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 #1

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The paper reports new particle formation (NPF) events observed at the High Altitude Cloud Physics Laboratory (HACPL) in Mahabaleshwar in Western India. They measured nucleation and growth rates as well as condensation and coagulation losses. The authors further analyze under what conditions NPF occurs by using a detailed case analysis and a cluster analysis. The paper concludes that NPF is favored by low relative humidity and when air masses reach the site from central India. Using the NanoMap method it is estimated that NPF events occur several hundred kilometers upwind of the site.

The paper presents an interesting data set on NPF. However, many claims and conclusions I could not see and follow, e.g. the determination of CCN to NPF (details see below). Furthermore, many conclusions are not well established and over-interpreted. The paper needs substantial improvements following the detailed comments below.

Line 218: the sharp decrease occurs between 4-6h according to Figure 3a and there-fore before sunrise (Figure 2). This looks like a change of air mass as also seen in the change of hygroscopicity. It would also be more helpful to present absolute humidity in Figure 2 to check for air mass changes.

Response:

Thank you for the detailed check of the timing of events and suggestion to present the absolute humidity. We agree that there is some difference in the timing of events. Indeed, the decrease in total Aitken and accumulation mode number concentration that takes place until 08:00 in the morning is not caused by an increase in boundary layer height, since sunrise is not until 07:30, which is too late.

Absolute humidity (see figure below for 12th December, 2016) unfortunately could not add any any additional information in to the analysis. Nevertheless, the decrease in concentration between 05:00 and 08:00 is not due to a change of air mass, since the air mass trajectories (extracted using HYSPLIT model) and wind directions (figure given below) are stable throughout the day. Rather it is an effect of decreasing pollution within the same air mass. We have changed the text accordingly in the revised manuscript to make this more clear.

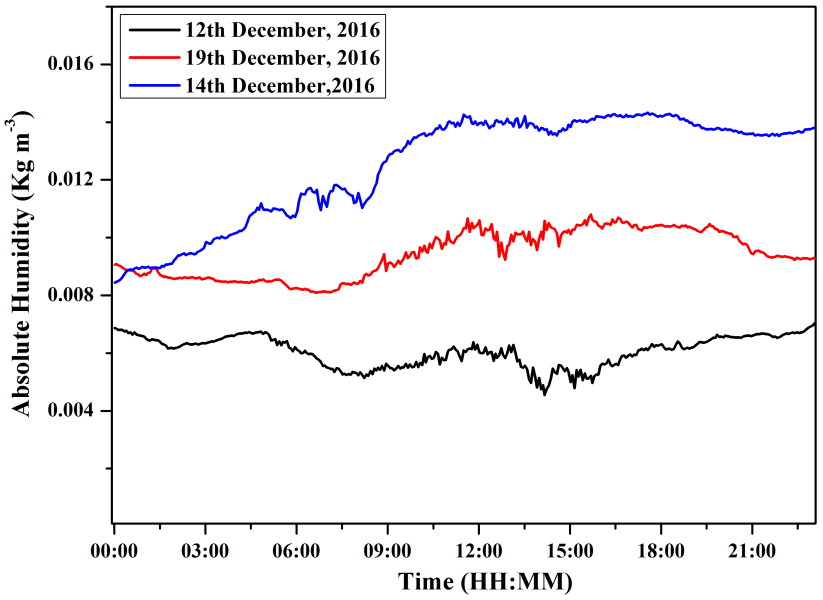


Figure: Diurnal variation of absolute humidity on 12th, 14th and 19th December, 2016.

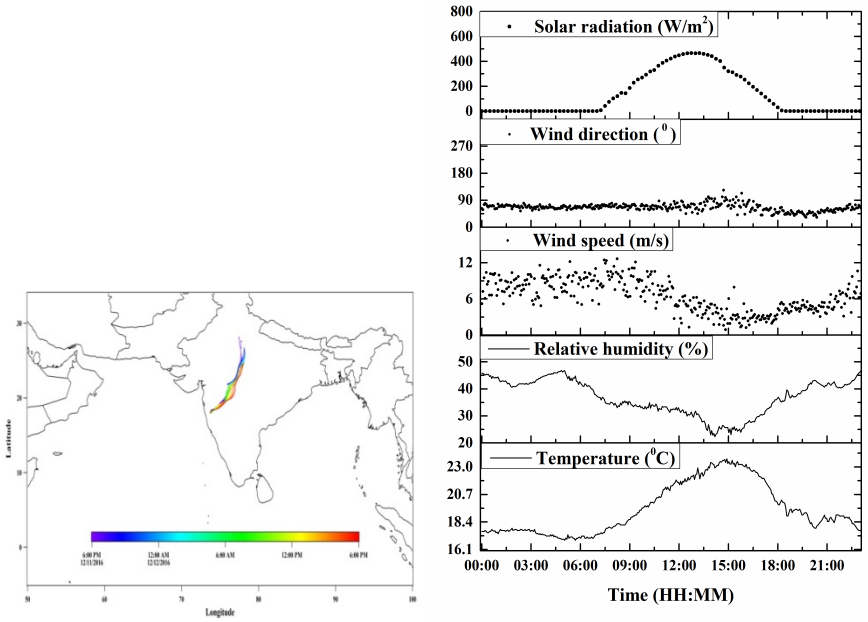


Figure: HYSPLIT airmass back trajectories (Hourly; left panel) and diurnal variation of meteorological parameters (right panel) on 12th December, 2016. **Date and time given in back trajectory plot is in UTC.**

To check whether absolute humidity is a sole marker for air mass change, we have checked the diurnal variation of absolute humidity on 14th and 19th December as well. It was found to vary along the day on 14th December but the airmass back trajectory and wind direction appears to be constant (figure given below). However on 19th December, the absolute humidity varied during daytime consistent with the change in airmass and wind direction (figure given below). The absolute humidity showed variation

same airmass (12th and 14th December, 2016) as well as different airmass. This is why absolute humidity may not be considered as a primary indicator for airmass change as it gets affected by evaporation, transpiration, condensation, precipitation, moisture, etc. within a same air mass.

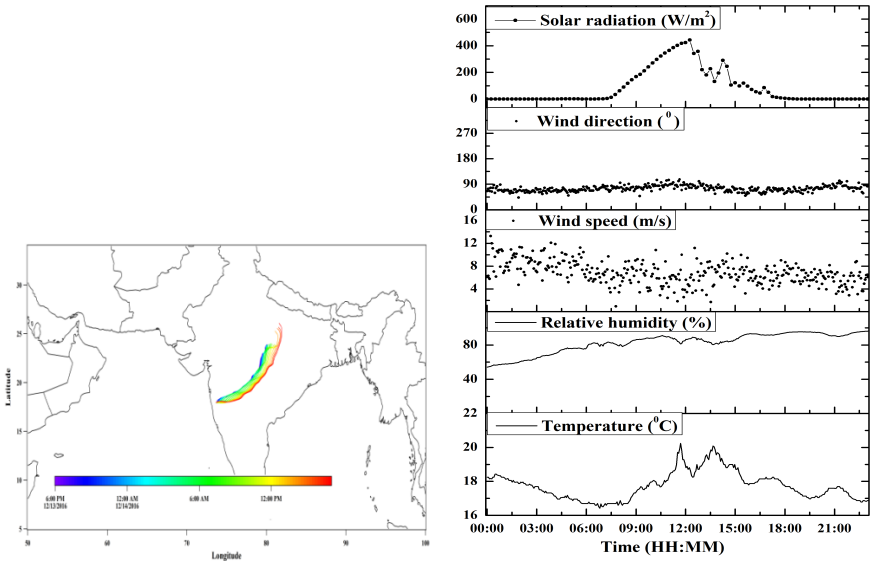


Figure: HYSPLIT airmass back trajectories (Hourly; left panel) and diurnal variation of meteorological parameters (right panel) on 14th December, 2016. **Date and time given in back trajectory plot is in UTC.**

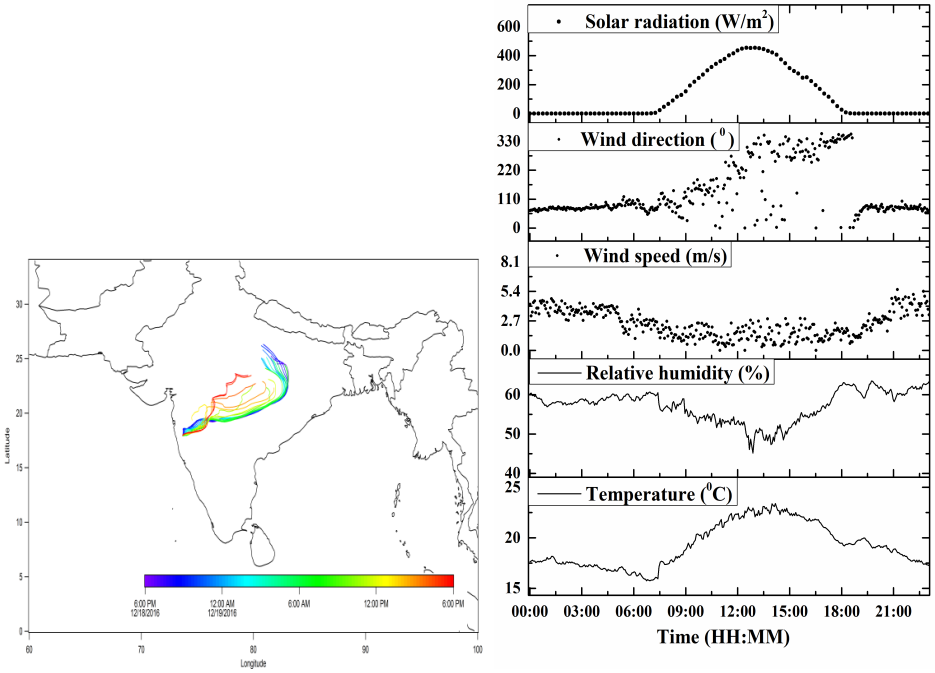


Figure: HYSPLIT airmass back trajectories (Hourly; left panel) and diurnal variation of meteorological parameters (right panel) on 19th December, 2016. **Date and time given in back trajectory plot is in UTC.**

Line 225: sunrise is at 7.30h and NPF is seen at 11h. This is not 60-90 minutes later. Probably you mean estimated start of NPF.

Response: The reviewer is right that we meant estimated start of NPF at 1.5 nm diameter. We only have measurements starting from 5.14 nm diameter, i. e. almost 2 hours after the formation of 1.5 nm diameter particles.

We have clarified in the manuscript that the formation of 1.5 nm diameter particles takes place around 09:00 to 09:30, almost 2 hours after sunrise at 07:30. And that the NPF is not visible in our size distribution measurements until around 11:00 since it takes approximately 2 hours for the particles to grow from 1.5 nm diameter to the lowest detectable size of 5.14 nm diameter in our size distribution measurements.

Line 229ff: What time period do you take for the average values? By the way I do not consider 20-24 C as hot.

Response: The solar radiation value given earlier was for the nucleation time (11:00-12:00 hrs). The values of wind speed, relative humidity were given as the average value during 12:00 to 17:00 hrs. To match the time periods, the parameters are now given as the average between 12:00 and 17:00 hrs.

We accept the temperature between 20-24 ºC is not considered as hot. Therefore, we will remove the term 'hot' and revise the statement as "The less humid and stable weather condition tends to favor the enhancement of atmospheric nucleation (Hamed et al., 2011)."

Line 233: With a GR of 2.5 nm/hr it is impossible to reach 40 nm in 6 hours.

Response: The authors accept that it is impossible to reach 40 nm in 6 hours. Since we have calculated 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 5-900nm 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 248: How do you know that sulfuric acid is driving nucleation? It could also be organics. Furthermore, it could also be other parameters like availability of nucleating species.

Response: The authors accept that there could be other parameters also. It may not be correct to argue the role of sulfuric acid as there are no observations of sulfur dioxide or sulfuric acid during the measurement period. With this line we tried to depict one of the possible way that how relative humidity can affect the NPF formation. Hamed et al., 2010 have showed that high relative humidity tends to cut down the availability of atmospheric oxidants (OH). Based on this study, we have also rephrased this line as "High relative humidity results in lowering of OH radical (important oxidant) in the ambient air which in turn limits the availability of nucleating species (sulfuric acid, organic vapors etc.)"

Line 195: this GR is for particles larger than 5 nm. However, for smaller particles GR is usually quite slower due to the Kelvin effect (see Kulmala 2013).

Response: The reviewer is right that GR is normally lower for sub-5-nm diameter particles than for particles >5 nm diameter. However, in the absence of sub-5-nm diameter particles, we have approximated the GR from 1.5 nm diameter to 5 nm diameter with the average GR found for particles

between 5 and 25 nm diameter. Hence, this might be a systematic overestimation of GR and therefore an underestimation of time needed for growth between 1.5 and 5 nm diameter. Besides, for individual days the time needed for growth between 1.5 and 5 nm diameter might be very different from the average time (1.5 h), hence again leads to bias.

On most of the time only a small error in comparison to other uncertainties in parameters calculated in this study, since the time needed for growth between 1.5 and 5 nm diameters is only 1.5 h. Nevertheless, we have stressed in the manuscript that the 1.5 h is only an approximation to the realistic value, since we lack data below 5 nm diameter.

Line 256: The CS is only a factor 2 higher on non-NPF days. This is not a much higher value.

Response: The authors agree that CS value on non-NPF day is not a much higher value. Further as suggested by Reviewer 2, we have also calculated the average CS value for all non-NPF days as 4.2±1.9 $*10^{-2}$ s^{-1}.

Based on calculated average value of the CS for strong (now referred to as Type 1a NPF days) NPF and non-NPF days respectively within one standard deviation, we have come to the conclusion that the CS on non-NPF days is slightly higher, and that this is one of the contributing, but may not be a crucial reason for the appearance of strong NPF days.

Line 263-264: 9:30 to 11:00h is the assumed time of formation of particles, while 11:00 to 13:30 h is the observed formation. Make this clear.

Response: Thank you for the query. 9:30 to 11:00 h is the possible time for nucleation (formation of 1.5nm particle) and 11:00 to 13:30 is the observed formation because of the lack of data below 5.14 nm. Therefore, we observed the nucleation after 11:00 h. We have now clarified this statement in the manuscript.

Line 266: The decrease in aerosol mass happens before. When NPF starts, PNC and aerosol mass are already low.

Response: In our study, we have observed that conditions with low PNC and low aerosol mass concentration favored NPF formation. We accept that PNC and aerosol mass was already low and therefore rephrased the line as “During the first time window, aerosol mass concentration and PNC were found to be at its minimum.”

Line 269: What do you mean by “formation of new particles is governed by the nature of pre-existing aerosol particles”?

Response: Thanks for the comment. Authors would like to rephrase the above mentioned sentence as "formation of new particles may be governed by the chemical nature of pre-existing aerosol particles". A study by Pikridas et al., 2014 has reported that nucleation events occur only when particles are neutral in nature as compared to NH_3 limited nucleation in sulfate-rich environments. Following the same concept, we have also calculated the particle acidity for NPF and non-NPF days. The calculated particle acidity shows acidic nature of particles on non-NPF day while neutral nature on NPF day. Based on this we have concluded that the particle acidity may also be one of the influencing factors for NPF formation.

Line 270: Is this the equivalent ammonium to anion ratio? What time interval does this cover? Only after 9h?

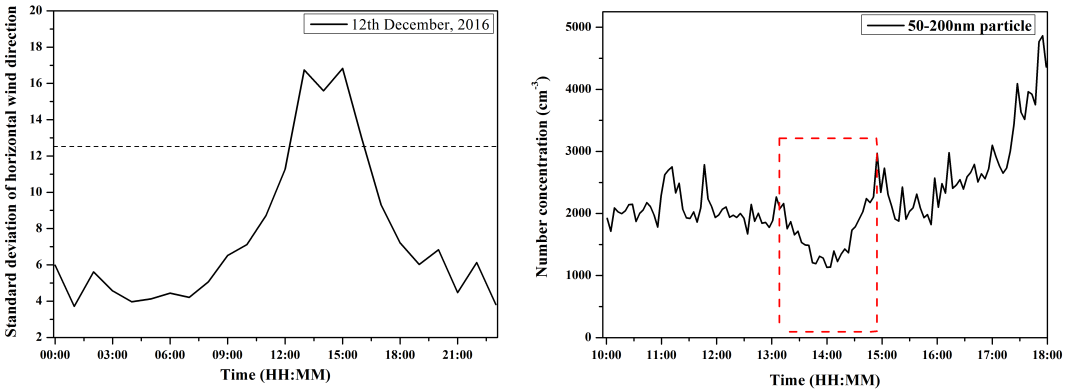
Response: Yes, this is the equivalent ammonium to anion ratio. This is the average value for the time period 09:00 to 11:00 hrs. We have added this information in the revised manuscript.

Line 278: organics increase before inorganics. How do you interpret that?

Response: In line 278, Authors intend to say that the mass concentration of aerosol increased 2 hours later than the increase in Aitken mode volume concentration (13:30 to 14:30 hrs.). The high organics concentration after 14:00 hrs is possibly due to primary emissions as secondary species like sulfate does not show any increase within the same time window. This information will be added in the revised manuscript.

Line 286: Much of the increase in aerosol mass is by HOA and BBOA and not due to additional mass from NPF. In Figure 1 it is seen that the concentration of particles 50-200nm increases after 14h. What can now be attributed to this increase and to particles grown in from NPF? What is the cut-off of the ACSM?

Response: The authors accept that the increase in aerosol mass may be contributed by HOA and BBOA. The increase in the concentration of particles 50-200 nm around 15:00 hrs may be attributed to the transition of sampling site from boundary layer influence to free troposphere (see graph below). The standard deviation of horizontal wind direction above 12.5 indicates the influence of atmospheric boundary layer. The dilution in the 50-200 nm particles (figure below) was observed when the site got influenced by boundary layer (13:00 to 15:00 h). The further increase in 50-200 nm particles after 16:00 hrs is possibly due to primary emissions (enhancement due to traffic emission and biomass burning), which is also reflected by the increase in concentration of organics (as mentioned in comment above). The further increase in 50-200 nm size particles after 18:00hrs is contributed by NPF.



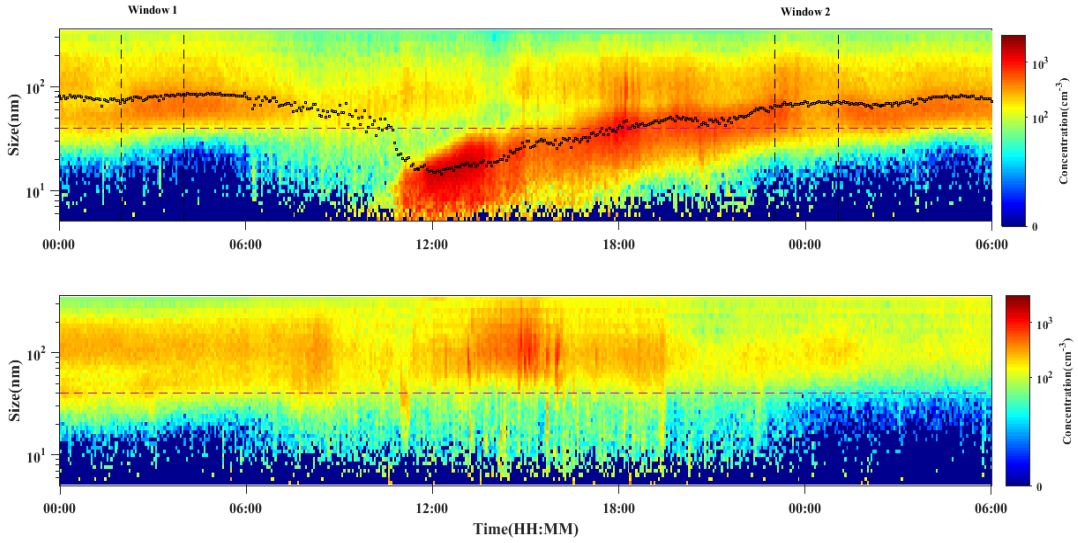
Line 289: this is speculation. CCN starts to increase already at 12h, one hour after observing NPF at 5 nm. How can these small particles be activated so early? Could it also be that particles in the 50-200 nm band start to grow due to condensation of organics and become CCN active?

Response: We agree with the reviewer that the non-NPF particles 50-200 nm diameter have contributed to the short-time peak of CCN around 12:00, and also to the more pronounced increase between 14:00 and 18:00. After this time period, and later during the night hours, the relative increase in CCN is due to an increase of NPF grown particles, since a large part of the NPF population has grown to sizes well above 40 nm diameter. We have changed the text in the manuscript accordingly in line with the comment of the reviewer.

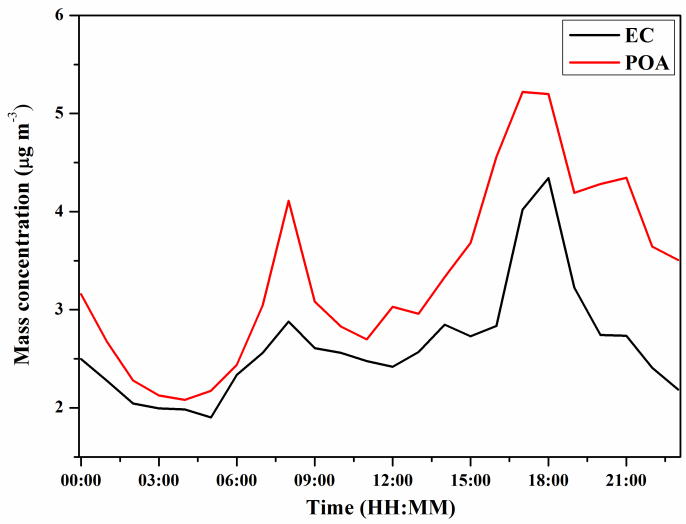
Section 4.3: There are several issues with the estimation of NPF to CCN. The authors say that they compare time window 2 with window 1 and that GMD > 40 nm. In Figure 1 these criteria cannot be met but calculations are given. The notation given for the different parameters (CCN/POA, etc.) is unclear

and not consistent. I had to consult the original publication to understand it. All values for delta (CCN/CN) are positive. I have a hard time to believe that the fraction of CCN is always larger shortly after nucleation (11:00-13:30h) than in the aged air mass when no nucleation mode CN are measured yet. This would mean that an extremely large fraction of nucleation mode particles (most particles are still <40 nm) activates. I also doubt that CCN/POA is a good measure for primary contributions to CCN. Along a trajectory POA decreases while CN may not change much. This pretends an increase in CCN fraction that is not real. As already mentioned above an increase in CCN may also be due to growth of 50-200nm particles. How do the authors account for this?

Response: Here we are somewhat confused with the comment about time window 2. Time window 2 is not around 11:00-13:30 hrs. From figure 1 it can be clearly seen that time window 2 is around midnight. The chosen criteria for evaluating the effect of NPF on CCN are followed for the two windows of Figure 1. The dashed line in Figure 1 represents the particle diameter of 40 nm and black dots represent the calculated GMD of particles. At this time, GMD is much higher than 40 nm diameter. But, since there is a chance to miss time window 2 in figure 1, we have also stressed the timing of time window 2 in the manuscript text.



We are limited with the direct measurement of primary emission tracers. Though we had EC measurements but the EC data was not available for all the NPF days. This is why POA has been chosen as a proxy for primary emission. We have compared the EC data with POA and it showed fair correlation (figure given below). The assumption of POA as primary tracer may add some uncertainty in the calculation but this error is not expected to be huge.



The parameter CCN/POA was calculated to assess the effect of fresh anthropogenic sources on the activation ratio (CCN/CN). Biomass burning and vehicular emissions are the major anthropogenic sources at this site (Mukherjee et al., 2018). Therefore POA was chosen as a marker of fresh emissions. The details of the methodology have been added in the revised manuscript. Further, the authors accept that all values for delta (CCN/CN) cannot be positive. Actually all the delta (CCN/CN) values were calculated as negative in this study and the negative sign was somehow missed in the header of the column in Table 2.

Section 4.4: this section contains many claims that can hardly be seen in the Figures and small variations in measurements are overly interpreted. Line 368: I do not see the decrease in Aitken mode concentration during increase of nucleation mode particles.

Response: Indeed, the increase mentioned for NPF particles between 11:00 and 14:00 in manuscript is not coinciding simultaneously with a decrease of Aitken mode particles. The decrease of Aitken mode particles is actually taking place earlier, already starting from around 09:00. We have not been clear about this, but have now explained it in the manuscript.

The authors would also like to mention that the Aitken mode number concentration decreased by 20% (from 2752 cm^{-3} to 2194 cm^{-3}) during the increase of nucleation mode particles.

Line 371: Onset of nucleation is usually around 9:00h. I do not see a sudden increase in Aitken mode particles. In addition, average Aitken mode concentration at that time is similar in cluster C2 and C3.

Response: Thank you for the comment. We have tried to answer the mentioned comment and next comment together as they are linked.

Line 372: It says: The diurnal variation of Nnuc particles exhibited high concentration during morning, afternoon and evening hours". I do not see high concentrations throughout the day. I also do not see the simultaneous peaks of nucleation and Aitken modes. There are time shifts.

Response: Both this comment and the previous one will be answered here. We are again sorry for over interpretation and over simplification of the timing of events.

It is enough that we rephrase the manuscript to say:

1. The PNC is in general more variable throughout the day for clusters C4 and C5 and nucleation and Aitken mode particles, which is indicating the influence of local pollution sources.

2. There is a clear morning rush hour traffic peak in the morning hours for C4 and C5 (figure S2), stronger than for C1, C2, and C3 likely contributing to inhibit the onset of formation, which normally takes place around 09:00 at the measurement site.

3. However, this does not rule out the onset of formation after the morning hours, as the Aitken mode concentration is decreasing in C4 and C5. We have no claim for the following statement, but the transport of air from foreign areas in clusters C4 and C5 might not allow for production of low volatile vapors needed to initiate NPF after the morning hours.

Line 398ff: Peak concentrations of nucleation mode are reached before 15:00h. Thus this increase in Aitken mode after 15:00h cannot inhibit NPF. More important than the particle concentration is the CS and the availability of condensing gases. The authors seem to assume that the latter are always similar, which is hardly justified.

Response: Thanks for the comment. Based on the influence of boundary layer at sampling site, we accept that the increase in Aitken mode after NPF cannot inhibit NPF. We have now removed this concept from section 4.4.

Line 422: On 12th December is the wind speed low during NPF. It is high before. The authors claim that NPF is suppressed by local emissions on 19th November. Later on, they pretend that NPF occurs up to hundreds of kilometers upwind. Thus, the nucleation mode particles are transported to the site and cannot be influenced by local emissions.

Response: Thanks for the comment. To assess the effect of local emissions on the nucleation process, we have also studied the influence of BL/FT at the sampling site. The formation of 1.5 nm particles is expected to occur at 9:00-10:00 hrs when the site is influenced by FT. The figure provided below shows that the site comes under the influence of BL after 10:00 hrs on 19th November, 2016. We believe that the effects of local emissions are pronounced only when the site is influenced by boundary layer. This phenomenon affected the intensity of the NPF on that day. We have also checked for the influence of BL/FT for other strong (now referred as Type 1a following Dal Maso et al., 2005), weak (now referred as Type 1b following Dal Maso et al., 2005) and non-NPF days and as a representative, 2 days of each type is given below.

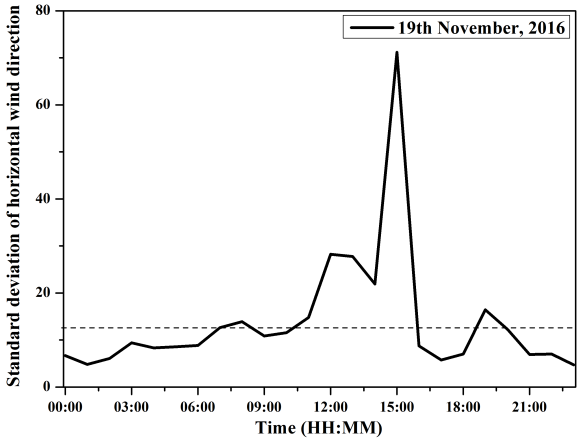


Figure: Diurnal variation of standard deviation of horizontal wind direction on 19th November, 2016.

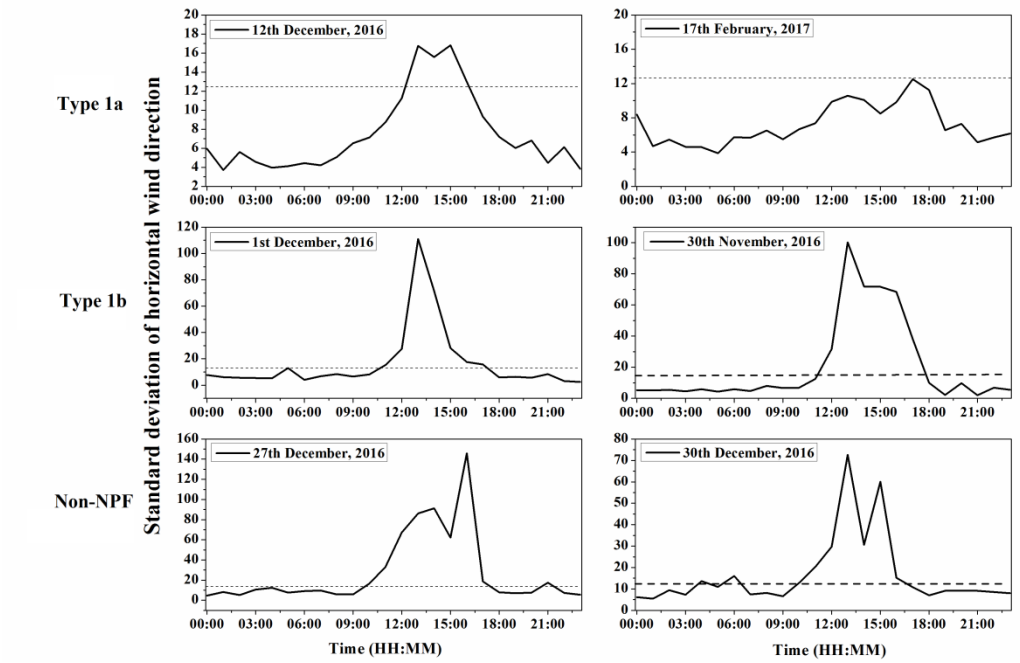


Figure: Diurnal variation of standard deviation of horizontal wind direction for 2 representative type 1a (upper panel), type 1b (middle panel) and non-NPF days.

The figure above shows that influence of FT at the sampling site favours nucleation and vice-versa.

Line 426: I wonder what else besides nitrate and sulfate can bind that much ammonia. This is hard to believe.

Response: The high molar ratio of ammonium to inorganic ions ~1.4 was observed on 19th November 2016 at the time of nucleation. During October-November, the plantation of strawberry is carried out in this region for which the fertilizer (mainly urea) is dissolved in water and is sprayed (high in ammonium) more often. This could be one of the possible reasons why we are getting high ammonium during the month of November.