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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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This manuscript investigates new particle formation (NPF) observed simultaneously at two sites in a polluted urban environment. The analysis is based high-time resolution measurements, which increases the originality of the results. The background for this study (section 1) as well as the used methods (section 2) are very well written. Contrary to this, there are serious problems in how many of the results, have been interpreted. As a result, a large part of section 3 needs substantial revisions, and most of the sections 3.4-3.6 need to be entirely re-written. My detailed comments in this regard are given below.

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

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and revise our manuscript accordingly.

Major comments:

The authors provide two very general statements based on their results: 1) reduced NPF at street site compared to rooftop during spring, and 2) enhanced NPF at street site compared with rooftop in winter. These finding are supported by only 1-2 cases (days) of observations, which is way too little to make this kind of a general conclusion.

Response: In revision, the authors will add “At the street site, the reduced NPF events always occurred in the springtime while the enhanced NPF events always occurred in the wintertime.”

The authors would like to believe the sufficiency and uniqueness of evidences are crucial to evaluate the quality of scientific studies. This is because the number of cases for gravitational wave observation in 2016 and a recent NPF study reported by Bianchi et al. (2016) was even smaller than those presented in this study. The authors thereby abide by a principle, i.e., it is theoretically reasonable, multiple-evidences supported and no exception against it, to justify our results on reduced NPF at the street site, i.e., 1) Considered the widely recognized the importance of condensation sink in new particle formation (NPF), reduced NPF at the street site is theoretically expected and repeatedly occurred in the springtime. The authors provided three types of evidences from different angles to confirm the reduced NPF rather than simple comparison between rooftop site and street site measurements, 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 dif-

ference of that on non-NPF days (Figs. 3 and 4 in the origin version). In addition, the authors also provided three types of evidences from different angles, rather than simple comparison between rooftop site and street site to confirm the enhanced NPF in the wintertime, 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).

According to the comments, the authors will revise the manuscript to make the unique evidences to be more obvious.

The used proxy for gaseous sulfuric acid (SA) concentration has two problems: 1) it has been developed and evaluated for moderately-polluted sites only, so its applicability in highly-polluted sites like this one may be questionable.

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 ambient air to the sampling site during the NPF 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 ambient air exactly meets the reviewer claimed, i.e., the proxy for calculating gaseous sulfuric acid (SA) concentration is applicable only under clean to moderately-polluted atmospheres. The authors thereby believe that our approach is consistent with the well-established knowledge and is thereby scientifically valid.

2) SO2 is measured at rooftop site only, so it is unclear how well this represents SO2 in the street site. Also, the ratio in the SO2 concentration between the street site and rooftop is likely to be different between spring and winter, and there is no means to

estimate this difference. As a result, the authors need to be very careful when making any interpretations that rely on estimated SA concentrations.

Response: The authors thank the comments. 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 apparent 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.

Class II NPF events have very low particle growth rates above 10 nm. All theoretical arguments indicate that >10 nm particles grow faster than smaller particles, and practically all observations on size-resolved particle growth rates support this view. This lead to a serious question: what is the origin of these particles? More specifically, if there are little condensable vapours to growth >10 nm, there should be even less vapors to grow smaller particles. One possible explanation for this is that particle of Class II originate from very local NPF, in which high local vapor concentrations initial nucleation and make the formed particles to grow very rapidly to a few nm, even to 10-20 nm. This rapid growth is then stopped due to atmospheric dilution of emitted vapors. This kind of process has been reported to occur in some coastal areas (Mace Head), in car exhaust to ambient air, and also close to other localised combustion sources. If

Case II event are caused by very localized sources, it is questionable to compare NPF between the street site and rooftop in such cases.

Response: The reviewer's first statement is probably contradictory to the truth. For example, the data results in Table 1 recently reported by Yu et al. (2016) fight against the reviewer's first statement. In the first publication on NPF events in Beijing (Wehner et al., 2004), the observed growth rate of new particles was as low as ~1 nm h-1. In the study, however, the formation of new particles started around 07:00 after sunrise and the initial size of newly formed particles was ~5 nm. The results also indirectly fight against the reviewer's statement. Theoretically, when the volume concentration of particles is considered, the amount of chemical species required for growing >10 nm particles was much larger than that for <10 nm particles. For example, the amount of chemicals required for growing particles from 10 nm to 12 nm was about six times larger than particles grew from 3 nm to 5 nm. Furthermore, the coagulation growth is important for <10 nm ambient particles while it is negligible for >10 nm ambient particles. As reviewed by Vu et al. (2015), the particle number size distribution (PNSD) of vehicle or combustion plumes character the typical peak number mode such as at 30 nm, 50 nm, 70-80 nm, etc. In our study, when the NPF events in Class II occurred, the nucleation mode particles overwhelmed and other particle modes were negligible. The duration period of Class II lasted for 4-8 hours with the wind speed >4m/s, suggesting they probably happened in regional scale. The authors have no idea to link NPF in the urban atmosphere of Beijing (an inland megacity where ocean-derived reactive iodides were unexpected) with those in rural coastal atmospheres, e.g., Mace Head where ocean-derived reactive iodides could be important precursors for NPF events. The authors may have no comments on the reviewer's speculation.

The authors use condensation sink (CS) in interpreting their results. This problematic. The particles are formed below 2 nm size (J<2), but the authors calculate the formation rate of 8 nm particles (J8). The value of J8 depends on 3 quantities. J<2, CS and the growth rate of particles below 8 nm. Since neither J<2 nor the sub-8 nm growth rate

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are known, it is impossible to infer how CS might affect J8 in the observed cases.

Response: The authors fully respect the reviewer's knowledge on the issue. However, the condensation sink has been widely used to argue the occurrence of NPF in literature when neither J<2 nor the sub-8 nm growth rate were not available, e.g., Kulmala et al. (2004, 2016).

The authors assumed that only biogenic organics could influence NPF and subsequent growth. Why? There certainly large anthropogenic emissions of organic vapours in this kind of environment, and the oxidation of such vapors is very likely to produce low-volatile compounds that could affect nanoparticle formation and growth.

Response: The authors never assumed "only biogenic organics could influence NPF and subsequent growth" in the manuscript. The role of oxidation products of biogenic VOC in NPF events have been 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."

Considering the points highlighted above, many of the interpretations made in sections 3.4-3.6 are not justified. The most problematic of these is section 3.6 which is highly speculative.

Response: The comments are general and don't contain helpful information for revision. The authors thank the reviewer's comments and try our best to respond and revise our manuscript accordingly.

Minor comments

I would recommend using terms other than short-term and long-term NPF events. In atmospheric time series, long-term usually means something that last for years or at least for months.

Response: Agree. It will be revised as "short-lived NPF events, regional NPF events" (Stanier et al., 2010; Jeong et al., 2010).

line 208: should be written: . . .only lasted for few minutes

Response: It will be corrected in the revision.

lines 254 and 270: did't detail is a strange expression. Please modify

Response: The sentences are indeed ambiguous and unnecessary. Therefore, it will be deleted in revision.

line 320: what is meant by ..reaction should proceed to solid state

Response: It will be revised as "reaction should proceed to solid state, i.e., the gases start to partition on the particle phase."

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