Response to reviewer #2

We appreciated referee#2's positive suggestions and constructive comments. Our point-to-point replies to the referee's comments are listed below.

Hong et al. presents a measurement report on wintertime new particle formation (NPF) in the rural area of North China Plain, exploring its influencing factors and possible formation mechanism. While NPF in urban cities of China are relatively well investigated, measurements in the rural areas are rather not enough to understand its underlying mechanisms. This manuscript is of great interest to readers of general aerosol formation, particularly in the NPF research. However, the following issues/concerns need to be addressed before it can be accepted for publication in the journal.

1. The sulfuric acid (SA) concentration in this study was calculated according to proxy proposed by Petaja et al. (2009). However, Lu et al. (2019) proposed a better proxy for estimating SA concentration in urban Beijing. It would be beneficial to compare both proxies for their performance since Petaja et al.'s proxy is based on measurements in boreal environments while Lu et al's one might be more applicable to the current study.

Response: We thank the reviewer for the suggestions and agree with the reviewer. We recalculated the SA concentration using the proxy proposed by Lu et al. (2019). All the corresponding figures, tables and discussion were modified accordingly.

2. This study measured only particle number size distribution and no potential nucleating precursors (e.g., sulfuric acid, amines, carboxylic acids) were measured. A SA-DMA mechanism was proposed based on the similarity of correlations of the particle formation rate with sulfuric acid concentration for this study and for the Cloud studies. It seems that proposing such a mechanism based solely on this similarity does not make any sense, providing no any measured DMA concentration in this area. In addition, how can the authors ensure the base is DMA rather than any other amines?

Response: We agree with the reviewer that without direct measurements of potential nucleating precursors, it might be improper to make such a strong conclusion regarding the nucleation mechanism. Therefore, we focused more on the comparison of the NPF between our study and that observed at urban Beijing. For example, we did more analysis by calculating the 72-hour back trajectories of air masses arriving at our site as well as at urban Beijing. We found that that the transport paths of the air masses arriving at our site was roughly similar to that of urban Beijing, both originating from Siberia area where concentration of gaseous pollutants and particulate matter was typically quite low, which is shown as an example on the date of 7 Dec 2018 in Fig. 1 below. Together with the fact that NPF concurrently occurred at urban Beijing during the same days, we hypothesis that NPF events during these days at current region might be a regional phenomenon, most likely sharing the same or similar nucleation mechanism. This further suggests that SA-DMA nucleation, which was confirmed for urban Beijing, could potentially be the dominating mechanism for GC site. We agree that our previous conclusion sounds quite arbitrary and we thereby rephrased our statement in this section, as shown below:

On line 297-305:

"*To further understand the dominating nucleation mechanism in the rural atmosphere of NCP in*

China, we plotted the measured formation rate of 1.3 nm particles ($J_{1.3}$) against the simulated H_2SO_4 concentration and compared the results to previous studies conducted in different environments, as shown in Fig. 4. As illustrated by the significant correlation between the concentration of sulfuric acid and the particle formation rates, sulfuric acid is considered to be the driving species in the initial steps of NPF as confirmed conventionally. However, the obtained $J_{1.3}$-H_2SO_4 relationship for current environment appeared to deviate largely from those obtained by other studies. If only referring to the slope of the $J_{1.3}$-H_2SO_4 relationship, our results seem to approximate most to the ones measured by these CLOUD (The Cosmics Leaving OUtdoor Droplets chamber) experiments based on the mechanism of H_2SO_4-DMA nucleation. However, without the direct measurements of other potential precursors, the molecules stabilizing H_2SO_4 clustering still remain unclear."

On line 307-317:

"*Comparing the particle formation rates reported in different environments in China, our results were of the similar magnitude as that in Beijing (Cai et al., 2021), an urban site in the NCP. It has to be noted that their study was conducted during a much longer time and completely covered the measurement period of our study. More importantly, during the five days of events in our study, NPF concurrently occurred at their measurement site (Liu et al., 2020). Additionally, for these five event days air masses arriving at our site followed similar transport paths to that at urban Beijing, both originating from Siberia areas, where concentration of gaseous pollutants and particulate matter was typically quite low, through the northwest of the observational sites. Taking both evidence, we hypothesis that NPF events during these days in this area might be a regional phenomenon, sharing the same or similar nucleation mechanism. Cai et al. (2021) and Yan et al. (2021) further concluded that H_2SO_4-DMA was the dominating nucleation mechanism for urban Beijing with an additional support from the measured C2-amine concentration. Considering the similarities between these two sites, we speculated that the clustering of H_2SO_4 with DMA may also dominate the nucleation process at our site during winter, though future work is needed to verify current hypothesis.* "

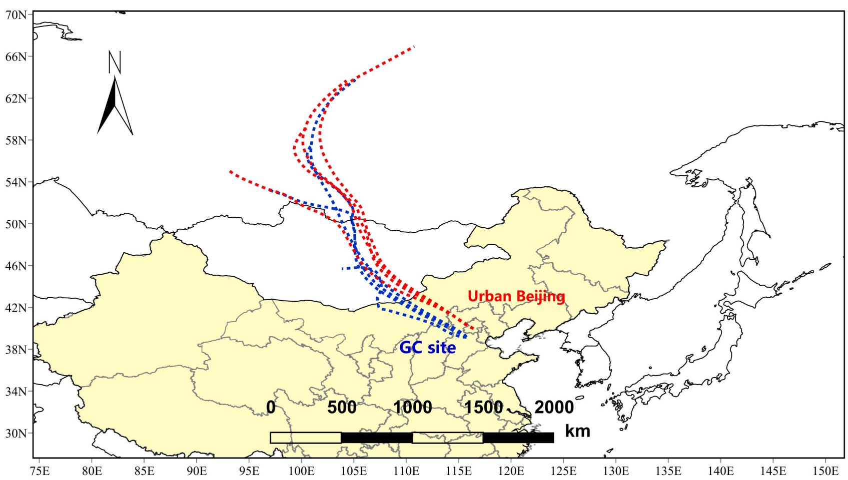

Figure 1: 72-hour back trajectories of air masses arriving at our GC site as well as urban Beijing on December 7, 2018.

3. The exclusion of SA-acid mechanism was based on Figure S1 which show a bad correlation between J and SA*diacids. However, the rationale needs to be validated since concentrations of both SA and diacids varied in the correlation plot, leading to violation of thermodynamic roles. This approach is not convincing.

Response: Thanks for the comments. We agree with the reviewer and thus did more data analysis regarding the temporal pattern of these precursors concentration instead of only looking at the correlation plot. As illustrated in Fig. 2 below, the concentration of these four dicarboxylic acids during NPF events were in general lower than that during non-event days, on which sulfuric acid was also abundant that clustering of these two precursors should be more favored but NPF still did not occur. By further looking at the diurnal trend of the level of these precursors in the atmosphere for NPF days (shown in Fig. 3), we found that the rise in the SA concentration during day time of NPF events was not concurrently observed with or followed by the elevation of the diacids content. On the contrary, the signals of these diacids normally peaked during nighttime with the lowest level around daytime when NPF was typically initiated. Together with these evidence, we hypothesis that H_2SO_4-diacid may not be the dominating mechanism for the NPF of current environment. We rephrased the discussion in this section accordingly.

On line 325-336:

"*However, as illustrated in Fig. S4, the concentration of these four dicarboxylic acids during NPF events were in general lower than that during non-event days. Furthermore, during the daytime of events days when NPF was typically initiated, the signals of these diacids obtained from the I-CIMS did not show clear increase, unlike sulfuric acid, but rather elevated during the night time (see Fig. S5), being obviously different from the case of Pingyuan. Hence, the involvements of diacids during the initial steps of nucleation under current rural atmosphere might not hold. This statement does not necessarily mean that our previous inference was incorrect, but on the other hand, provides some hints that though NPF events in the NCP is regional, there might be no uniform theory but multiple mechanisms coexisting to explain its feature with the dominating one varying upon different emission patterns or meteorological conditions.*"

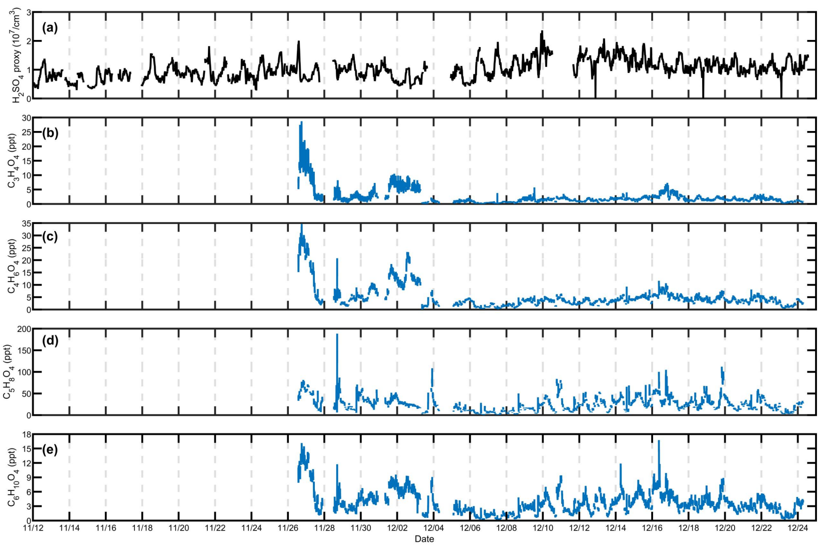

Figure 2: Measured concentration of these four dicarboxylic acids as well as the concentration of SA proxy during our study.

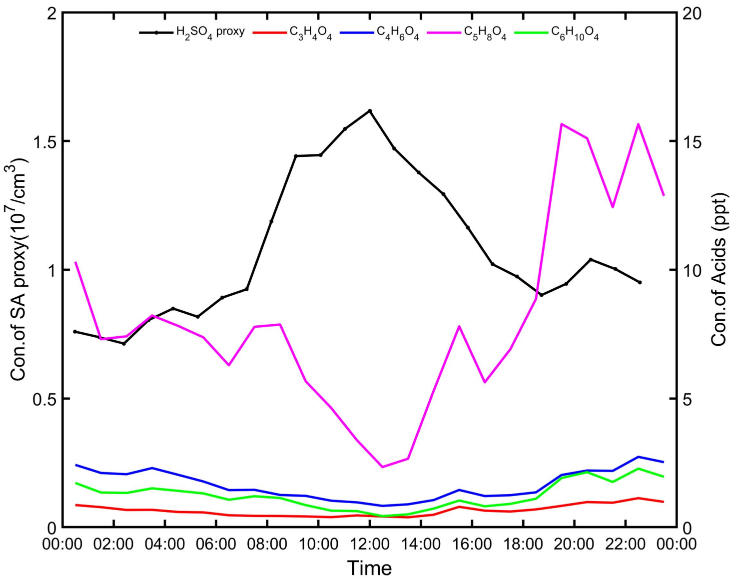

Figure 3: Diurnal trend of the concentration of SA as well as these dicarboxylic acids in the atmosphere for NPF days.

4. The authors conclude that the controlling factor for NPF is the condensational sink which is based on qualitative comparison of CS characteristics between the measurement site and urban Beijing. However, some quantitative representations are needed to make sure the CS indeed is the most important factor for determining the occurrence of NPF at the site.

Response: Thanks for the comments. Here, we used a dimensionless criterion, *I*, proposed by Cai et al. (2021) to quantitatively represent our conclusion that the controlling factor for NPF is the condensational sink. The description of *I* (we added a new section in the data processing part) and corresponding results and discussions were added in the revised manuscript. The calculated *I* as a function of the condensational sink was also shown here for clarification.

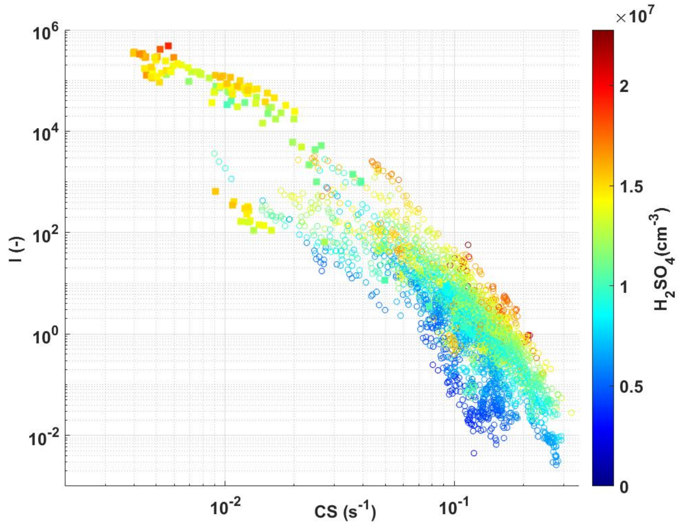

Figure 4: The demensionless criterion, *I*, as a function of CS. The colorbar indicates the concentration of H_2SO_4. The squares indicate NPF days while the circles are for non-event days.

After line 206:

"*Sect 2.3.5 Indicator for the occurrence of NPF*

Previously, McMurry et al. (2005) proposed a dimensionless criterion, L, to predict the occurrence of NPF events in the atmosphere. After being validated in diverse atmospheric environments (Kuang et al., 2005; Cai et al., 2017;), L has been used to investigate the governing factors for NPF events under typical atmospheric conditions. Upon recently, Cai et al. (2021) proposed a new indicator, I, on the basis of L, which only considered H_2SO_4 to drive the growth. The new indicator was calculated by further taking into account the condensation of other species, for instance, amines and has been suggested to be a good quantitative representation for the occurrence of NPF after comparing with L for NPF events observed at urban Beijing (Deng et al., 2020). The detailed information to calculated I can be found in Cai et al (2021)."

Line 361-390:

"*Was this also true for rural atmosphere in the NCP? By comparing with non-event days at our site (see Fig. 5a), we noticed that H_2SO_4 level was not significantly higher but sometimes even lower than that during non-event days. In other words, the abundance of H_2SO_4 did not always lead to NPF; and it was only when CS was significantly lowered that the event became more likely to occur. This strongly demonstrates the similarity between our site with urban Beijing, that CS would be the limiting factor for the occurrence of NPF. However, we noticed that there were a very few cases (two cases) that CS was somewhat quite low, being quite close to that under those event days, yet NPF still did not occur. The most plausible explanation for this could be on the one hand the lowered H_2SO_4 concentration at these days (as shown in Fig. 5a) and on the other hand the other nucleating species rather than H_2SO_4 may not be always enough to initiate nucleation at this site.*

As previously stated that the dimensionless criterion, I, is a good quantitative indicator to predict whether an NPF occurs or not during a certain day, we plotted I against the condensational sink for NPF days and other days under different H_2SO_4 level. Cai et al. (2021) found that the larger the I value, the higher frequency that NPF events occurred for both urban Beijing and Shanghai, which was also clearly revealed by our results. On the one hand, as shown in Fig. 5b, the largest I values were mostly observed for NPF days, confirming its feasibility in predicting the occurrence of NPF events. On the other hand, the obtained I anti-correlated with CS quite well, while the influence from the available H_2SO_4 was not obvious. This strongly suggests that CS was the dominating factor governing the appearance of NPF events at current environment, being highly consistent with the feature in Beijing."

Below are rather minor:

- There are lots of typos, ill-sentences through the manuscript which need to be corrected.

Response: Thanks for the comments, we went through the manuscript and corrected all relevant ill-sentences.

- L39, at an urban site

Response: Thanks for the comments, we changed to "*at an urban site*".

- L61 and throughout the text, H2SO4 needs subscript for 2 and 4. There are lots of such typos in the text for H2SO4 and other molecular formula

Response: Thanks for the comments, we went through the manuscript and corrected all typos relevant to subscription.

- L61, sulfuric acid molecules, follow a plural form

Response: We added "*molecules*" after "*sulfuric acid*".

- L67, newly form

Response: We changed to "*newly formed*".

- L73-74, I don't think the chemical composition of 1-3 nm particles has been speciated thus far.

Response: Thanks, we agree and we deleted "*as well as the chemical composition*" in the sentence.

- L80, important contributors to atmospheric nucleation

Response: We changed "*participating in*" to "*to*".

- L84, formation

Response: We changed "*formations*" to "*formation*".

- L137-138, I think 3080 include DMA inside

Response: We deleted "*, a differential mobility analyzer (DMA, model TSI 3081)*" in the sentence.

- L188&198, where, ???

Response: We deleted the comma after "*where*".

- L203, particles in new mode? What does this mean?

Response: We revised the whole paragraph as:

"*Days of NPF events was classified according to the method proposed by Dal Maso et al. (2005) and Kulmala et al. (2012), in which (a) a burst in the concentration of sub-3 nm particles or clusters was observed and (b) these particles had a continuous growth over a time span of hours (e.g., usually more than ten hours). If no clear growth of these newly formed particles (sub-3 nm particles) can be identified, the day was classified as an undefined day. The day without both the burst of sub-3 nm particles and their subsequent growth was considered as a non-event day.*"

- L207, discussion

Response: We changed it to "*Results and discussion*".

- L208, section 3.1.

Response: We added "*3.1*" before "*General characteristics of NPF at GC site*".

- L215, at the current site

Response: We added "*the*" before "*current site*".

- L222 & others, lower than, not “compared to”

Response: We changed “*compared to*” to “*than*”.

- L226, what are they referred to?

Response: We changed “*They*” to “*Yue et al. (2009) and Wang et al. (2013)*”.

- L253&others, “Note that” is simple than “It has to be noted that”

Response: We changed “*It has to be noted that*” to “*Note that*”.

- L256-257, it is hard to understand this sentence

Response: We revised the sentence to:

“*It has to be noted that most atmospheric formation rate reported in China was based on the measured formation rate at relatively larger size, i.e., 3-10 nm, which is so called the “apparent” particle formation rate. In order to derive the formation rate of critical clusters from the “apparent” particle formation rate (Kulmala et al., 2017), the nuclei GR or GR at sub-3 nm is needed but usually remains unclear.*”

- L262, formation rates vs those

Response: We used “*formation rates*” in the revised manuscript.

- L266, in those polluted atmospheres

Response: We changed “*in those polluted atmosphere*” to “*in those polluted atmospheres*”.

- L288-289, that clause is ambiguous here

Response: We revised the sentence to:

“*This could be attributed by the high CS or CoagS at those polluted environments as the growth of small particles is limited, which are more vulnerable to the coagulation scavenging.*”

Reference

Cai, R., Yan, C., Worsnop, D. R., Bianchi, F., Kerminen, V-M., Liu, Y., Wang, L., Zheng, J., Kulmala, M., & Jiang. J., (2021) An indicator for sulfuric acid–amine nucleation in atmospheric environments, Aerosol Science and Technology, 55:9, 1059-1069, DOI: 10.1080/02786826.2021.1922598.

Lu, Y., Yan, C., Fu, Y., Chen, Y., Liu, Y., Yang, G., et al. (2019). A proxy for atmospheric daytime gaseous sulfuric acid concentration in urban Beijing. Atmospheric Chemistry and Physics, 19(3), 1971–1983. https://doi.org/10.5194/acp-19-1971-2019.