Point-to-point responses to anonymous referees #1 and #2

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We thank anonymous referees for their helpful comments to revise the manuscript. We are also grateful to the referees for recognizing the originality of this work. Point-to-point responses are given below.

Anonymous Referee #1

This article deals with observations of new particle formation and nano-particles in an urban atmosphere in China. The article is clearly written, the methods are explained in sufficient detail and the presented data is new and interesting for the scientific community. In places, the article could be shorter and more focused, as it struggles to combine a lot of detailed information and many different parameters.
The article fits to the scope of the journal and it presents a contribution to our understanding of the dynamics of the small particles in a megacity. Therefore I recommend it to be published after the following concerns/comments have been addressed.

Re:
The manuscript not only reports general characteristics of new particle formation in our urban atmosphere, but also deals with some methodology, findings and theoretical interpretation. This made the manuscript appear long and less focused. Considering this, as well the suggestion from the referee #2, we chose to shorten some unnecessarily long paragraphs and Figure 4, and divide Section 3 in more parts.

General comments:

1. *It does not make sense to report the size with 2 decimals (of nanometers). The sizing accuracy is not that good. I strongly advice for using 1.4nm instead of 1.38nm (and so on) everywhere in the article and figures (also J1.4 and not J1.38).*

Re:
We have changed the 2 decimals of sizing diameters to 1 decimal throughout the text and figures

2. *Chapter 2.2. rows 5-15. I agree that fluctuations in the total concentration that are faster than the scanning cycle can lead to a background concentration after the inversion. However, from your references, at least in the studies conducted in the boreal forest, there is often a clear scanning cycle also outside nucleation events indicating presence of sub-3nm particles or ions, which cannot be explained solely by fluctuations.*

Re:
We thank the referee for pointing out the observations in the boreal forest showing clear scanning cycle outside nucleation events. Actually, we also saw nighttime scanning cycle on 4 March 2015, which did not eventually develop to NPF event. But these observations do not conflict with our definition of "background concentration": we first ruled out all periods with visible scanning cycles, and then we defined the rest of periods with only fluctuations as "background concentration".

3. *p. 18660, rows 11-19 and chapter 3.2. Have you thought about an effect due to chemical composition? It is well known that organic substances activate less readily in DEG (see e.g.Kangasluoma et al. 2014), so this could lower the detection efficiency at smallest sizes and therefore lead to the 'upside volcano' shape. Is there any evidence suggesting there was more organics involved in NPF on type B events? At least later you mention that in winter (when B events were common) you got higher J with the same H2SO4…*

Re:
It is a good thought that organic composition may lead to lower activation efficiency of smallest particles. If true, it means our PSM measurement suffered a negative artefact due to a lot of "invisible" small particles. To verify this, the chemical composition information of small clusters is need, which is out of the instrument capability of this study. However, we can contribute one argument against this hypothesis: it is accepted in general that larger new particles have a higher mass fraction of organics than smaller new particles in NPF. If organic substances activate less readily in DEG, the particles in larger bins should have even lower detection efficiency than the smaller bins. Therefore, the increasing n(D_p) with D_p (i.e. upside down volcano) could not be simply due to negative artefact of PSM detection.

This argument is now added to the last paragraph of chapter 2.2.

4. *Chapter 2.3. You could shorten the article by omitting the first part of this chapter (p. 18660 row 20- 18661 row 11) and Fig. 4. It would be enough to say that due to high GRs, you chose to use GDE instead of appearace time method. I don't see that Fig. 4 produces a lot of new information to the reader.*

Re:
We have now removed Figure 4. The first part of this section has been shortened accordingly, but some basic background information is retained as below:

"Conventional appearance time method determined growth rates (hereafter, *GR*) during the initial period of NPF by finding the time steps when newly-formed particles appeared at certain size bins and calculating the *GR* from the time differences between successive size bins

(Kulmala et al., 2012; Lehtipalo et al., 2014). This method was often not applicable to the NPF event with high *GR* below 3 nm, e.g., 0.26 nm/4 min (i.e. 3.9 nm h^{-1}) with size intervals 0.26 nm and scanning time intervals 4 minutes in our measurements. Furthermore, sub-3 nm particles were often generated persistently throughout the daytime period. Maximum concentrations in the sub-3 nm size bins could appear a few hours later than the onset of nucleation. Therefore, we were not able to pinpoint correctly maximum or 50% maximum concentrations at the onset of nucleation."

5. *Chapter 3.2 is very long, and would benefit from either shortening it or dividing it in parts.*

Re:
We have now divided Section 3.2 into 2 sections to discuss nucleation rate and growth rate respectively.

6. *Chapter 3.2-3.3: Have you ruled out that (self-) coagulation cannot cause the local maximum in the GRs?*

Re:
The GR value was calculated based on the GDE method. In Eq. 1 we had calculated coagulation production and coagulation loss terms. At the local maximum sizes, condensational growth must be large enough to balance the particle number concentration change (dN/dt) and coagulation terms. Therefore, the local maximum GR must be resulted from high condensational flux, not self-coagulation.

These had been explained in section 2.3 (methodology)

7. *Chapter 3.4: I think your explanation for the 'missing banana' is plausible. However, you should also look at the air mass trajectories, if this can explain the difference between type 1 and 2 events. For seeing continuous growth on a measurement site, you need to have nucleation taking place on a regional scale (not only locally).*

Re:

We checked the air mass trajectory differences between Type B1 and B2 events. Compared with Type B1, Type B2 was characterized by long range transport trajectories from far north of China and Mongolia. Those lumped trajectories showed little interruption of wind direction. In addition, the meteorological and chemical parameters (high solar radiation flux and wind speed; low temperature; low $PM_{2.5}$ and SO_2, NO_2, CO and O_3, as shown in Figure 6) collectively suggested that Type B2 was typical regional event in quite uniform air masses.

Now at the end of the 1st paragraph of Section 3.4 we added:

"We first examined the air mass trajectory differences between Type B1 and B2 events. Compared with Type B1, Type B2 was characterized by long range transport trajectories from far north of China and Mongolia. Those lumped trajectories with little wind direction interruption imply that the air mass was quite uniform. In addition, meteorological and chemical parameters (high solar radiation flux and wind speed, low temperature, lower $PM_{2.5}$ and SO_2, NO_2, CO and O_3, Fig. 6) collectively suggested that Type B2 was typical regional event in uniform cold air masses. Therefore, the interrupted growth of new particles was not likely to be a result of nonuniform air mass."

8. *You could comment in the conclusions how the emission control in summer was affecting your data (this is of general interest also outside nucleation experts).*

Re:
We added the following comment in the first paragraph of conclusion section:

"In summer, strict emission control measures during the 2014 Youth Olympic Games resulted in relatively low $PM_{2.5}$ and anthropogenic trace gases (SO_2, NO_2, CO and O_3) levels. Infrequent nucleation was thus limited by both low concentrations of gaseous precursors and high temperature and RH in summer.

Specific comments:

1. *Introduction, p. 18654, row 26. I would say just 'formation of clusters' (instead of homogenous nucleation of thermodynamically stable clusters, which is an outdated view of the process), see also the articles about nucleation mechanism from the CLOUD experiments (Kirkby et al.,2011;Almeida et al. 2013; Schobesberger et al., 2013; Riccobono et al. 2014).*

Re:
Thanks for pointing this out. We now changed it to "formation of clusters"

2. *End of Introduction: The aims of your study are stated quite vaguely. I would consider using more concrete language, for instance: (1) provide new information about the initial steps on NPF in a polluted environment, (2) find possible limiting factors, which explain the seasonal and diurnal variation… But this is just a suggestion.*

Re:
We have now used more concrete language like this:
"Our aim was to (1) provide new information about the initial steps of NPF based on size- and time resolved nucleation rate and growth rate measurements, and (2) find possible limiting

factors behind the seasonal and diurnal variations of nucleation events in the polluted urban atmosphere."

3. *Methodology, p. 18657, row 6-9 complex sentence. What was actually moved?*

Re:
We rephrase the sentence:
"As part of an intensive summer campaign (12 August–12 September 2014), the summer measurement was conducted at a local governmental meteorology observatory platform (32.06^{o}N, 118.70^{o}E) that is 14km south to the NUIST site ((2) in Fig. 1). The instruments were housed in an air conditioned trailer, using exactly the same sampling inlets as the NUIST site."

4. *The first sentence of chapter 2.2 is a bit complicated. Reformulate e.g. to: 'a criterion -- was that the total particle concentration reading followed the supersaturation scanning cycle so that the highest concentrations were measured at lowest cut-off sizes.'*

Re:
We rephrase the sentence:
"A criterion was set to determine whether the nCNC detected sub-3nm particles in the atmosphere. The criterion was that total particle concentration reading of followed the supersaturation scanning cycle of PSM so that the highest concentrations were measured at lowest cut-off sizes (as shown in Fig. 2 in Lehtipalo et al., 2014)."

5. Conclusions, p. 18674, row 9: can occur à occurred

Re:
We corrected the word.

5. *Check when to use definite/indefinite article and singular/plural forms throughout the article.*

Re:
We have now checked the definite/indefinite article and singular/plural forms throughout the article.

Anonymous Referee #2

This manuscripts analysis sub-3 nm particle formation in a polluted environment. The paper is definitely original and it appears scientifically sound. The text is well organized and relatively easy to read. While the paper is rather long, it contains plenty of material worth publishing and discussing. Therefore, I see no major need for shortening the text. I have a few, mostly minor, recommendations for revising the paper.

Scientific issues:

1. *Section 1. The paper might benefit from adding a few fresh references on i) nucleation experiments that have aimed to get insight into atmospheric nucleation mechanism, and ii) modeling/field studies investigating the importance of atmospheric nucleation on CCN production.*

Re:
We have now rewritten the first paragraph of Section 1:

"New particle formation (NPF) is an important source of secondary aerosols in the atmosphere (Seinfeld and Pandis, 2006). Field studies and model simulations have consistently shown that NPF can enhance cloud condensation nuclei (CCN) concentrations and contribute significantly to the global CCN production (Wiedensohler et al., 2009; Yue et al., 2011; Wang et al., 2013; Spracklen et al., 2008; Pierce and Adams, 2009; Merikanto, 2009; Yu and Luo, 2009; Matsui et al. 2013). NPF is a two-stage process consisting of formation of clusters and subsequent growth to detectable sizes (McMurry et al., 2005; Zhang et al., 2012). Recently, chamber experiments have made substantial progress in revealing the fundamental processes involved in particle nucleation and growth (Kirkby et al., 2011; Almeida et al., 2013; Schobesberger et al., 2013; Riccobono et al., 2014; Ehn et al., 2014; Kürten et al., 2014). However, consistent theories are still under investigation to quantify the processes physically, chemically, and dynamically (Kulmala et al., 2013, 2014) ..."

2. *Section 2.2. The authors define sub-3 nm particle formation events based on increases in particle number concentrations in this size range, and then divide these event into 4 classes (A1, A2, B1, B2). This is perfectly fine, as there no well-established terminology for such event when starting from sub-3 nm neutral particles. However, in order to avoid confusion among readers, it would be important to mention, or discuss shortly, the other nucleation event even classifications used commonly based on either DMPS/SMPS measurements, or ion measurement. Furthermore, I would encourage the authors to call their events as "sub-3nm particle events" throughout the manuscript, since the vast majority of literature reporting on "nucleation events" based their analysis on particles size distribution measurements not extending to below 3 nm.*

Re:
Now in Section 2.2 (at the end of first paragraph, page 18660) and Conclusion section (first paragraph), we have pointed out clearly the relationship of our classification and traditional NPF definition:

"For the size range > 3 nm, depending on whether a banana-shape growth was seen, we further defined Type A1/A2 and Type B1/B2 events: in Type A1 and B1 events, particles eventually grew to CCN-active sizes, while in Type A2 and B2 events banana-shape particle growth to CCN-active sizes was not seen. Therefore, Type A1 and B1 events were equivalent to conventional NPF events based on either DMPS or SMPS measurements."

"We observed atmospheric nucleation events on 42 out of total 90 observation days, but particles could grow to CCN-active sizes on only 9 days that was equivalent to conventional NPF events."

We thank the referee's suggestion to use "sub-3 nm particle event" throughout the manuscript. In essence, our "sub-3 nm particle event" is more close to nucleation than previous literature not extending to below 3 nm. Now in Abstract we change the second sentence to

"Sub-3 nm particle event, equivalent to nucleation event, occurred on 42 out of total 90 observation days, but new particles could grow to cloud condensation nuclei (CCN)-active sizes on only 9 days."

In other places throughout the manuscript, we still hope to use "nucleation event", because we have explained in sufficient detail in the manuscript the relationship between "sub-3 nm particle event" and "nucleation event" (e.g., Section 2.2). Anyway, future literatures will update their definition of nucleation event with the development of instrument extending to sub-3 nm.

3. *Section 3.1. The authors mention one nocturnal sub-3 nm event in their observations. Such nocturnal events seem to be rather rare, but have reported in a few other investigations. The authors should mention that their finding is not unique, and also include a couple of references discussing earlier observations on this phenomenon.*

Re:
Now in the last paragraph of Section 3.1, we added the discussion of nocturnal nucleation references:

"…This implied the existence of certain dark nucleation source. There are a number of observations that have also shown nighttime particle formation events in various atmospheric conditions (Junninen et al., 2008; Lehtipalo et al., 2011; Lee et al., 2008; Ortega et al., 2009, 2012; Russell et al., 2007; Suni et al., 2008; Svenningsson et al., 2008; Yu et al., 2014), but the

mechanisms behind the nocturnal nucleation are yet still highly speculative. With our instrument capability in this work, we could not deduce any valuable information on the nocturnal nucleation mechanism, except that we found the air mass on 04 March was relatively clean (both *CS* and gases, mean *CS*: 0.15 s^{-1}), and temperature and RH (mean: 4.4^{o}C and 33%) were favorable for nucleation."

4. *Section 3.2, last full paragraph on page 18667: Please make clear for the reader that the organic vapor concentrations referred to in this context are not measured by any means, but estimated values based on theoretical understanding on sub-3 nm growth and therefore subject to uncertainties in i) the derived growth rate, ii) the theory by which the growth was related to the origanic vapor concentration, as well as iii) proxy based sulphuric acid concentration which also contributes to this growth.*

Re:
We have changed the last paragraph of Section 3.3 to adopt the suggestion of the referee:

"It should be noted that the organic vapor concentrations C_∞ referred to in this study were not directly measured, but estimated based on Eq. (2). Aerosol dynamic processes, such as nucleation, coagulation, and the condensation growth of H_2SO_4 and water vapors, were not considered explicitly in Eq. (2). In addition, bulk thermodynamics was applied in Eq. (2) for extremely small clusters/particles of sub-3 nm sizes. Therefore, although our calculation provided an possibility to explain the size dependence of growth rate observed in the polluted urban atmosphere, the organic vapor concentrations C_∞ in this study was subject to uncertainties in (1) the growth rate derived from the GDE method, (2) the theory by which the growth rate was related to the organic vapor concentration, and (3) H_2SO_4 level which also contributed to the initial growth."

5. *Section 4. I agree on the statement on calling for a robust proxy development for sulphuric acid in polluted environments. At the same time, however, the authors should bring up the need for developing means to estimate/measure ELVOC in such environments as well.*

Re:
We added the following sentence in the last paragraph of Section 4:

"The study also brought up an urgent need for developing means to measure or estimate activating organic vapor (i.e. ELVOC) levels in the initial growth stages of atmospheric NPF."

Technical issues:

1. *I think that a 2-digit accuracy would be more appropriate for the reported quantities (J, GR, vapor concentration). 3 digits, and especially 4 digits, seem too accurate to me.*

Re:
We have now changed 3 and 4 digits of *J* and *GR* to 2-digit accuracy.

2. *I am not sure if the authors use quite correctly the term "limiting factor" (section 3.1, lines 9-11 on page 18665) or "limiting" (section 3.4, lines 4-6 on page 18673). Any quantity may limit a process in two ways: it may be too small (in case it favors this process like radiation seem to favor nucleation) or it may be too large (in case it suppresses the process like condensation sink does for nucleation). Please check out this point in section 3.1. What it comes to section 3.4, the authors apparently mean that there was a lack of condensable organic vapors other than ELVOCs, and therefore particles >3 nm did not grow as effectively as in days when more such vapors were present.*

Re:
We agree with the referee that both promoting and suppressing quantities may limit a process. There are lots of literatures that called both types of quantity "limiting factor" (e.g., Nilsson et al., 2001; Wu et al., 2007; Boy et al., 2008; Lehtipalo et al., 2010). In our conclusion and abstract, we had explained in more detail the influence of every quantity (shown below). Therefore, we think it is appropriate to use the term of "limiting factor" in Section 3.1 and 3.4 that are pointed out by the referee.

"In summer, infrequent nucleation was limited by both low concentrations of gaseous precursors and high temperature and RH. In more polluted winter and spring atmosphere, precursor supply was not limiting anymore; nucleation can occur once meteorological conditions were favorable (i.e. low CS and temperature/RH, higher solar radiation). However, for the further growth of sub-3nm particles to CCN-active sizes, anthropogenic gaseous precursors again became limiting factors."

Nilsson, E. D., Paatero, J., and Boy, M.: Effects of air masses and synoptic weather on aerosol formation in the continental boundary layer, Tellus Ser. B, *53*(4), 462-478, 2001.

Wu, Z., Hu, M., Liu, S., Wehner, B., Bauer, S., Mabling, A., et al.: New particle formation in Beijing, China: Statistical analysis of a 1-year data set, Journal of Geophysical Research: Atmospheres, *112*(D9), D09209, doi: 10.1029/2006jd007406, 2007.

Boy, M., Karl, T., Turnipseed, A., Mauldin, R. L., Kosciuch, E., Greenberg, J., et al.: New particle formation in the fronet range of the Coloardo Rocky Mountains, Atmos. Chem. Phys.,

8, 1577-1590, 2008.
Lehtipalo, K., Kulmala, M., Sipilä, M., Petäjä, T., Vana, M., Ceburnis, D., et al.: Nanoparticles in boreal forest and coastal environment: a comparison of observations and implications of the nucleation mechanism, Atmos. Chem. Phys., *10*, 7009-7016, 2010.

3. Please reword.

Page 18663, line 3: should be ". . .will also be shown in the next section."

Page 18664, line 21: should be ". . .will be discussed later. . ."

Page 18667, line 18: please define the table. Table 1?

Page 18668, line 14: should be "rapidly"

Page 18671, line 26: should be "summarizes"

Page 18672, line 27: ". . .than on Type B2 event days."

Re:

Thanks for pointing these out. We have corrected these grammar and typeset issues accordingly.