Interactive comment on "New Particle Formation at a High Altitude Site in India: Impact of Fresh Emissions and Long Range Transport" by Vyoma Singla et al.

Anonymous Referee #2

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In their work, Singla et al., have studied new particle formation events that have been observed at "high altitude" in India. During the measurement time they observed 47 NPF events. The data have been recorded using a ToF-ACSM, a WRAS and a CCNC, actually not the best set of instruments to study those type of processes. The authors calculated formation rate and growth rates for the most important events (10 events) and found quite high value. Despite that the conclusions of the paper and the scientific message is not very clear neither new.

After a careful read of the manuscript I would not recommend this work to be published in ACP at this current form. I would also add that there is no new information on what we know already about NPF. Especially considering the fact that most of the conclusions don't have evidence in the manuscript.

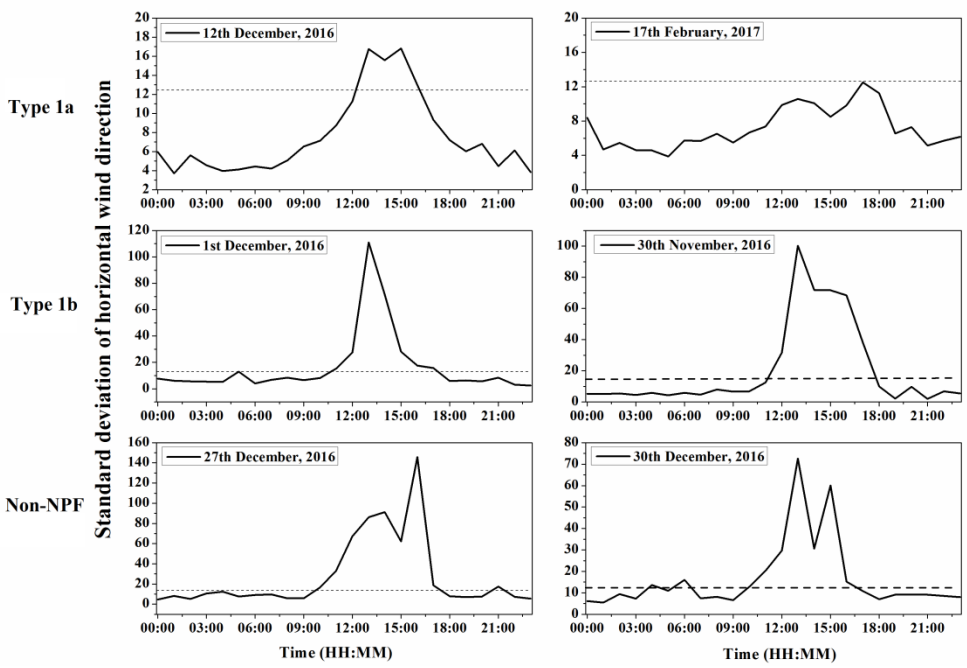
Response: Authors would like to thank the reviewer for his comments and suggestions. We admit that the previous version of the manuscript is not very clear enough with conclusions, and we have taken steps to make the conclusions clearer and removed non-conclusive facts. We would like to state that we don't claim to search for the mechanisms behind NPF formation, but wish to convey that that there are environmental factors favorable for the onset of formation and continued growth of NPF particles. Without this information it is difficult to undertake a study looking for the mechanism behind NPF formation in this region. Hence, our study is an important preparation for future studies, where we can select proper instrumentation and investigate the mechanisms leading to NPF and growth in this region. We also understand that GR and FR analysis has been performed before in other regions and that this is not novel. But, not many reports are there over this geographical area and we have no idea previously where, when and how NPF are formed in this region. Since how NPF are formed are not known, and models do not predict these NPF satisfactory in new regions where measurements have not been performed before, more information from new sites are necessary. And we made some new interesting analyses which are novel, for example the NanoMap analysis and cluster analysis highlighting the importance of aged continental airmass.

Below I reported few major concerns

In the title, the authors mention new particle formation at high altitude. After that, there is basically no reference anymore on the height of the sampling site. What does it mean high altitude? Are the measurements done in the free troposphere (FT) or in the planetary boundary layer (PBL)? This needs to be explained in the manuscript. It is fundamental to understand where all these particles going after are been formed. The lifetime in the free troposphere is larger than in the PBL making their climate impact very different. Without this information is actually useless to know the altitude especially because around the globe high and low altitude can mean totally different scenario. See for example the study conducted from Martine Collaud Coen et el., (2017) (https://www.atmos-chem-phys-discuss.net/acp-2017-692/). I would recommend the authors to look deeply in the newest literature focusing on new particle formation /

nu-cleation at high altitude / free troposphere. Here just few papers (Rose et al., ACP 2017, Garcia et al., ACP 2015, Tröstl et al., JGR 2016, Venzac et al., PNAS, 2008)

Response: Authors thank the reviewer for suggesting related references. As suggested, an attempt was made to see whether our observation site is influenced by planetary boundary layer or free troposphere. Following the methodology of Rose et al., 2017 (as suggested by the Reviewer), we have calculated the standard deviation of horizontal wind direction. It was observed that during strong (now referred to as type 1a) NPF events, the site stays in free troposphere at the time of NPF formation and influenced by boundary layer only after NPF (~ 13:00 hrs). In case of weak NPF days, the observation site comes under the influence of boundary layer at the time of nucleation which is probably affecting the intensity of NPF and subsequent growth of newly formed particles. During non-NPF days, the observation site comes under the influence of atmospheric boundary layer generally during the morning hour (~ 10:00 hrs) which is expected to inhibit the nucleation process. The diurnal variation of standard deviation of horizontal wind direction for few days is given below for reference.



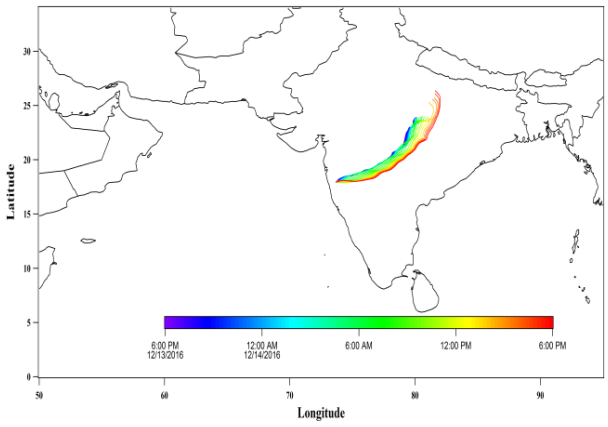
Bianchi et al., 2016 have given the observational evidence that highly oxygenated molecules (HOMS) can initiate the NPF process in addition to sulfuric acid–ammonia nucleation at high altitude sites. We have also observed the high degree of oxygenation for LV-OOA (low volatile oxygenated organic aerosol) during this time period (f44 ~ 0.4 Mukherjee et al., 2018). The diurnal variation of horizontal wind direction (graph below) during strong NPF days show that the site is in free troposphere up to 12:00 hrs. Since the site is in free troposphere, we would expect minimum influence of local activities. Therefore the formation of strong NPF at our site under the influence of free troposphere indicates the likely presence of highly oxygenated molecules (HOMS) at our site which may be acting as a fuel for NPF. However, without strong observational evidence, this argument is very difficult to establish with current measurement limitation.

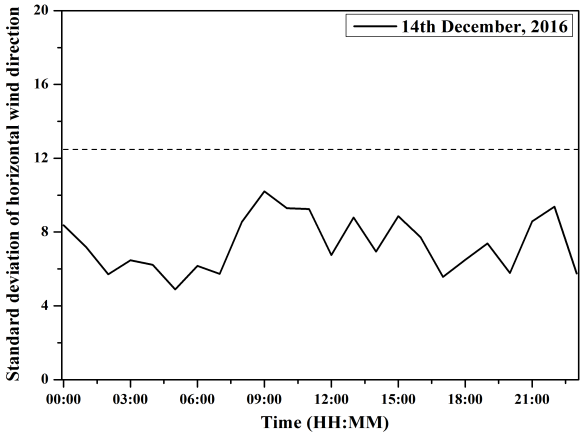
In the abstract, but in general in the whole study, the authors' just report a series of numbers and characteristics of the most prominent NPF events. However there is no a clear message on the mechanism behind the NPF events or newer information on this process. Additionally, in the manuscript, there are basically no indications that support their conclusion. For example in the abstract they reported: ": : :.New particle formation (NPF) events were observed on 47 days and mainly associated with these north-easterly air masses and high SO2 emissions and biomass burning activities, while weaker or non-NPF days were associated with westerly air masses and relatively higher influence of local air pollution: : :." This is not confirmed by any of the data shown here.

Response: It is true that we don't make any claim to present a mechanism for the new particle formation. However, we have focused on to present the environmental conditions favorable for NPF, in this case SO_2 emissions and biomass burning activities in the region. We have proven this circumstantial evidence of NPF dependent on this regional pollution in chapter 4.4. However, we will summarize our findings from chapter 4.4 in the chapter (it is relatively long) to make it clearer about our conclusions from this chapter.

Additionally, in the abstract, they reported:". A closer examination of strong NPF events showed that low relative humidity and solar radiation favored new particle formation". It is very common to see NPF correlating with radiation therefore nothing new but here as well there is no evidence that the Relative humidity is affecting NPF. Changed in RH could just reflect a change in air mass.

Response: Thanks for the comment. Although it is well known that solar radiation often favors new particle formation at other sites globally, it is worth mentioning also for this specific geographic region. We have already shown the variation of RH for NPF and non-NPF day in Figure 2. High RH on non-NPF day itself is the evidence that RH is affecting NPF formation. Hamed et al., 2011 showed that high relative humidity tends to limit the concentration of available precursor gases by reducing the oxidant concentration (OH). Moreover, change in RH or absolute humidity may reflect a change in air mass but the relationship between them is not linear. There are many factors like evaporation, transpiration, condensation, precipitation and moisture etc. which can change the RH or absolute humidity within a same air mass. To see the possible influence of RH on NPF, other factors like airmass and PBL were also looked into for 14th December 2016. It can be seen from the figure (below) that the hourly HYSPLIT backward trajectory and wind direction (Figure 2 of manuscript) hardly shows any change in airmass throughout the day and the site resides in free troposphere (evident from the diurnal variation of σ_θ). Still we are unable to see any NPF activity. This depicts the effect of high humidity on NPF formation.





As mentioned already, the authors have a good set of instruments but unfortunately it is not the proper one to study NPF. They would need a chemical ionization mass spectrometer (CIMS) in order to measure sulfuric acid concentration or organic precursor concentration. Additionally, Since they based the conclusion on the SO2, would be important to have a monitor to measure this gas as well. Then it is extremely important to measure also physical propertied of the aerosol smaller than 5 nm, the most critical size when study NPF. Obviously it is difficult to measured all this parameters however would be good if the author would mention that in the text. For this kind of studies I believe that most of the conclusions can't be driven with the instruments used in this study. ToF-ACSM is a very good instrument but the cutoff of the instrument is far too big to say something about nucleation. Here I would recommend the author to look for the latest study on NPF that have been conducted at the CLOUD chamber in CERN and their instrumentation.

Response: Thanks for the suggestion. Again, we would like to point out that it is not our aim to provide mechanisms on the onset of NPF. Nevertheless, we agree that we should discuss the areas which we are lacking at present in the revised manuscript. Author also agrees that CIMS is one of the ideal instruments to study the NPF events but here we have tried to investigate the NPF formation with best possible resources available. We are using ACSM (cut off size ~40nm) as a proxy to see the change in mass concentration due to NPF formation, if any. The intention is not to draw any big conclusion using ACSM data rather to highlight the possible effect of NPF event on ambient aerosol mass loading.

Additional major comments:

Formation rates: when comparing no NPF day with NPF day would be important to calculate J5 for the non NPF days as well.

Response: Thanks for the comment. However, we cannot calculate J5 for the non-NPF days since there is no formation of new particles.

Growth rates: In order to explain a GR of 2.5 nm/h or more at such size, you would need lots of H2SO4. This is probably not possible if you are not in a plume of an air mass with very high H2SO4 concentration. More considerations need to be done here as well and probably organics would play a major role as well.

Response: We agree with the reviewer that the growth rate of 2.5nm/h at nucleation size mode has to be supported by both high H_2SO_4 and highly oxygenated organics as well. In Mukherjee et al., 2018 we have reported LV-OOA with f44 ~0.4 which is quite high. It is also proven from the cluster analysis and concentration weighted trajectory (CWT) analysis that the site is influenced by long range transport from Central India region. The chances of availability of highly oxygenated molecule are quite high which may serve as a fuel to NPF formation under suitable meteorological conditions. The CIMS observation will be ideal to check the role of organics in NPF.

Lines 268 to 275: the statements reported in these lines are not confirmed by the data. There is no evidence that the neutralized nature of aerosol favored nucleation. Additionally, the study mentions that NH3 plays a major role in those events. They based this conclusion on the fact that during the non-events,

ammonia is taken up by the acidic aerosol. Although the ammonia scavenging by the acidic aerosol might be real, there are no evidence the NH3 is driving NPF.

Response: The nature of pre-existing particles was calculated in terms of particle acidity. The authors have provided the value of particle acidity for both NPF and non-NPF days as 1.08 and 0.88-0.90 respectively. The study by Pikridas et al., 2014 has reported that nucleation events occurred only when particles were neutral while lack of NH_3 can limit nucleation in sulfate-rich environments. We are not deriving the conclusion that the NPF is driven primarily by the ammonia, but the availability of ammonia can be one of the factors which may drive NPF formation.

Pikridas, M., Riipinen, I., Hildebrandt, L., Kostenidou, E., Manninen, H., Mihalopoulos, N., ... & Pandis, S. N. (2012). New particle formation at a remote site in the eastern Mediterranean. *Journal of Geophysical Research: Atmospheres*, *117*(D12).

Additionally because of the nature of the ACSM the paragraph is 4.2 is not very useful in order to understand NPF. Also the diameter has to be defined. Is it Electrical mobility or aerodynamic diameter? If Electrical the cut off is around 40-50 nm otherwise around 75 nm. Additionally, if the aerodynamic diameter is converted the authors need to mention the density approximation that they used to make such conversion. Summarizing the ACSM can't say that the aerosol measured comes from NPF or not. As far as it is shown in this data, it can come from any sources. Therefore once more there are no evidences of the statements at the end of the paragraph (from line 286 – 292).

Response: The quoted particle diameter range measured by ACSM (~40-1000 nm for PM_1 lens) is vacuum aerodynamic diameter. Measurements of the particle transmission were made with material of known density. For our instrument we have used NH_4NO_3 and the density of 1.72 g cm^{-3} was used in the conversion. In the case of NH_4NO_3 (non-spherical and crystalline), an additional correction factor was used to convert the material density to the particle density which is called as shape factor. The shape factor for our instrument was determined by comparing particle time-of-flight in an AMS system for the material with an unknown shape factor with a solid spherical particle (i.e. polystyrene spheres).

It is true that the chemical compounds measured by the ACSM come from a variety of sources. But, as we have suggested also to reviewer no. 1: the mass fraction originating from NPF grown particle is increasing with increasing time after onset of formation, and during the night, a considerable part of ACSM measured chemical mass comes from NPF grown particles compared to other particle sources. This can be evidenced by observing the grown NPF particle mode during evening and night hours. We have clarified this in the manuscript.

4.4 Cluster analysis The paragraph is quite long, vague and here as well the statements are not supported by the data. It is very difficult to believe that NPF is triggered by biomass burning without further evidence, chemical information and source appointments.

Finally, as the reviewer 1 mentioned already, most of the conclusions reported here are not supported by the data.

Response: Thanks again for reminding us about making the goals clear for our data. We would like to repeat that we don't claim to search for the mechanisms behind NPF formation, but wish to convey that that there are environmental factors favorable for the onset of formation and continued growth of NPF

particles. Without this information it is difficult to undertake a study looking for the mechanism behind NPF formation in this region. Hence, our study is an important preparation for future studies, where we can select proper instrumentation and investigate the mechanisms leading to NPF and growth in this region. We have also tried to explain the cluster analysis on the basis of aerosol chemical composition, particularly in terms of organic aerosol components (HOA, BBOA and OOA).

Minor Issue:

Paragraph 2.1 Measurement site. Here would be very helpful to explain what are the major sources around the site and if the site is situated in the planetary boundary layer, free troposphere or some layer in between. I also assume that this depend on the season and on the time of the day.

Response: We have already described the major sources around our site in Mukherjee et al., 2018. We have added the major sources around the observation site in the section 2.1 of the revised manuscript. We have added information on whether the site is situated in the planetary boundary layer or free troposphere. We have given few graphs related to this comment in earlier response.

Line 230: Usually cold temperatures favour nucleation not hot. (Kikrby et al., Nature, 2011)

Response: Author agrees with the comment. The line is rephrased and may read as "This less humid and stable weather condition tends to favour the enhancement of atmospheric nucleation (Hamed et al., 2011)."

Line 233: How can be that a particle that is 5 nm big and grow at 2.5 nm/h reach 40 nm in 6 hours?

Response: The authors accept that it is impossible to reach 40 nm in 6 hours. Since we were calculating the growth rate in the size range 5-25 nm, we cannot derive the above conclusion. Now we have calculated the growth rate in the size range 5-900 nm and accordingly revised the statement as "The particles were continuously formed at 5 nm diameter for a minimum of 2 hours and then grew at a rate of 5.1 nm hr^{-1}."

Line 255 :" The CS on NPF days was much lower than on non-NPF days (4.2 - 4.4*10-2 s-1). " The difference in CS between event and no event doesn't seems to be much lower. They are actually comparable. I would consider using more non-event days in the data analysis. One option would be to take an average of many them.

Response: The authors agree that CS value on non-NPF day is not a much higher value. As suggested, we have also calculated the average CS value for all non-NPF days as $4.2 \pm 1.8*10^{-2}$ s^{-1}. Indeed, a factor 2 is not much higher. Based on calculated average value of the CS for strong NPF and non-NPF days within one standard deviation, we have come to the conclusion that CS on non-NPF days is slightly higher, and that this is contributing, but maybe not a crucial reason for the appearance of strong NPF days.