C. Chou, A.K. Bertram, E.T. Quintana, L.A. Maldonado, A. Garcia-Reynoso, M. Si, and V.E. Irish (2019): Ice Nucleating Particles in a Coastal Tropical Site. *Atmos. Chem. Phys.*, 19, 6147–6165, doi: 10.5194/acp-19-6147-2019

Cabrera-Segoviano, D., Pereira, D. L., Rodriguez, C., Raga, G. B., Miranda, J., Alvarez-Ospina, H., and Ladino, L. A.: Inter-annual variability of ice nucleating particles in Mexico City, *Atmos. Environ.*, 273, 118964, <https://doi.org/10.1016/j.atmosenv.2022.118964>, 2022.

Line 569: You write “such as particle morphology, coating, and degree of aging”. Already, the two sites show quite similar INP concentrations (besides for larger INPs which were higher in concentration at the southern site on one day). Why go deeper into these effects, as your data suggests that you should look at larger (micron-sized) particles and their origins, first. Remove this statement, as it does not fit your results.

A: The reviewer is right. The text was modified as follows. **Lines 662-665**: “Although the present work shows that air pollutants such as PM<sub>2.5</sub> and ozone can be linked with the ice nucleating abilities of urban aerosol particles, it is important to understand the role and the origin of the super-micron particles as they are a large contributor to the MCMA INP population”

Lines 570-571: To draw the connection to cirrus clouds here is VERY far fetched, given the altitude at which cirrus form. It is a long way (and a lot of mixing) from an emission at a location in a city to the cirrus cloud level. Delete this sentence.

A: The sentence was deleted.

Lines 558-562: The first of the two sentences is correct for your (and earlier) results on chemical composition. However, your study does not show a convincing connection to INPs

(for reasons discussed above). Therefore, the second sentence in the paragraph is highly misleading and needs to be removed or strongly revised.

A: The idea was modified as follows. **Lines 648-652:** “Although the distance between both sampling sites is just 16 km, aerosol sources and atmospheric processes linked to particle formation and aerosol aging (e.g., gas-to-particle conversion, organic coatings, and photochemistry) are quite different. This implies key local implications in particle characteristics (i.e., chemical composition, particle morphology, and particle size) that could impact the INP concentration.”

#### **Minor and editorial comments:**

Line 53: “along” seems wrong in this context. Replace.

A: Corrected.

Line 57: You give values in terms of concentrations to describe the difference between the two measurement sites. Additionally giving percentages here would be very helpful to contextualize this information.

A: Corrected.

Line 75: How is the meteorological situation in the MCMA? Please add at least the main wind direction or describe typical daily wind direction patterns.

A: Corrected.

Line 85: MPC -> MPCs

A: Corrected.

Line 126: Which PM? As you use different inlets, please already mention this restriction here by giving the different size ranges (PM<sub>2.5</sub>, PM<sub>10</sub>, total suspended particles) you collected.

A: Corrected.

Line 147: What is the meaning of the different colors of the monitoring stations (green and yellow)? If this does not matter, maybe only use one color.

A: Corrected on Figure 1.

Lines 154-155: How is the condition of this ecological reserve at the time of your measurements? Dried out? Blooming? Green? Describe briefly.

A: Corrected.

Line 169: Change “INP abilities” to “INP samples”.

A: Corrected.

Line 186: “used to collect bacteria and fungi identification”: It certainly collected also other particles. And it certainly does not collect “identification”. Revise.

A: Corrected.

Line 192: “(Campbell and Davis)”: Is this the company who built the meteorological station? Or a publication describing it? Add this information.

A: Corrected.

Line 210: “the 47mm Teflon filters” -> You likely mean the MiniVOL samples here. Please add this information.

A: Corrected.

Lines 216 and 219: Why did you put the anions and cations in brackets?

A: Corrected.

Line 229: “all the particle samples” -> Please add more precisely which samples were used for this.

A: Corrected.

Line 231: Change from “(Espinosa et al., 2012)” to “Espinosa et al. (2012)”.

A: Corrected.

Lines 347-348, Caption of Fig. 3: Replace “northern and southern particles” with “for the measurements done at the northern and southern site”.

A: Corrected.

Line 364-365 (Caption of Fig. 4): Were all three data-sets (given in green, yellow and red) collected during a high pollution episode, or only the latter? Clarify!

A: Corrected on Figure 3.

Line 370: Delete “the” before “urban”.

A: Corrected.

Line 459: “notorious” sounds strange in this context -> exchange by a better word.

A: Corrected.

Line 496: Did you measure “fungi” or “fungal spores”? (If needed, check the whole manuscript.)

A: We measure fungi genera CFU concentration.

Line 533-534: How about vice versa: Were there bacteria and fungi at the southern site that were not present at the northern site? This seems to be expectable, as the southern site seems to be closer to vegetated areas.

A: Corrected.

SI Line 22: Please format the SI such, that tables are all visible on one page. This may mean to have empty space in between, but it increases readability enormously.

A: Corrected on SI.

SI Line 44: “the” should not be bold.

A: Corrected on SI.

SI Fig. S4: Show this plot on an extra page with larger panels (maybe two columns x 3 rows). The way it is now, it is difficult to see details.

A: Corrected on SI Fig. S4.

SI Fig. S6 and S7: Either show the same section in all three of the panels on display, or overlay the firemap with the trajectories. (This is related to one of the main comments.)

Personally, I would prefer if all trajectories were shown together with the fire map. If you agree to do so, you can color e.g. the north data in aqua (instead of blue) and magenta (instead of red). Then all trajectories are visible.

It will become easier to judge to which extent fires may have influenced the measurement sites, and from which directions air masses came to your two measurement sites.

A: Corrected on SI Fig. S7.

### Literature:

Cabrera-Segoviano, D., Pereira, D. L., Rodriguez, C., Raga, G. B., Miranda, J., Alvarez-Ospina, H., and Ladino, L. A.: Inter-annual variability of ice nucleating particles in Mexico city, *Atmos. Environ.*, 273, 118964, <https://doi.org/10.1016/j.atmosenv.2022.118964>, 2022.

Tarn, M. D., et al. (2018), The study of atmospheric ice-nucleating particles via microfluidically generated droplets, *Microfluidics and Nanofluidics*, 22(5), doi:10.1007/s10404-018-2069-x.

Ullrich, R., C. Hoose, O. Möhler, M. Niemand, R. Wagner, K. Höhler, N. Hiranuma, H. Saathoff, and T. Leisner (2017), A New Ice Nucleation Active Site Parameterization for Desert Dust and Soot, *J. Atmos. Sci.*, 74(3), 699–717, doi:10.1175/jas-d-16-0074.1.

Wang, B., Lambe, A. T., Massoli, P., Onasch, T. B., Davidovits, P., Worsnop, D. R., and Knopf, D. A.: The deposition ice nucleation and immersion freezing potential of amorphous secondary organic aerosol: Pathways for ice and mixed-phase cloud formation, *J. Geophys. Res.*, 117, 2012JD018063, <https://doi.org/10.1029/2012JD018063>, 2012.