Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-1151-AC2, 2020

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Investigating three patterns of new particles growing to cloud condensation nuclei size in Beijing's urban atmosphere" *by* Liya Ma et al.

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Received and published: 11 August 2020

Anonymous Referee #1

This study investigated patterns and characteristics of atmospheric new-particle formation events in Beijing. The authors categorized these observed events into three classes based on the number size distributions of the newly-formed particles. Further, by combing the size distribution with the speciation of measured or modelled gas and particle-phase pollutants, the authors discussed the contribution of organic and inorganic compounds to particle growth during different type of events.

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Discussion paper

The manuscript focus on the topic of new-particle formation in the urban atmosphere, trying to address critical questions that whether or not the newly-formed particles can grow to the CCN size, and what conditions/species control the grow process. The scope of the manuscript is thus suitable for ACP, and the data the authors presented are ample and interesting. However, the interpretation of some key results is questionable and leads to unrigorous conclusions. Major revisions and improvements are needed before this manuscript can be considered for publication as an ACP paper.

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

Major comments:

1) The authors defined three classes. "Class I was characterized by no apparent particle growth" makes sense, this class might indicate either a lack of supersaturated condensable vapors so that particles don't grow, or a too high condensation sink so that small particles don't survive. But is there a better way to classify the rest events? Particles are larger than 50 (or 75) nm doesn't necessarily mean they are good CCNs; and there are so many factors (chemical, physical or meteorological) that can determine whether or not the particles grow over 50 (or 75) nm. Classifying the events just based on the "cut-off" size doesn't really help modelers or lab experimentalists to understand the real atmosphere. Please justify the classification or improve it.

Response: Thanks for your comment. Previous studies in various atmospheric environments showed that particles' ability to act as CCN is largely determined by aerosol size at normal ambient super-saturation when the size of atmospheric particles is smaller than 60-80 nm (Dusek et al., 2006; Li et al., 2015; Zhu et al., 2019). However, chemical composition, particle mixing states, meteorological conditions, etc., may affect the activation of particles to CCN with diameters beyond 60-80 nm. In our previous studies, we found that newly formed particles sometimes encounter a growth threshold around 50 nm, which can't be explained by the meteorological conditions (Man et al., 2015, Zhu

et al., 2014, 2017, 2019). Therefore, we use the particle "cut-off" size as classification criteria. In the revision, we will add more justification and improve it to better service other researchers.

2) From the surface plot of these NPF events (e.g. Fig 2a, e; Fig 3a, e; Fig 4a), I don't see any significant band of pre-existing particles. Were these events all observed in very clean days? Or is it because the linear color scale veil the background particles? Please do change to the log color scales.

Response: Thanks for your suggestion. We have changed the liner color scale to the log color scale (see the revised manuscript), and the pre-existing particles are more obvious in the revised figures.

3) The author stated that many growth events lasted for over 10 hrs or even a whole day. Was there any primary emission mixing with the newly-formed particles, e.g. from vehicles, restaurants or factories? Is it true that there was only condensational growth without mixing during the whole period? Please discuss this and also show O:C from the AMS measurement to verify the statement.

Response: Thanks for your comment. We use a high-time resolution particle sizer, i.e., FMPS, to measure the particle number size distribution (PNSD) in 1 s time resolution. The high time resolution of FMPS can allow clearly identify the signals of newly formed particles from preexisting ambient particles, e.g., freshly emitted particles from combustion, as well as the mixing process of the different types of particles (Liu et al., 2014; Man et al., 2015; Zhu et al., 2017, 2019). According to our previous studies (e.g. Zhu et al., 2017, ACP) and the review paper by Tuan et al. (2015), the PNSD of traffic emissions are characterized by two peaks, i.e., about 16 nm and 30 nm, and intermittently lasts a few seconds or minutes (Figure 1). Figure 2 (will be added in new supporting information) shows the fresh industrial emissions and/or the cooking emissions. During the NPF events (e.g. Figure 3), COA occasionally influences the new particles signal, and the growth of new particles was consistent with the increase in LO-OOA and MO-

OOA. Therefore, we argued that the growth of new particles depends largely on the condensational growth.

4) About the AMS measurements, the sampling site is 8 km away from Peking University, how long does it take for an air parcel transport from one site to the other? Roughly one hour maybe? How well does the AMS result represent the particle composition at Peking University? I think this question need to be better addressed in order to discuss the spatial heterogeneity.

Response: NPF events are regional occurred. In our study, the average duration of NPF events was 10 hrs., and the wind speed was approximately 4-6 m/s. There was only half hour delay for air parcels sweeping from one site deployed the AMS to another site deployed the FMPS. Under such wind speed, the chemical components in PM1.0 measured by the AMS mainly represented regional characteristics. However, local emissions may also contribute to then to some extent. In our previous study (He et al., 2002), the chemical composition of PM2.5 at two sampling sites in the zone of Beijing were generally consistent. The uncertainty will be added in the revised manuscript.

5) AMS measured the bulk PM_1.0, how well does the chemical composition in PM_1.0 represent the species drive the sub-100 nm particle growth? Were there any aerodynamic diameters measured by AMS at the same time? Discuss more about the uncertainty here.

Response: Thanks for the question. Ideally, the real-time chemical composition of sub-100 nm particles would be the best to explain the growth of new particles. The data was not available in this study unfortunately. In our previous observation using AMS, the real-time chemical compositions of sub-100 nm particles have large artifacts. AMS measurements for these small particles may be not reliable. We thereby combined all chemistry information to explain the growth of new particles. In the revised manuscript, the uncertainties will be added in section 2.1.

6) Page 4, line 20, Equation 4, I don't find the exact same equation in the references

the authors cited here. Using averaged particle number concentration over the whole growth period can bring in large uncertainties. Newly-formed particle is prone to coagulation loss; this means particle number concentration at D_pg1 will be much higher than that at D_pg2, and the Mass required will be overestimated. Please justify the equation, or calculate the particle mass concentration for each FMPS scan and also take the coagulation into account.

Response: Agree. A more accurate calculation should be adopted to gain the required mass for particle growth. During the new particle growth period, the number concentration may decrease due to the dry deposition, diffusion and dilution effects, and the particle coagulation. In the revised manuscript, we will calculate the range of required mass according to the integral particle number concentration at Dpg,1 (N1) and Dpg,2 (N2). The formula will change to

Massrequried = 4/3ïĄř [(Dpg2/2)3 - (Dpg1/2)3] * N1 * ïĄš ∼4/3ïĄř [(Dpg2/2)3 - (Dpg1/2)3] * N2 * ïĄš

7) Was there a special reason to sum up O3 and NO2 instead of discussing them separately? NO2 is not always associated with O3, it could come from primary emission such as vehicle exhaust.

Response: In China, previous study showed that the primary on-road vehicular NO2/NOx ratio was less than 2%, and NO was the main exhaust gas (Yao et al., 2005). Heavy duty vehicles are allowed to enter urban areas in Beijing only after 20:00 but not in daytime. Considering the NO-titration of O3 (O3+NO→NO2+O2), we use the sum of O3 and NO2 to represent the oxidizing capacity.

8) The authors briefly mentioned seasonal variation, but didn't dive into the details in, for example, wintertime events. A recent study (Wang et al., 2020, Nature 581 (7807), 184-189) show that NH4NO3 could help the newly-formed particles grow and survive in winter. So, it's intriguing to know that the authors observed that the newly formed particles didn't grow during wintertime events, but it would be more important

to understand why they didn't. Was it because of a lack of supersaturated condensable vapors, or a too high condensation sink?

Response: Wang et al. (2020) performed the experiments in the CLOUD chamber with scrupulous cleanliness and minimal contamination, and found NH4NO3 can drive the newly-formed particles grow to the larger sizes. However, NH4NO3 were less likely formed during winter daytime NPF period in Beijing because of low products of HNO3 and NH3 in ambient air. In the chamber study reported by Guo et al. (2020, PNAS, 117, 7, 3427-3432), new particles grew rapidly to about 50 nm in the clean chamber, but they grew much slowly in the polluted chamber, in which the sizes of new particles less than 20 nm (Figure 1 in Guo's paper). Based on Guo's study, the lack of growth of new particle during wintertime was due to the high condensation sink. This will be added in the revision.

9) Please discuss more about the model uncertainty, sensitivity test, etc.

Response: In the revised manuscript, we have added the model uncertainty and sensitivity test in section 3.2, The model results generally could meet the benchmark criteria of above four species (US-EPA, 2007), with correlations of higher than 0.51 (Table S1). The concentrations of SO42- and NH4+ had been slightly overestimated (with Normalized Mean Bia (NMBs) and 12%, 6%), while the concentrations of NO3- and OOA were underestimated (with NMBs of -29% and -39%).

10) The authors used many sentences describing the particle growth/shrinkage processes vs time, e.g. "However, the shrinkage occurred as early as 15:20-17:20 on 11 June.". Yet these sentences contain very limited information. I would suggest the authors go through the whole manuscript and reword these sentences by discussing more deeply about the environmental conditions or the causes of these different types of growth.

Response: Thanks for the comment. In the revised manuscript, the relationship between the meteorological conditions and the new particle growth types will be dis-

cussed in detail.

Minor comments: 1) Page 1, line 17: “11/27” (and hereinafter) should be something like “11 out of 27”.

Response: Corrected.

2) Page 1, line 22: “: : : in the remaining NPF events”, please add the number here.

Response: Corrected.

3) Page 2, line 26: “survival probability ratios”, “survival probability” would be better.

Response: Corrected.

4) Page 3, line 9: should the coefficient be size-dependent?

Response: The coefficient was dependent on the particle number concentration, no the particle sizes.

5) Page 3, line 13: “During the other observational periods: : :”, please specify the date.

Response: Corrected.

6) Page 6, line 8: “to a negligible level; in Scenario 2”, the semicolon should be period.

Response: Corrected.

7) Page 6, line 10: “: : : may not represent two NPF events occurring in one day.”, why? They look very much like two events.

Response: In the revised manuscript, this sentence will be modified to “This phenomenon can be explained by the spatial heterogeneity of NPF, or it can represent two NPF events that occurred in one day.”

8) Page 6, line 14: “. . . associated with wind direction changes in the late afternoon or nighttime.”, please specify the wind directions, and discuss if the sources of pollutants

changed.

Response: We will add the wind speeds and wind directions in the supporting information.

9) Page 7, line 14: "... from 9-22 nm to 23-69 nm...", please reword it.

Response: This sentence will be modified to "the initial Dpg of newly formed particles were 9-22 nm, and they grew to 23-69 nm in the daytime".

10) Page 8, line 29: "uparticulate" should be "particulate".

Response: Corrected.

11) Page 9, line 19: "... need to confirm this.", should be "... are needed to confirm this."

Response: Corrected.

12) Page 9, line 30: "stopped the growth", should be "stopped growing".

Response: Corrected.

13) Page 10, line 17: "The observed concentrations of OM and NO3- largely oscillated and had no increasing trends after 21:00, although Dpg increased from 60 nm to 75 nm in one and half hours.", explain this.

Response: In the revised manuscript, we will change OM to OOA, and discuss the variations of OOA during particles growth. In this case (Figure 4), OOA reaches its maximum at 22:20 and is consistent with the increasing of Dpg.

14) Page 12, line 5: "The slope further suggests that an increase of 10 ppb in Ox likely causes an increase of 5 nm in Dpgmax.", I would suggest removing it.

Response: We will remove this sentence in the revised manuscript.

15) Page 12, line 23: "When the estimated CS were compared, the averaged value

was 1.8±2.0×10-2 s-1, 2.1±1.5×10-2 s-1 and 2.0±1.2×10-2 s-1. . .", the deviations are too large to provide detailed information, I would suggest removing it.

Response: We will remove this sentence in the revised manuscript.

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Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-1151, 2020.

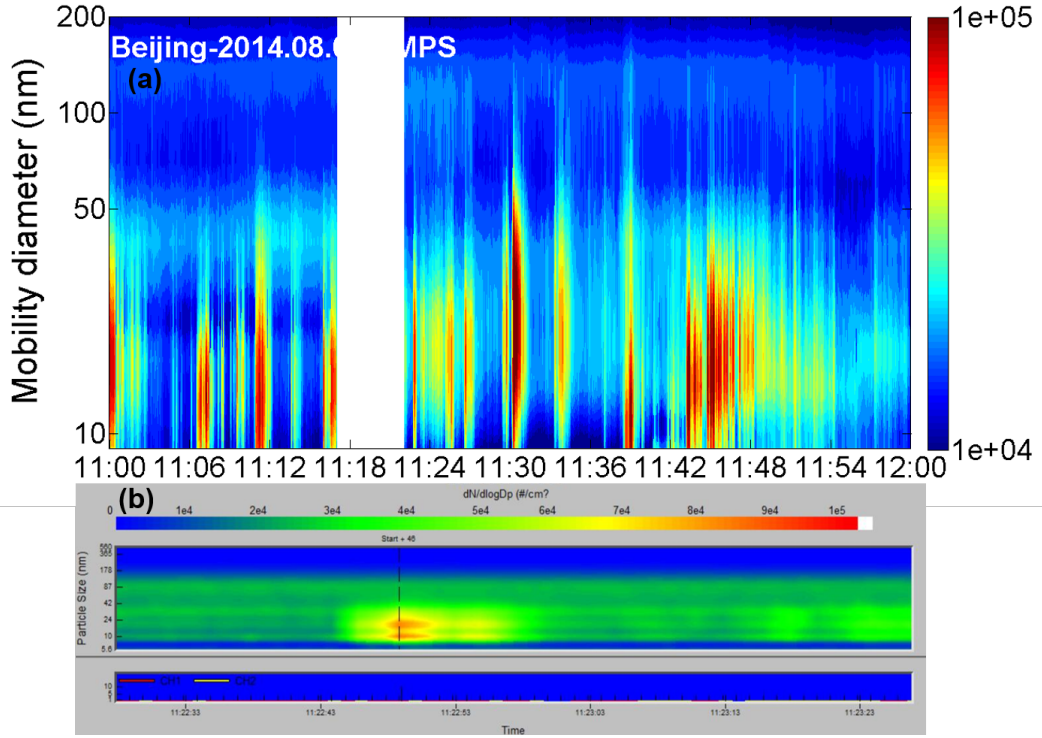

Fig. 1. Contour plot of traffic emissions (a) and the raw FMPS data of the vehicle spikes (b)

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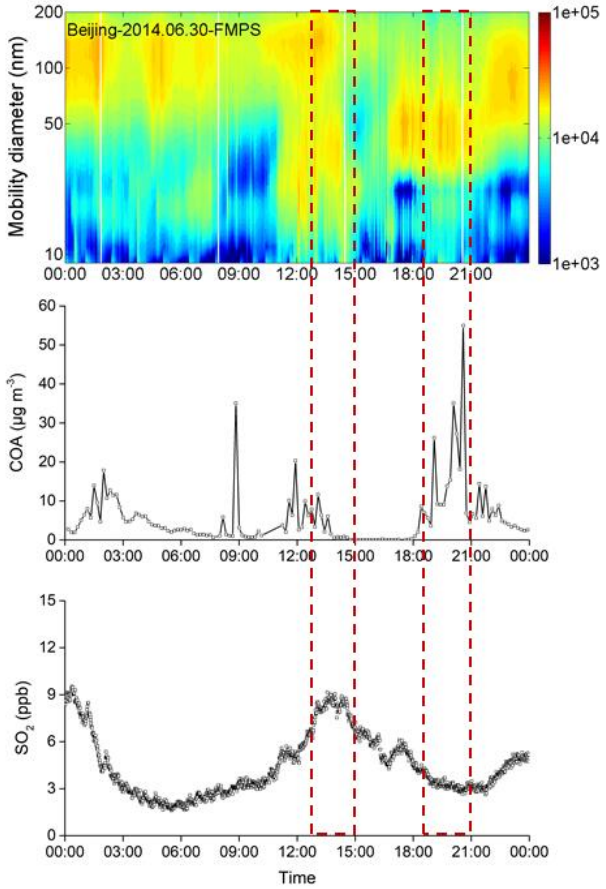

Fig. 2. Fresh industrial emissions with high SO2 (12:30-15:00) and the cooking emissions with increased cooking OA (COA, 18:20-21:00)

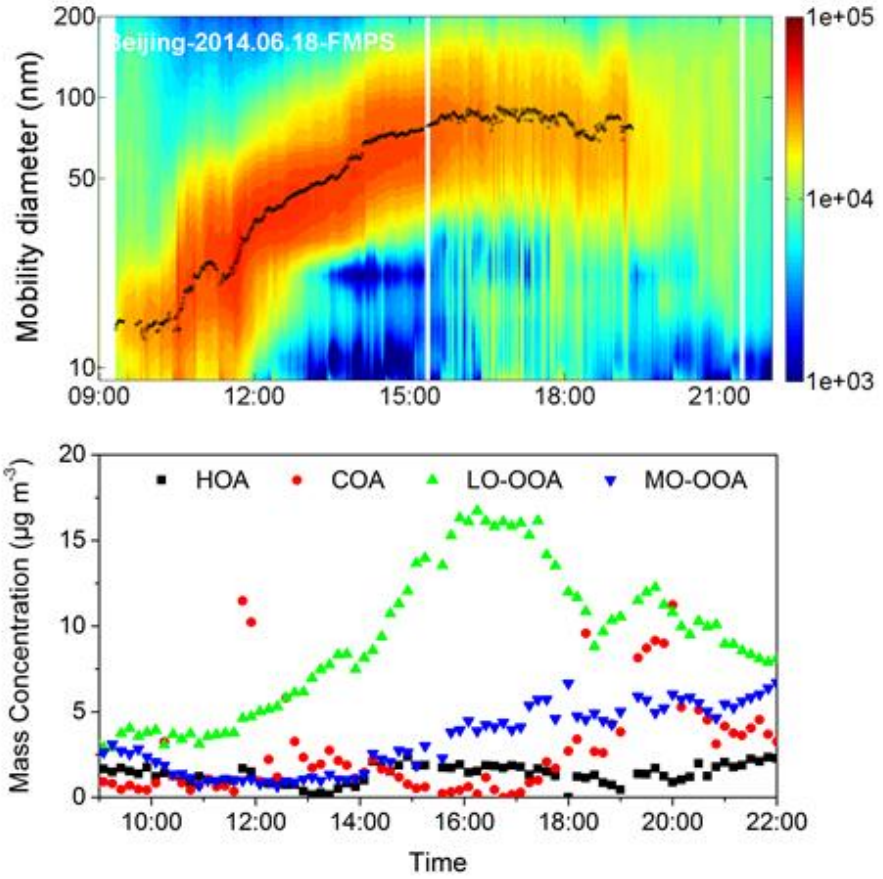

Fig. 3. NPF event and the variations of hydrocarbon-like OA (HOA), cooking OA (COA), less oxidized oxygenated OA (LO-OOA) and more oxidized oxygenated OA (MO-OOA) on June 18, 2014

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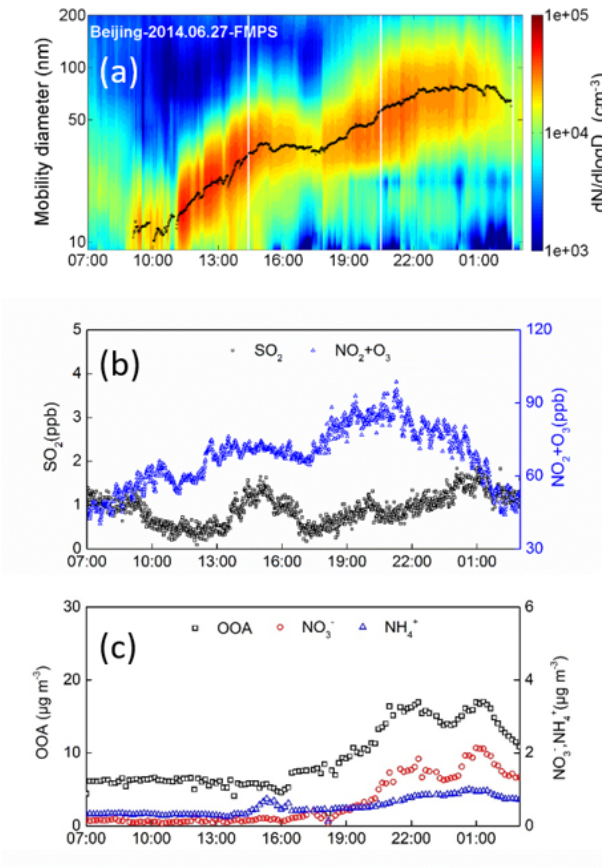

Fig. 4. NPF event that occurred on 27 June 2014 ((a) contour plot of the particle number concentration; (b) time series of the observed mixing ratios of SO2, NO2+O3 (c) time series of observed OOA, NO3- and N

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