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# Comment on acp-2022-822

Anonymous Referee #1

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Referee comment on "New particle formation in the tropical free troposphere during CAMP$^2$Ex: statistics and impact of emission sources, convective activity, and synoptic conditions" by Qian Xiao et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-822-RC1, 2023

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Xiao et al. present an in-depth analysis of potential NPF in the free troposphere (FT) sampled during 19 research flights within the Camp$^2$Ex campaign investigating the phenomenology of NPF in the tropical free troposphere. Using k-means clustering and the ratio of enhancement in methane to that in CO for grouping the observed appearances of sub-10 nm particles into background, biomass-burning related and urban influenced. Investigations of NPF in the FT are of high relevance as NPF might be a major source of CCN especially over the open oceans and the tropics and the mechanisms leading to NPF in the FT are still poorly understood due to the complex interplay of emissions, oxidation pathways, updrafts, and cloud processing of precursor vapors. Therefore, I find the presented manuscript well-suited for publication in Atmos. Chem. Phys. However, while the general approaches chosen in the manuscript are solid, I am currently missing the clarity in the results section due to too many Figures and some potential misconceptions which need to be addressed before I can recommend publication in Atmos. Chem. Phys.

Major comments:

- One general concern, which needs to be at least thoroughly discussed in the manuscript, is that the authors often connect the observation of sub-10 nm particles (elevated $N_{>3nm}/N_{>10nm}$ ratio) directly to the observed external conditions and link this occurrence of "NPF" to them. However, in the FT new particle growth rates might be just in the order of <1 nm $h^{-1}$, which means that the observation of 3-10 nm particles could originate from particle formation processes which already occur over several hours (up 15-20 hours, if we assume GR=0.5 nm $h^{-1}$ and the growing nucleation mode to be located at around 8-10 nm, which is not resolved by the simple $N_{>3nm}/N_{>10nm}$ ratio due to missing size-distribution information). In that case, the current conditions under which the sub-10 nm particles are observed might not at all representative for the conditions under which the new particles might have been forming. The authors should discuss potential implications of this within their analysis.
- As this study focusses on NPF it would be very useful to use the quantity of condensation sink (CS in $s^{-1}$, as defined by Dal Maso et al. 2015) instead of surface area. If the CS is even calculated using assumptions on the hygroscopicity of FT particles, it would much better represent the actual sink of condensable vapors and, related to it, the coagulation sink of newly formed clusters. This would incorporate the RH information into that parameter (high RH means also even higher sink typically at the same dry aerosol surface area. Related to that: Do FIMS and LAS actually dry the sample? I am missing that information from the Methods section). This would

significantly help to relate the observations of sub-10 nm particles in the FT to NPF at many other locations where CS is reported. Related to comment 1) a comparison of CS to a potential GR then also directly gives an approximation of the survival probability.

- I am missing the clarity in the analysis, especially from Section 4 onwards, where I find many Figures difficult to read (and potentially unnecessary for the main text), while other Figures would have been helpful. I have some major points here:
  - My biggest scientific concern related to that is that the authors often compare conditions of NPF of a certain cluster and/or attributed air mass origin with conditions of no-NPF at the same altitude. However, as altitude is not the only variable which leads to the classification of a certain NPF event in a certain cluster and/or attributed air mass origin, this comparison is in my opinion not very useful. I thus suggest leaving the no-NPF periods from Fig. 4b-f and delete Fig. 9 (I think Fig. 8 already shows the most important conclusion for Section 4.3.1).
  - 6 and Fig. 11, Fig. 12 are in my opinion supportive material but no major results and could easily be moved to the SI. I also consider Fig. 1 not as the most important Figure to start the manuscript with. It remains unclear what is meant by "sampling data count". Why not put color the bar plot with the amount of background, biomass-burning and urban emission related NPF and no-NPF observed during the flight and add it as an additional panel to Figure 2.
  - To put all the flights and observations into a clearer relation I suggest making an additional version of Figure S1 (maybe a second panel), where all flights are represented as black lines when no NPF is observed and colored when NPF is observed with the same coloring as in Fig. 4a (blue for background, yellow for urban and red for biomass-burning). Moreover, please add a legend to the already existing panel relating the current colors to the number of the RF. Please also improve the resolution of that Figure significantly to make it better readable. If all the updates are made according to my suggestions, Fig. S1 could even move to the main MS as it gives the reader a quick geographical overview. Please also indicate the position of Manila on the map!

Minor comments:

Page 2, 56-57: Please provide a reference for that statement.

Page 3, line 90: "from the perspective of galactic cosmic rays". What is this supposed to mean? GCRs are known to enhance NPF of weakly binding systems such as $H_2SO_4$+$NH_3$ and HOMs. The work of the CLOUD team (Kirkby et al., 2011 and 2016, Nature) should be mentioned as they have provided the most thorough investigations of the role of GCRs in NPF so far.

Page 3, line 107: In accordance with the guidelines of ACP, please refrain from citing unpublished references. See guide for authors: "Works cited in a published manuscript should be published already, accepted for publication, or available as a preprint with a DOI".

Page 5, line 134-135: "combined size distribution from multiple instruments, including FIMS and LAS". Are FIMS and LAS the only instruments combined here than delete "multiple instruments, including", or were there other instruments incorporated in that combined size distribution than mention them explicitly before. Were the size-distributions just added as the instruments covered different size-ranges or was there some combining instrument inversion applied?

Page 5, line 149: How is the uncertainty of the ratio defined? By the variance of the data within the 10 second interval, or by some pre-set error on the estimates of $N_{>3nm}$ and $N_{>10nm}$? Please specify.

Page 6, line 160-161: Such periods are often called “undefined” in typical NPF studies.

Table 2: It could be useful to also give the data ranges for the different mean values and clusters.

Page 7, line 183-189: In the absence of an accessible version of DiGangi et al. (see above comment) this needs to be more detailed as this is a central part of how the different NPF occurrences have been specified.

Page 7, line 186: Here you speak about 4 regimes, but mixed urban/biomass burning is not mentioned again at any later stage in the manuscript and does not appear in Fig. 4.

Page 8, line 221-223: If we call these events undefined, this could be used here and would make the sentence better accessible to the reader.

Page 9, line 233: “impact” might not be the best word to use here as surface area and airmass as NPF is a result of airmass, surface area and other factors. Maybe “interplay”?

Figure 2: As you discuss the panels in the different order in the text, it makes sense to swap the current panels b and c.

Page 10, line 271: “was elevated compared to all the other other clusters” is also true and maybe even more important.

Page 10, line 272: These were the MT flights. Could be mentioned that those were at overall different meteorological conditions.

Page 11, line 275: should be 1, 3 and 4!

Page 13, line 329 – Page 14, line 344: This paragraph is difficult to follow and rather lengthy. As I suggest moving Fig. 6 to the SI, it could be shortened: The main message here is: cluster #1 has high UV, occurs at noon and has a higher CS. In contrast, cluster #2 has low UV, is at the morning and has a lower CS. Investigation of the occurrence of times with such low CS shows that such periods occur more often in the early morning than in the late afternoon and the NPF frequency for mornings is higher than for the late afternoons, which indicates that the newly formed particles are indeed formed in the early morning and are not related to NPF from the previous day.

Page 16, line 398-399, Fig. S4: I do not see these trends from Fig. S4. N>100 nm seems to be quite similar between the two periods. What do you mean by “as high as when NPF was absent”. Please clarify. Please also change the x-axis label of the Fig. S4 (strange unit, what does 27 hours mean? Just put a normal time axis there).

Page 17, line 402: Here the focus could be more on NPF by adding “(…) and mixtures of sulfuric acid ammonia and organic vapors are shown to be efficient new particle formation agents (Lehtipalo et al., 2018, Sci. Adv.)” right after the reference to Ahern et al. (2019).

Page 23, line 503: Please also refer to newer studies investigating NPF in highly polluted environments, e.g. Yao et al., 2018 (Science).

Page 23, line 504-506: Could temperature be decisive here? Especially when organics are involved in the formation process there is an interplay between the degree of oxidation and volatility which both depend strongly on temperature. If oxidation occurs at lower altitudes and high T, highly oxygenated molecules might form which are however still not able to condense onto the smallest clusters at that temperature, but during updraft and cooling of the airmass this might become possible. This should be discussed in the

manuscript. You could refer to Stolzenburg et al. 2018 (PNAS) for these competing processes.