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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.

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General Comments:

In this work, Zhu et al. presented new particle formation (NPF) events observed at both a street site and a rooftop site using two TSI 3091 FMPS during both spring- and winter-time. The authors reported two major findings: 1) NPF was enhanced at the street site during wintertime due to seasonal street canyon effects; 2) Photochemically oxidized biogenic organics might contribute significantly to the growth of >10 nm particles. Overall, the manuscript is fairly well written and the subject of the research is certainly within the scope of Atmospheric Chemistry and Physics (ACP). The unique feature of this work is the high time-resolution (1Hz) observations of particle number

size distribution (PNSD). It does provide an advantage in NPF research. This is an interesting study but the reviewer feels that there are several issues needed to be further addressed before the manuscript can be considered for publication in ACP.

Response: The authors thank the reviewer's comments and try our best to address the issues point-by point.

Specific Comments:

1. L27: I do not have too much confidence that the authors can draw a conclusion of "seasonal effects" from several days of NPF events. It is more like a case study. After all, there were no summer and autumn observations.

Response: Agree. The findings obtained in this study were mainly related to direct and indirect effects of largely changed ambient temperature. It will thereby revise as "temperature effects" in revision.

2. L30: "The oxidation of biogenic organics. . .apparent growth." There is no clear evidence of strong biogenic VOC emission at the sites. The authors may want to look into the anthropogenic VOC emissions, such as traffic-related VOC emissions.

Response: 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 and may act as important precursors 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."

3. NPF event consists of both nucleation and the ensuing particle growth. It would be more reasonable to replace "NPF rate" with "nucleation rate".

Response: In our study, the authors calculated the apparent formation rate of new particles >8nm. "Nucleation rate" currently refers to the formation of <1-3 nm new particles and clusters with more novel technologies available for measuring <3 nm particles. The authors prefer to use apparent formation rate (FR) in revision.

4. L235-240: The authors used "25% minimum coefficient of variation (CV) of particle number concentration" as an indicator to eliminate vehicle emission spikes from the NPF dataset. If possible, I suggest the authors also use NOx as an indicator of vehicle emission plumes. For example, did the particle number concentration spikes show any correlation with NOx time series?

Response: NOx 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 as an indicator of vehicle emission plumes to deduct primary traffic particles. It does not work because the one-minute time resolution is too low to successfully deduct primary traffic particles. To best of our knowledge, NOx analyzers are usually set for operating in one-minute time resolution and the data of NOx may suffer from the same problem. An example is presented to illustrate the problem for using BC to deduct

primary traffic particles.

During the entire sampling period on 22 December 2010, BC shows no correlation with the nucleation mode PNC (Fig. 1a). During a few short periods, the BC spikes appeared to be visibly consistent with the PNC spikes as shown in Fig. 1b. However, the correlation obtained was much poor, e.g., during the period of 10:30-12:30 (Fig. 1c). This is not surprised because the aethalometer reported the instantaneous value of BC in one minute, but the vehicle spikes physically occurred in a few seconds (Fig. 2). Under such poor correlation, the regression equation is invalid to accurately deduct primary traffic particles.

5. As described by the authors that the street site was "18 m away from the curb of a heavy traffic (Chengfu) Road at the northwestern area in Beijing", it would be necessary not only to remove spikes of vehicle emissions but also to take into account the small particles transported from further down the road, which may be not as distinct as the spikes caused by passing by vehicles but would certainly raise the background level of $\sim$10 nm particles.

Response: When the authors calculated the new particle formation rate, we use the difference of nucleation mode PNC after and before the PNC increasing period. The background level of $\sim$10 nm particles can be eliminated and does not affect our calculation results.

6. L280-290: Ambient temperature changed substantially from spring to winter as indicated in the experimental section. The authors may also want to consider the role of weather in affecting the nucleation rate.

Response: On the same day, ambient temperature at the street site and on the rooftop can be reasonably assumed to be same by considering only $\sim$500 m distance between. Considered ambient temperature alone, it should not be the direct cause for the reduced or enhanced NPF at the street site relative to the rooftop site.

7. L285: In northern China, SO2, especially during wintertime, may also come from domestic heating, which can substantially increase SO2 emission. The authors may want to include this possibility.

Response: The authors thank the comments. L285 will revise to: “2) In December, the mixing ratios of SO2 were much larger than those in April mainly due to the domestic heating.” More information will be added in the revised section 2.3: “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. 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.

8. Section 3.5: Clear particle growth observed at a ground site is often associated with a regional NPF event. The short burst of nucleation events reported here may indicate that the air parcels were frequently disrupted by the urban micrometeorology conditions, which should be further investigated.

Response: In section 3.5, the duration period of Class II NPF events lasted for 4-8 hours when the wind speed larger than 4m/s. This strongly implied the Class II NPF events were likely to occur in a regional scale. Similar to Class II NPF events with the particle growth to be undetectable presented in this study, extremely low growth

rate of newly formed particles ($\sim$ 1nm h-1) in Beijing was also previously reported by Wehner et al. (2004). In our unpublished data, the authors simultaneously observed Class II NPF event and NPF event with extremely low growth rate at $\sim$240 km distance (Fig. 3, the case will also be presented in Supplementary). In the last three years (data unpublished), we had simultaneous observations of NPF events at 100-500 km distance. The authors obtained six cases based on simultaneous observations at two locations, i.e., one case featured by Class II NPF vs Class II NPF, four cases featured by Class II NPF vs NPF with an extremely low growth rate, one case featured by Class II NPF vs NPF with “banana shape” particle growth. The authors strongly believed that Class II NPF events lasted for 4-8 hours should be considered as regional NPF events.

References:

Fruin, S. A., Winer, A. M., and Rodes, C. E.: Black carbon concentrations in California vehicles and estimation of in-vehicle diesel exhaust particulate matter exposures. Atmos. Environ., 38(25), 4123-4133, 2004.

Hoyle, C. R., Boy, M., Donahue, N. M., Fry, J. L., Glasius, M., Guenther, A. Hallar, A. G., Huff Hartz, K., Petters, M. D., Petäjä, T., Rosenoern, T., and Sullivan, A. P.: A review of the anthropogenic influence on biogenic secondary organic aerosol. Atmos. Chem. Phys., 11(1), 321-343, 2011.

Meng, H., Zhu Y. J., Evans G., and Yao X. H.: An approach to investigate new particle formation in the vertical direction on the basis of high time-resolution measurements at ground level and sea level. Atmos. Environ., 102, 366-375, 2015a. Meng, H., Zhu, Y. J., Evans, G., Jeong, C. H., and Yao, X. H.: Roles of SO2 oxidation in new particle formation events. J. Environ. Sci., 30, 90-101, 2015b.

Ortega, I. K., Donahue, N. M., KurtelÀąn, T., Kulmala, M., Focsa, C., and VehkamalÌĺki, H.: Can Highly Oxidized Organics Contribute to Atmospheric New Particle Formation? J. Phys. Chem. A, 120(9), 1452-1458, 2015.

Riccobono, F., Schobesberger, S., Scott, C. E., Dommen, J., Ortega, I. K., Rondo, L., Almeida, J., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Downard, A., Dunne, E. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hansel, A., Junninen, H., Kajos, M., Keskinen, H., Kupc, A., Kürten, A., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Nieminen, T., Onnela, A., Petäjä, T., Praplan, A. P., Santos, F. D., Schallhart, S., Seinfeld, J. H., Sipilä, M., Spracklen, D. V., Stozhkov, Y., Stratmann, F., Tomé, A., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Vrtala, A., Wagner, P, E., Weingartner, E., Wex, H., Wimmer, D., Carslaw, K, S., Curtius, J., Donahue, N. M., Kirkby, J., Kulmala, M., Worsnop, D. R., and Baltensperger, U.: Oxidation products of biogenic emissions contribute to nucleation of atmospheric particles, Science, 344, 717-721, 2014.

Schobesberger, S., Junninen, H., Bianchi, F., Lönn, G., Ehn, M., Lehtipalo, K., Dommen, J., Ehrhart, S., Ortega, I. K., Franchin, A., Nieminen, T., Riccobono, F., Hutterli, M., Duplissy, J., Almeida, J., Amorim, A., Breitenlechner, M., Downard, A. J., Dunne, E. M., Flagan, R. C., Kajos, M., Keskinen, H., Kirkby, J., Kupc, A., Kürten, A., Kurtén, T., Laaksonen, A., Mathot, S., Onnela, A., Praplan, A. P., Rondo, L., Santos, F. D., Schallhart, S., Schnitzhofer, R., Sipilä, M., Tomé, A., Tsagkogeorgas, G., Vehkamäki, H., Wimmer, D., Baltensperger, U., Carslaw, K. S., Curtius, J., Hansel, A., Petäjä, T., Kulmala, M., Donahue, N, M., and Worsnop, D. R.: Molecular understanding of atmospheric particle formation from sulfuric acid and large oxidized organic molecules. Proc. Natl. Acad. Sci., 110(43), 17223-17228, 2013.

Tröstl, J., Chuang, W. K., Gordon, H., Heinritzi, M., Yan, C., Molteni, U., Ahlm, L., Frege, C., Bianchi, F., Wagner, R., Simon, M., Lehtipalo, K., Williamson, C., Craven, J. S., Duplissy, J., Adamov, A., Almeida, J., Bernhammer, J. A. K., Breitenlechner, M., Brilke, S., Ehrhart, S., Dias, A., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Gysel, M., Hansel, A., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Keskinen, H., Kim, J., Krapf, M., Kürten, A., Laaksonen, A., Lawler, M., Leiminger, M., Mathot, S., Möhler, O., Nieminen, T., Onnela, A., Petäjä, T., Piel, F. M., Miettinen, P., Rissanen,

M. P., Rondo, L., Sarnela, N., Schobesberger, S., Sengupta, K., Sipilä, M., Smith, J. N., Steiner, G., Tomè, A., Virtanen, A., Wagner, A. C., Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P. L., Carslaw, K. S., Curtius, J., Dommen, J., Kirkby, J., Kulmala, M., Riipinen, I., Worsnop, D. R., Donahue, N. M., and Baltensperger, U.: The role of low-volatility organic compounds in initial particle growth in the atmosphere, Nature, 533, 527-531, 2016.

Wehner, B., Wiedensohler, A., Tuch, T. M., Wu, Z. J., Hu, M., Slanina, J., and Kiang, C. S. Variability of the aerosol number size distribution in Beijing, China: New particle formation, dust storms, and high continental background. Geophys. Res. Let., 31, L22108, 2004.

Zhang, R., Wang, L., Khalizov, A. F., Zhao, J., Zheng, J., McGraw, R. L., and Molina, L. T.: Formation of nanoparticles of blue haze enhanced by anthropogenic pollution. Proc. Natl. Acad. Sci., 106(42), 17650-17654, 2009.

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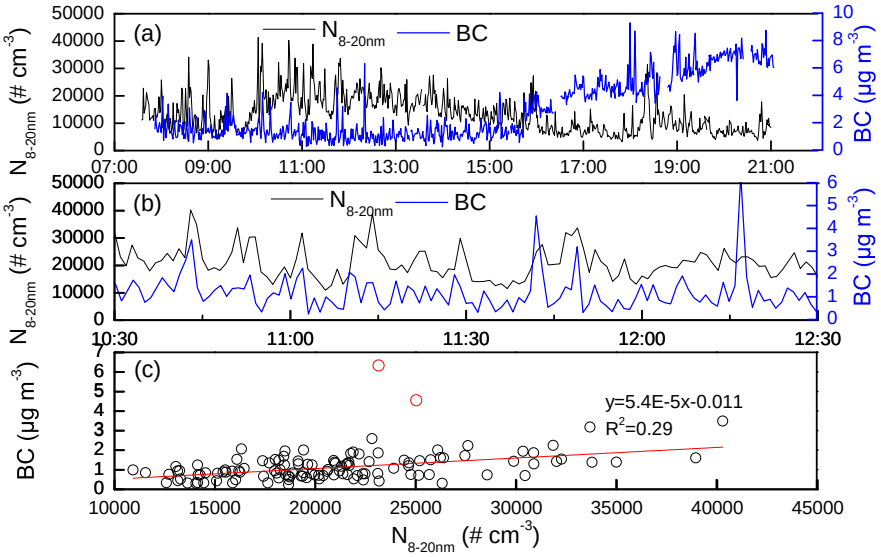

Fig. 1. The nucleation mode PNC and BC on 22 December, 2010. (a, b: time series of nucleation mode PNC and BC; c: relationship between nucleation mode PNC and BC during 10:30-12:30)

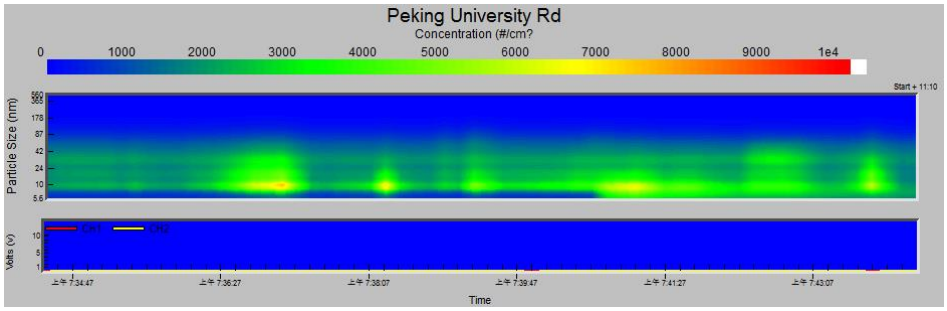

Fig. 2. Raw FMPS data showing vehicle spikes.

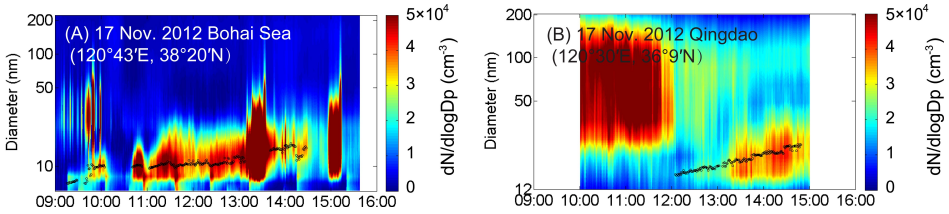

Fig. 3. Simultaneous observed Class II NPF event and NPF event with extremely low growth rate at ∼240 km distance.