Interactive comment on “Observations of Particles at their Formation Sizes in Beijing, China” by Rohan Jayaratne et al.

Response to Comments from Anonymous Referee #2

General comments:

For this paper, the authors employed a Neutral cluster and Air Ion Spectrometer (NAIS) to investigate the early steps of new-particle formation (NPF) events in Beijing, China, over a period of 3 months. Specifically, observations were made down to particle (or cluster) sizes of about 2nm. NPF events in large, polluted urban areas, in particular in E Asia, are a current subject of atmospheric research (e.g. Kulmala et al., 2017). To my knowledge, this is the first report on deploying an NAIS in a Chinese megacity for this purpose, and it constitutes one of recent attempts of improving on the observations of NPF in such environments by directly measuring in the sub-3 nm size range (cf. Cai and Jiang, 2017; Yu et al., 2016). As such, the study is timely and of interest to the scientific community engaged in this field, and I recommend its publication in Atmospheric Chemistry and Physics.

Response to General Comments

We thank the reviewer for these positive comments and are glad to note that he/she feels that the paper would be of interest to the scientific community engaged in this field, and for recommending that, subject to the changes below, it is suitable for publication in Atmospheric Chemistry and Physics.

Major Comments 1

Before that however, I recommend a major revision to take care of some important issues.

My main concern with the study in its present form is the treatment and discussion of the NAIS measurements for the sub-3 nm size range. The treatment, presentation and interpretation of these data need to be brought into a form more rigorously consistent within the paper itself, as well as with best-practices recommended by the community (Manninen et al., 2016) – in particular as the corresponding results are a major selling point here.

Comments regarding sub-3 nm measurements:
Lines 109-110: “The NAIS … can detect particles down to a size of 0.8 nm”:
My main point is that the NAIS can actually *not* be used to measure *neutral* compounds down to this size, so this statement is misleading in its current form. The NAIS does detect ions with the corresponding mobility, but due to the interference from charger ions it is deemed not possible to determine concentrations of neutral clusters for the smallest size bins. Quoting Manninen et al. (2016), which is cited also in this paper (line 137), “the particles below about 2 nm cannot be reliably distinguished from the corona-generated ions. Typically, the lowest detection limit for the NAIS in the particle mode is between 2 and 3 nm depending on the corona voltage and on the properties and composition of carrier gas (environmental conditions).” Details can be found in their paper and references therein. At one occasion later, the authors appear to consider this instrumental limitation, e.g. section 2.2.3.

Response to Major Comments 1

We agree with these comments and accept that the NAIS has a problem in differentiating between charged and neutral particles and clusters at sizes below 2.0 nm owing to the presence of corona-generated ions as pointed out by Asmi et al. (2009), Manninen et al. (2011) and Manninen et al. (2016).

We will address this issue by making the following changes to the paper:

1. Considering the limitations of the NAIS in measuring total particle and cluster concentrations at sizes smaller than 2 nm, we will restrict our observations to particles that are larger than 2.0 nm.
2. This will result in the smallest size bin (1.6-2.0 nm) being excluded from the particle analyses.
3. We estimate that this will decrease our charged and neutral PNC values by about 5%. We will make this change right through the manuscript.
4. In Table 2, we will remove the two columns showing charged and neutral cluster concentrations.
5. In Figure 7, we will remove the three points below 2.0 nm and insert a note in the caption cautioning against using the data below 2.0 nm.
6. Similarly, in Figure 2(a), we will insert a note stating that the data below 2.0 nm should be treated with caution.

In addition, we will incorporate the following changes to the text:

Lines 109-110: we will remove the text "can detect particles down to a size of 0.8 nm" and amend the sentence as follows:

"The NAIS is specifically designed to monitor particle formation as it can detect clusters and particles down to a size of 0.8 nm"

Line 136 - : We will insert the following text:

"However, Asmi et al. (2009), Manninen et al. (2011) and Manninen et al. (2016) have pointed out that the lowest detection limit for the NAIS in the particle mode is about 2.0 nm owing to the presence of corona-generated ions. Therefore, at sizes smaller than 2.0 nm, the NAIS cannot reliably distinguish between charged and neutral particles Therefore, Manninen et al. (2011) specified the lowest detection limit of the NAIS to be 1.6 and 1.7 nm for negative and positive ions, respectively, and 2.0 nm for neutral particles. Therefore, in this study, we will restrict our observations to the particle size range 2.0-42 nm."

Section 2.1.1 Line 165 - : we will amend the text as follows:

"..where N is the number of particles in the size range 2.0 -10.0 nm."

While changing the definition of the lower end of N from 1.8 nm to 2.0 nm affected the total PNC in that size range by about 5%, it did not affect the decisions regarding the identification of any of the NPF events.

Line 170: The text will be changed to

"The starting times of an event was determined by using the time of sudden increase in total PNC in the size range 2.0 – 10.0 nm."

Line 223: The text will be changed to

"…we exported the number concentrations of particles obtained from the NAIS in 14 bins in the size range 2.0 – 42.0 nm."

Major Comments 2

Section 3.4 (including Fig. 5 and Table 2) discusses charged vs. neutral "cluster" and "particle" concentrations. Here, the authors need to state what is their definition of "cluster" and "particle". And in light of the above, they might need to reconsider if total neutral cluster concentrations (as implied in section 3.4) can even be derived from the NAIS measurements! The discussions throughout section 3.4 may have to be revised. E.g., depending on those definitions, could the observed decreases of "neutral clusters" for NPF days (e.g. Fig. 5b) be explained by instrument response to a change in environmental conditions?

Response to Major Comments 2

We will provide the conventional definitions of clusters and particles from the literature in our introduction. In Section 3.4, we will restrict our analysis to particles larger than 2.0 nm. This will result in the smallest size bin (1.6-2.0 nm) being excluded from the particle analyses. We estimate that this will decrease our charged and neutral PNC values by about 5%. We will make this change right through the manuscript. The sub-heading title will be changed to "*Charged Particles*". All references to cluster concentrations will be removed. In Fig 5, we will remove Fig 5(b) that shows the neutral and charged cluster concentrations. Fig 5 will now show only the neutral and charged particle concentrations.

In Table 2, we will remove the two columns showing charged and neutral cluster concentrations.

Major Comments 3

Figure 2, top panel, and Figure 7:
As a consequence, I would argue that particle size distribution data below 2 nm shouldn't even be shown. The concentrations at the size bins <2 nm are subject to instrumental factors, not necessarily resulting from actual variations in the concentrations of sub-2 nm neutral clusters (particles). Hence, their display here could prompt an unaware reader to draw wrong conclusions about the actual population of sub-2 nm neutral clusters.

Response to Major Comments 2

In Figure 7, we will remove the three points below 2.0 nm and insert a note in the caption cautioning against using the data below 2.0 nm.

Similarly, in Figure 2(a), we will insert a note stating that the data below 2.0 nm should be treated with caution.

Other comments:

Comment 1

Line 68: Kulmama should probably be Kulmala – also in later instances for this reference.

Response 1

In the journal paper the name has been mis-spelt as 'Kulmama". Correcting this is bound to affect the citation count and we will seek the advice of the Editor on this matter and make the change, if required.

Comment 2

Speaking of which, the recent paper by Kulmala et al. (2017) is relevant to this study and should be brought to attention in the introduction. As condensation sinks were calculated for this study, it might be useful even to shortly discuss the authors' findings in light of the conclusions of that paper (see e.g. lines 237-239).

Response 2

We agree. We will include the following text in the Introduction:

"A recent paper by Kulmala et al. (2017) attempts to explain the occurrence of NPF under highly polluted conditions by combining direct observations and conceptual modelling. They hypothesized that the apparent discrepancy may be explained if the coagulation rate of molecular clusters by particles is significantly less than their collision rate or if the clusters grew much faster than is normally expected".

In the discussion section, we will also consider the dimensionless parameter, p, defined by Kulmala et al. (2017) and compare the value estimated from our results in the present study with the value predicted by Kulmala et al. (2017) for a polluted city like Beijing.

Comment 3

Also, it could be interesting to compare the results here with those in Yu et al. (2016). Therein, they report in particle formation and growth rates during NPF events in Nanjing, also down to sub-3nm sizes.

Response 3

We agree. We will include the formation rate and growth rate values found by Yu et al. (2016) in Nanjing by inserting the following text into the discussion section:

"These values may be compared with that found by Yu et al. (2016) in the urban atmosphere of Nanjing, China. They studied eight NPF events using a nano-condensation nucleus counter system capable of measuring particle size distributions down to 1.4 nm and estimated initial

and peak particle formation rates of 210 and 2500 cm^{-3} s^{-1}, respectively. The formation rates showed good linear correlation with a sulfuric acid proxy".

"Yu et al. (2016) determined a relatively high local maximum growth rate of 25 nm h^{-1} in Nanjing, China.

Comment 4

Lines 277 & Fig. 3, line 287:
"Haze days" seems to be used interchangeably with "no-NPF days". Are they? If so, that point should be made clearer. If not, it may be feasible to mark them in Fig. 3. The various types of day are actually defined later on (lines 325-329). I suggest moving this definition to an earlier place, and then shortly mention it again later.

Response 4

In Figure 3, the NPF days are shown as red full markers. The points shown in white hollow markers are all other days, including normal (no-NPF) and haze days. We will change the figure caption to read "other days" instead of "No-NPF Days".

Also, we will move the definition to the methods section and shortly mention it again at this point.

Comment 5

Line 318: "attachment to existing particles"

Response 5
This sentence will be removed when the discussion on cluster concentrations is excluded.

Comment 6

I would have expected this process be more pronounced on the *no*-NPF days, when condensation sinks were higher.

Response 6

This statement will also be removed when the discussion on cluster concentrations is excluded. However, we calculated the condensation sinks for no-NPF days and found that it was 0.006 s^{-1}, which is not significantly higher than the corresponding value on NPF days (0.005 s^{-1}). However, the condensation sink on haze days was 0.060 s^{-1}, which is significantly higher than both normal days and NPF days. We will insert the following text into the end of section 3.6 on condensation sinks:

"The value of the condensation sink during NPF events (0.005 s^{-1}) was not significantly different to the corresponding average values during other times on NPF days and on normal days with no NPF (0.006 s^{-1}). However, the mean condensation sink on haze days (0.060 s^{-1}) was significantly higher than both these values."

Comment 7

Line 378: “previous have not been able”
I assume the authors refer to their novel measurement of particles in the 2-3 nm allowing them to more accurately calculating the coagulation sink (CoagS) for particles down to 2 nm. That’s technically OK, but one would expect those small particles (i.e. in the 2-3 nm range for instance) to play a minor (negligible?) role in determining CoagS. How much is the value obtained here improved (increased) by the possibility to take the 2-3 nm range into account?

Response 7

Equation (5) for the formation rate considers the particles in the size range 2-3 nm. The rate of change of the number of particles in this size range was not available to previous workers. We use this, together with the coagulation sink of the particles in the size range 2-3 nm ($CoagSd_p$) to calculate the formation rate. The coagulation rate CoagS refers to the entire particle size range and this value is, as the reviewer points out, much larger than $CoagSd_p$ in the size range 2-3 nm. However, we thank the reviewer for this comment as it shows that the text was not very clear. We will modify the text to make this as clear as possible.

Minor comments:

Comment 8

Abstract, 2nd sentence: The statement should be clarified. From what are the estimated characteristics different in the case of restricted measurements?

Response 8

We will re-word this sentence as follows:
“Estimated characteristics of NPF events, such as their starting times and formation and growth rates of particles, are more accurate when the detection size of particles is smaller”.

Comment 9

Lines 152-153: It may be interesting and instructive for the reader to hear, in short, about the nature of the problems encountered.

Response 9

This sentence will be replaced by the following text:
“Data was lost on nine days owing to various problems such as the loss of power, software malfunction and a blocked filter during a haze event.”

Comment 10

Line 263: Does this t-test result apply to the whole measurement campaign, or just the subset shown in Fig. 2? In the latter case, would it change when applied to the whole period?

Response 10

This was for the subset shown in Fig 2. However, when we consider the entire monitoring period, the corresponding difference was even more significant. We have added the following sentence:

"The corresponding difference was even more significant when considering the entire monitoring period where the mean daily values of $PM_{2.5}$ on NPF days and the other days were 21 $\mu g\ m^{-3}$ and 143 $\mu g\ m^{-3}$, respectively."

Comment 11

Line 297: "are more likely …" than what else?

Response 11

We have amended the text as follows:
"Thus, the observed haze events are unlikely to be caused by in-situ new particle formation and more likely to be due to particles carried by the wind into the city or being prevented from escaping due to temperature inversions in the atmosphere".

Comment 12

Lines 329-332, Table 2: The source of the uncertainty of 20% has remained unclear to me. Maybe the authors can rephrase.

Response 12

We agree that the statement is unclear. We will replace it with:

"The values shown are the means of the average $PM_{2.5}$ concentrations over all the 24-hour days. The daily mean values varied from day to day, especially on days with NPF events or haze events mainly due to the different durations of these events. We estimated the standard deviation about these mean values to be 20%".

Comment 13

Most figures have a gray background and odd dark-gray or blank frames. They would look better without any that.

Response 13

We will remove the grey background and frames around all figures.

Comment 14

The text/numbers in the color bar in Figures 2 and 7 are difficult to read and lack units.

Response 14

We will improve the quality of the numbers on the color bars and include units (cm^{-3}).

References:

Asmi, E., Sipilä, M., Manninen, H., Vanhanen, J., Lehtipalo, K., Gagné, S., Neitola, K., Mirme, A., Mirme, S., and Tamm, E.: Results of the first air ion spectrometer calibration and intercomparison workshop, Atmospheric Chemistry and Physics, 9, 141-154, 2009.

Kulmala, M., Kerminen, V.-M., Petäjä, T., Aijun, D., and Wang, L.: Atmospheric Gas-to-Particle Conversion: why NPF events are observed in megacities?, Faraday Discussions, 2017.

Manninen, H., Franchin, A., Schobesberger, S., Hirsikko, A., Hakala, J., Skromulis, A., Kangasluoma, J., Ehn, M., Junninen, H., and Mirme, A.: Characterisation of corona-generated ions used in a Neutral cluster and Air Ion Spectrometer (NAIS), Atmospheric Measurement Techniques, 4, 2767, 2011.

Manninen, H. E., Mirme, S., Mirme, A., Petäjä, T., and Kulmala, M.: How to reliably detect molecular clusters and nucleation mode particles with Neutral cluster and Air Ion Spectrometer (NAIS), Atmos. Meas. Tech. Discuss, 2016.

Yu, H., Zhou, L., Dai, L., Shen, W., Dai, W., Zheng, J., Ma, Y., and Chen, M.: Nucleation and growth of sub-3 nm particles in the polluted urban atmosphere of a megacity in China, Atmospheric Chemistry and Physics, 16, 2641-2657, 2016.