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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Simultaneous measurements of new particle formation in 1-second time resolution at a street site and a rooftop site" *by* Yujiao Zhu et al.

Yujiao Zhu et al.

xhyao@ouc.edu.cn

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This manuscript presents a field measurement of new particle formation (NPF) events in urban Beijing, China. The deployment of Fast Mobility Particle Sizers (FMPs) is unique and could deliver new insights into NPF, if interpreted properly. Overall, this manuscript describes interesting phenomena that NPF was enhanced in winter at a street site comparing to a close rooftop site, whereas NPF was less pronounced at the street site in spring. The explanation for these observation, unfortunately, is not well justified, and requires a major work over again. Here are my detailed comments.

Response: The authors thank the reviewer's comments and try our best to respond and revise our manuscript accordingly.

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Discussion paper

Main comments,

1. Micro-meteorology could be a major player that explains the difference between the street site and the rooftop site, which is not discussed at all in the current manuscript. Potentially, the loss of nanoparticles due to the surfaces along the street canyon is a factor too.

Response: The authors believe the turbulence dispersion to be more important than advection diffusion at the street site under a strong synoptic wind. The authors didn't measure wind direction and wind speed at multiple street locations and the authors didn't think one point observation of wind direction and wind speed can full reflect the complicated micro-scale wind field at the street site. The authors thereby reluctantly speculated the influence of the complicated micro-scale wind field on the observed particle number concentrations between the rooftop site and street site.

Through a deep data analysis, the authors additionally provided two types of unique evidences which were less affected by micro-meteorology at the street site as well as the simplest evidence, i.e., the simple comparison between the rooftop site and street sites, to confirm the reduced and enhanced NPF at the street site in different seasons. The authors found that the sufficiency and uniqueness of three types of evidences were not fully recognized by the reviewers because their challenges mainly focused on the simplest evidence. This means the authors' presentation strategy has to be improved to make the three types of evidences more obviously.

In revision, the authors will clarify that the reduced NPF always occurred at the street site in the springtime. Three evidences from different angles will be itemized as Evidence 1, 2 and 3, i.e., Evidence 1: The lower particle number concentration (PNC) of nucleation mode particles at the street site mainly because of a shorter initial burst time. Evidence 2: The authors used the PNC at the street site subtracting the corresponding PNC at the rooftop site to calculate the difference. The authors then obtained the second evidence: the negative difference of nucleation mode particles against the

positive difference of Aitken mode particles on NPF days. Evidence 3: Using the same approach, the authors obtained the third evidence: the negative difference of nucleation mode particles on NPF days against the positive difference of that on non-NPF days (Figs. 3 and 4 in the origin version).

In addition, the authors will clarify that the enhanced NPF always occurred at the street site in the wintertime. Three evidences from different angles will be itemized as Evidence 1, 2 and 3, i.e., Evidence 1: The significantly larger PNC of nucleation mode particles at the street site and a larger apparent formation rate of new particles mainly because of a shorter initial burst time. Evidence 2: The positive difference of nucleation mode particles in the wintertime against the negative difference of nucleation mode particles in the springtime on NPF days. Evidence 3: The larger positive difference of nucleation mode particles on NPF days against that on non-NPF days in the wintertime (Figs. 5 and 7 in the origin version).

We agree that the loss of nanoparticles due to the surfaces along the street canyon can be a potential factor of the reduced NPF in the springtime. In revision, We will revise L225 as: “Several factors can lead to the reduced NPF events at the street site, i.e.., 1) a larger condensation sink because of more pre-existing atmospheric particles from primary emissions; 2) tall buildings along both the sides of urban streets providing additional surface areas to scavenge gases and atmospheric particles (Yao et al., 2011); 3) vehicle-emitted NO reacting with RO2 and suppressing NPF (Wildt et al., 2014).

2. The inter-comparison between two FMPSs showed some differences, and the authors decided to use one FMPS as a reference and correct the number concentration of the other one. How did they decide which one is “the one” to trust? Nevertheless, number concentrations are used to calculate formation rates, growth rates, and condensation sink. This could lead to a major uncertainty in the discussion for nucleation mechanism.

Response: As reported by Zimmerman et al. (2015), an independent measurement

of CPC simultaneously with FMPS can be used to accurately correct the FMPS data. The reference has been cited in the manuscript. In this study, a CPC was operating simultaneously with a FMPS at the street site and the FMPS was thereby used to correct the other. The two FMPS were then processed the second-step correction proposed by Zimmerman et al. (2015). The total particle number concentration of the FMPS at the rooftop site was multiplied by a correction factor which was equal to the minutely averaged ratios of the FMPS and CPC data at the street site. The calculated value and the CPC data was used to complete the third correction for the FMPS data at the rooftop site and at the street site, respectively. This will be clarified in revision.

3. The FMPSs were placed downstream of dryers, which indicates that the measured size distributions could be of from the atmospheric ones. This at least eliminates the role of relative humidity to a certain extent. Even for particles in the size ranges of 10-20 nm, the uptake of H2O is one of the major pathways for particle to grow.

Response: Relative humidity (RH) varied from 13% to 49% during NPF event days in the wintertime and below 55% during NPF event days in the springtime. At such RH levels, the growth factor of 10-20 nm particles (assume to be (NH4)2SO4) were less than 1.02 (Hämeri et al., 2000). This will be added in revision.

4. The mixing ratio of SO2 was only measured at the rooftop site. How about CO? It might be possible to deduce a street SO2 simply by the mixing ratios of CO. The current assumption that concentrations of SO2 are identical at the two sites are not acceptable, and could lead to mis-interpretation.

Response: The authors thank the comments and the SO2 concentration at the two sites indeed needs more interpretation.

In this study, CO was not measured at the street site. However, black carbon (BC) was measured by a potable aethalometer at the street site and BC is also a good indicator of traffic emission (Fruin, et al., 2004; Meng et al., 2015 a,b). The authors tried to use BC to deduce the traffic-related SO2 at the street site. In revision, we will add

"The sulfur content in the gasoline and diesel was limited <50 ppm at those years. The measured BC spikes were lower than 5 μg m-3 during the NPF periods. The maximum contribution of traffic-related SO2 at the street site was roughly estimated to be 1.3 ppb according to the results in our previous studies (Meng et al., 2015 a,b)". In the wintertime, the ratio of traffic-derived SO2 to the observed values was less than 1/4 and the observed values were overwhelmingly contributed by domestic heating. The uncertainty by assuming SO2 at the street site same as the rooftop site should be minor in the wintertime and it should not affect our conclusion because the formation rates of new particles at the street site were increased by 3-5 times against the rooftop site in the wintertime. In the springtime, the contribution of traffic-related SO2 might significantly increase the mixing ratio of SO2 at the street site. However, the reduced NPF was observed at the street site. The possible underestimation of SO2 at the street site further solidified our analysis results, i.e., a strong scavenge effect at the street site likely existed and caused the reduced NPF.

5. The authors focused on the oxidation of biogenic organics when discussing the growth of >10 nm particles. In an urban environment such as Beijing, wouldn't anthropogenic VOCs be more concentrated? Are there any measurements that point the authors to biogenic VOCs instead of anthropogenic ones? How will the interpretation

Response: The authors thank the comments. The role of oxidation products of biogenic VOC in NPF events were widely studied in field experiments, chamber and modeling studies, and quantum chemical calculations (Schobesberger et al., 2013; Riccobono et al., 2014; Ortega et al., 2015; Tröstl et al., 2016). According to the established knowledge, the authors argued the potential importance of oxidized biogenic VOC in growing newly formed particles in this study. The north and northwest directions of the sampling site subject to mountain areas have a high percentage of land-covered forests. Extensive biogenic VOC is theoretically expected in spring may act as important precursor in NPF. During the NPF periods, the north or northwest wind dominated and carried less polluted or even clear ambient air from mountain areas to the sampling site, e.g., the

mixing ratio of SO2 was < 3 ppb in the springtime and < 5 ppb in the wintertime during the periods of NPF events.

The role of oxidized anthropogenic VOCs in growing >10 nm newly formed particles is still poorly understood (Zhang et al., 2009; Hoyle et al., 2011). Considering the knowledge gap and lack of related data in this study, the authors are reluctantly to discuss the possibility in this study. Following the reviewer's comments, in the context, the authors will add "Theoretically, oxidized anthropogenic VOCs could also participate in the growth of newly formed particles while the study is limited (Zhang et al., 2009; Hoyle et al., 2011). The role of oxidized anthropogenic VOCs needs further study."

6. Throughout the manuscript, the authors are presenting J8, which is fine. However, particles bigger than 8 nm are larger enough that they don't really reflect the nucleation mechanism, instead, a combination of nucleation and subsequent growth, especially growth mechanisms, might actually determines how many particles were measured.

Response: Different reviewers clearly had different views on the apparent formation rate of new particles. As a compromise by considering all reviewers comments, J8 will be used in revision. We will add additional interpretation: "Noted that J8 reflects a combination of nucleation and subsequent initial growth of new particles." in the explanation of new particle formation rate.

Minor comments,

7. (Page 8), clearly define long-term NPN, short-term NPF, Class I NPF, and class II NPF.

Response: The authors thank the comments. The authors would like to correct "long-term NPF events, short-term NPF events" to "regional NPF events, short-lived NPF events" following Stanier et al. (2010) and Jeong et al. (2010). Regional NPF events represent NPF events occurred lasting longer than 1 hour, and short-lived NPF events represent the NPF periods was less than 1 hour. When new particles showed "banana

shape" growth, and the new particles grow to larger than 30 nm, we define as Class I NPF event. When the new particles showed no apparent growth and the particles diameter was about 11 nm, we define as Class II NPF event. In this study, the duration of NPF events in Class I and Class II were lasting longer than 1 hour, which belong to the regional NPF events.

8. (Page 10, Line 225), how about NO in the winter? Wouldn't NO be always higher in the street canyon?

Response: Theoretically, NO could be always higher in the street canyon not only in the springtime but also in the wintertime by considering on-road traffic emissions closer to the street site. The enhanced NPF at the street site implied that the enhanced effects overwhelming the reduced effects. A revision will be done to reflect this argument.

9. (Page 13, Lines 280-287), the argument on H2SO4 is just speculation. Many factors determines H2SO4. Also, why is SO2 from on-road vehicles negligible comparing to the background?

Response: In this study, the NPF events occurred under the north or northwest wind direction with wind speed >4m/s. The north or northwest wind carried less polluted or even clear air to the sampling site during the NPF event periods, e.g., the mixing ratio of SO2 was < 3 ppb in the springtime and < 5 ppb in the wintertime during the periods of NPF events. Less polluted or even clear air exactly meets the criteria of equation (4), i.e., the proxy for calculating gaseous sulfuric acid (SA) concentration is applicable under clean to moderately-polluted atmospheres.

In revision, the authors use BC to deduce that the traffic-related SO2 was less than 1.3 ppb (details can be found in the response to comment 4). In the wintertime, the maximum contribution of traffic-related SO2 to the observed values was roughly estimated as 1/4 and the observed values were overwhelmingly contributed by domestic heating. In the springtime, the contribution of traffic-related SO2 might significantly increase the mixing ratio of SO2 at the street site.

10. (Page 15, the last paragraph), I am certainly not convinced by the discussion here. Different nucleation mechanisms probably explains NPF events in Beijing, Qingdao, and marginal seas of China. Again, J8 is not a good indicator for nucleation mechanisms. By definition, NMIoNP stand for "the net maximum increase of nucleation mode PNC". I don't see a clear connection between NMIoNP and J8. A cutoff of 8 cm-3 s-1 could be arbitrary. The correlation will not be bad if a cutoff of , say, 7 cm-3 s-1, was chosen.

Response: Theoretically, the formation rate of new particles alone has no direct relationship with the environmental and climate effects of new particles. However, NMIoNP defined as "the net maximum increase of nucleation mode PNC" is directly related to the environmental and climate effects of new particles. Thus, it is important to establish the link between NMIoNP and J8.

Considered 1) formation rate of new particles, e.g., J= kNucOrg[H2SO4]m[NucOrg]n (Zhang et al., 2012), 2) the subsequent particle growth, and 3) H2SO4 vapor to be necessary for nucleation in ambient air except at sea beach, two scenarios are considered. One is: H2SO4 vapor is relatively sufficient against NucOrg and J8 is thereby mainly determined by availableness of NucOrg. A good correlation is theoretically expected for J8 and NMIoNP. The other scenario is: NucOrg is relatively sufficient against H2SO4 vapor and J8 is thereby mainly determined by availableness of H2SO4 vapor. J8 could be high, but the total yield of new particles could be low because of a rapid consumption of H2SO4 vapor. A poor or no correlation is theoretically expected for J8 and NMIoNP.

The authors found when the formation rate less than 8 cm-3 s-1, the new particle yield increased with the increasing formation rate. Of course, for any values <8 cm-3 s-1, the statement is valid. The authors didn't find any logic problem.

11. In supplementary, coefficient of variation (CV) is defined, but try to define "25% minimum", especially what "minimum" stands for. Also, why 1 16.6 nm cutoff chosen in

the following session?

Response: The authors revise the description of 25% minimum CV as: “Coefficient of variation (CV) is the ratio of standard deviation to mean for particle number concentration in every 60s. We sort the data sequence in an order from the smallest to largest, and the minimum 25% values of CV reflect smaller changes of particle number concentration.”

N16.5nm used as the reference to conduct the deduction relied on two reasons: 1) Zhu et al. (2006) also observed the vehicle particle mode around 16 nm at 30 m downwind. 2) In this study, 10 nm-30 nm was the major mode in the vehicle particle size distribution, and 16.5 nm was the peak of this particle mode. This will be added in revision.

12. Proofread the manuscript.

Response: The authors are sorry for this and the language-editing will be processed before re-submitting.

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