A point-to-point response to referee #1

We thank you for your insightful comments to improve our work. A point-by-point response to the comments is given below. Your comments are shown in *red italics*. Our responses are given in black. Revised text is shown in blue in the response. Line numbers in the responses correspond to those in the revised manuscript.

1. This paper describes results from atmospheric nucleation studies in Chinese cities and its technical aspects appear to be at the state of the art in this area. While the manuscript is admirably succinct, it also admirably touches on all (at least most) of the aspects of the important information. Yet there are sentences that are difficult to understand, and it seems that some inferences and conclusions are not well-supported (the first may be causing some of the second.) The main conclusion of the paper is that H_2SO_4-DMA nucleation can explain the observations in these cities. A secondary one is that OOMs are needed to explain growth rates of newly nucleated particles.

Response:

Thank you for these positive and constructive comments. We have improved the writing and rewritten the sentences that were difficult to follow. We hope the revised manuscript clarifies the evidence for our main conclusions (see below).

2. Support for the main conclusion is not well presented. For example, line 165 states that SA-DMA was 'identified ' as the dominate (sic) NPF mechanism. This is not a finding if it is solely based on Figure 1 (correlation and causation are falsely linked.) For example, line 165 states that SA-DMA was 'identified ' as the dominate (sic) NPF mechanism. This is not a finding if it is solely based on Figure 1 (correlation and causation are falsely linked.) The analysis presented in section 3.2 is focused on teasing out SA and temperature dependencies. Should not a dependence on DMA be important for identifying SA-DMA nucleation? Figure S3 is mentioned as supporting the SA-DMA mechanism but on the face of it the $J_{1.4}$ sim.-meas. correlation is not good. Similarly for $J_{1.7}$ (figure 7b). For both of those, it looks like the measurements range over about 1/2 the orders of magnitude that the simulations do: this is not support for the mechanisms in the simulations. Assuming SA dimer is an indicator of SA-DMA nucleation, the best support is Figure 4 but SA_2 scaled is not presented here (confused by the text on lines 220-224.) Figure 5 does present SA_2 scaled instead. Good: it does show a decently strong temperature dependence (would be helpful to have data in Figure 4 colored by temperature also.) But two things are bothersome in this analysis: the above-mentioned dependence on DMA is washed away and details are scant on the reason behind the temperature dependence of the simulations (bond strength, and only for the SA.DMA cluster?)

Response:

We thank you for these constructive comments. To better support the main conclusions of this study, we have revised the manuscript in the following aspects:

(1) We have revised the description and implication of each figure, and removed misleading statements that are not supported by the figures.

(2) We have added a correlation analysis between neutral SA-DMA clusters and the number concentration of

sub-3 nm particles to provide support for SA-DMA nucleation.

(3) We have rewritten the discussions on the influence of DMA on nucleation.

(4) We have added statistics of the NPF frequency in different campaigns. The NPF frequency shows a strong negative correlation with temperature, providing support for the significant influence of temperature on atmospheric nucleation.

(5) We have expanded the discussion to better explain the inhibitory effect of temperature on NPF.

(6) We have added results of multiple field studies outside China, and compared them with those in this study, highlighting the main contributions and the global relevance of our work.

With these improvements, we think the support for our inferences and conclusions is clarified. We briefly summarize the main conclusions and their supporting evidence below:

Conclusion #1: SA-DMA nucleation can explain the observations in these cities. Supporting evidence includes:

(1) A good correlation between particle formation rate and [SA_1] was observed in our field measurements. The results for nucleation rate versus [SA_1] indicate highly efficient nucleation mechanisms, consistent with the curves from CLOUD experiments and other atmospheric studies under SA-DMA nucleation (Figure 1);

(2) Neutral clusters composed of SA and DMA were detected, and their signals were strongly correlated with the concentration of sub-3nm particles, demonstrating their involvement in cluster formation (Figure 2 and Figure S3);

(3) Both measured [SA_2] and particle formation rates aligned with theoretical predictions using the SA-DMA nucleation mechanism (Figure 4 and Figure S7);

(4) The dependence of NPF on influencing factors, namely temperature and [DMA], was also consistent with theoretical predictions (Figures 5-6 and Figure S5).

Conclusion #2: OOMs are needed to explain the growth rates of newly nucleated particles. This is supported by the fact that the growth contributed by SA and its clusters cannot explain the initial growth (1.4-1.7 nm), and the improved agreement between measured and predicted $J_{1.7}$ when the contribution of OOMs to particle growth was considered (Figure 7).

In addition to these two main conclusions summarized by you, the major implication of this study is given: SA-DMA nucleation can explain atmospheric NPF over a large spatial scale of polluted atmosphere, and temperature is a major cause for the difference in NPF characteristics at different locations. This is supported by:

(1) The sites span a broad geographic range and encompass a variety of urban and suburban environments (Figure S1).

(2) A negative correlation between NPF frequency and ambient temperature (Figure 3c-d).

(3) The dependences of NPF on [SA_2] and particle formation rate (Figure 5-6).

The specific comments are copied below to facilitate our point-by-point response.

2.1. For example, line 165 states that SA-DMA was 'identified ' as the dominate (sic) NPF mechanism. This is not a finding if it is solely based on Figure 1 (correlation and causation are falsely linked.) For example, line 165 states that SA-DMA was 'identified ' as the dominate (sic) NPF mechanism.

Response:

Thanks, we have revised the original statement "the dominate NPF mechanism in our campaigns was identified as SA-DMA" into "the observed nucleation is likely driven by SA and enhanced by strong stabilizing precursors such as DMA. Other nucleation mechanisms are unlikely to dominate under these conditions" (lines 172-173). Here we use the relationship between the particle formation rates and [SA_1] as supporting evidence for nucleation mechanisms. It was insufficient to 'identify' a nucleation mechanism with this evidence. We presented more evidence to support SA-DMA nucleation, and all the evidence has been summarized (lines 158-161):

"SA and DMA can explain the atmospheric nucleation observed at all sites. This finding is supported by the correlation between [SA_1] and particle formation rates, the composition of detected clusters, the alignment of simulated and measured nucleation intensity ([SA_2] and particle formation rates), and the dependences of NPF on temperature and [DMA]. The first two points are addressed in this section, while the remaining evidence will be discussed in Sect. 3.2 and Sect. 3.3."

2.2. The analysis presented in section 3.2 is focused on teasing out SA and temperature dependencies. Should not a dependence on DMA be important for identifying SA-DMA nucleation?

Response:

Thanks, we have added a paragraph on analyzing the role of DMA in NPF (lines 216-227):

"Besides SA, other potential precursors related to NPF in polluted regions including DMA, NH_3 and OOMs (Figure S4). These species are known to enhance SA-driven nucleation (Kirkby et al., 2011; Almeida et al., 2013; Riccobono et al., 2014) and promote particle growth (Tröstl et al., 2016). Increasing [DMA] considerably enhances SA_2 formation under fixed temperature ranges (Figure S5), and this effect diminishes as [DMA] approaches nucleation saturation (Almeida et al., 2013). This phenomenon supports the contribution of DMA to atmospheric nucleation and is consistent with the results from a flow reactor (Jen et al., 2014). In CLOUD studies, the contributions of OOMs and NH_3 to cluster formation were almost negligible in the presence of DMA (Kürten et al., 2018; Xiao et al., 2021). Given that our field measurements exhibited similar [NH_3] and relatively low [OOMs] compared to those in CLOUD experiments (Table 2), it follows that their effects are also minor under our ambient conditions. Despite the potential participation of other precursors, the observation-simulation agreement suggests DMA is a major base that stabilizes SA clusters (Figure S5). However, [DMA] and [NH_3] were not markedly elevated during NPF periods (Figure S4). The likely reason is that the suppression of NPF by high CS masked the enhancing effect of DMA and NH_3, as they were positively correlated with CS (r^2=0.31 and 0.39, respectively, Figure S6)."

2.3. Figure S3 is mentioned as supporting the SA-DMA mechanism but on the face of it the $J_{1.4}$ sim.-meas. correlation is not good. Similarly for $J_{1.7}$ (figure 7b). For both of those, it looks like the measurements range over about 1/2 the orders of magnitude that the simulations do: this is not support for the mechanisms in the simulations.

Response:

Due to the uncertainties in determining the measured *J* from the particle size distributions, and potentially the fact that our theoretical predictions were solely based on the SA-DMA mechanism, which may miss other influencing factors on NPF, we did not expect a good correlation between the measured and predicted *J* in real atmospheric studies. Instead, we focus on the consistency in the order of magnitude of the measured and predicted *J* values. We

argue that, considering the measurement uncertainties, this is an acceptable uncertainty range for atmospheric studies. We have added clarification on this point (lines 127-142 in the Supplement):

"There is an acceptable consistency between $J_{1.4,meas}$ and $J_{1.4,sim}$ when observational and model uncertainties are considered (Figure S7). Deviations reported in previous laboratory or field studies were typically within one order of magnitude (Kürten et al., 2018; Cai et al., 2021; Xiao et al., 2021), smaller than those in our study. This discrepancy likely arises from differences in uncertainty ranges. For a single observation, the measurement uncertainty is relatively low (Freshour et al., 2014), and the resulting simulation uncertainty can be controlled within a narrow range. However, our measurement spanned several years and involved multiple sites, may amplifying the overall uncertainty in $J_{1.4}$.

The uncertainty range of $J_{1.4,sim}$ need to be analyzed basically. Overall, the output range spans approximately three orders of magnitude, indicating high model sensitivity to input parameters. Theoretically, particle formation rate is approximately proportional to $[SA_1]^4$ in SA-DMA nucleation, and this relationship is particularly evident under high CS and high [DMA] (Cai et al., 2021). Considering the uncertainty of $[SA_1]$ merely (+100%/-50%, Table S1), the propagated uncertainty of $J_{1.4,sim}$ is estimated to be +1600%/-94%. Since there is no simple algebraic relation between [DMA] and $J_{1.4}$, their quantitative dependence need be inferred empirically. An urban study reflected that $J_{1.4}$ roughly varied in proportion to twice of the change of [DMA] (1-5 pptv) accounting for other influencing factors (Cai et al., 2021). Considering the uncertainty of [DMA] (+150%/-60%) merely, the uncertainty of $J_{1.4,sim}$ is estimated to be +400%/-80%. In short, by superimposing the uncertainty of input values, the overall uncertainty in modeled $J_{1.4}$, resulting from the propagation of measured precursor uncertainties, is quantitatively reasonable."

2.4. Assuming SA dimer is an indicator of SA-DMA nucleation, the best support is Figure 4 but SA_2 scaled is not presented here (confused by the text on lines 220-224.)

Response:

We agree with you that Fig. 4 serves as evidence supporting SA-DMA nucleation mechanism, and the discussion regarding $SA_{2,scaled}$ has been deferred to the next paragraph to maintain clarity and prevent readers being confused. Furthermore, an additional purpose of this figure is to evaluate the reliability of the model, thereby supporting the subsequent scaling of relevant parameters. We have revised this paragraph (lines 248-254) as:

"Figure 4 shows that $[SA_2]_{meas}$ is in accordance with $[SA_2]_{sim}$ when considering the uncertainties, indicating SA and DMA could explain the formation of SA_2. To be specific, $[SA_2]_{meas}$ is slightly lower than $[SA_2]_{sim}$ overall. Similar discrepancies between measured and simulated cluster concentrations have also been reported in CLOUD experiments (Kürten et al., 2014). This systematic underestimation is likely attributable to measurement errors, because not all SA_2 is fully detected, as some may dissociate within the mass spectrometer (Alfaouri et al., 2022). The observation-simulation comparison of $J_{1.4}$ is shown in Figure S7, where simulation results fall within acceptable ranges upon uncertainty analysis. The consistency between measured and simulated parameters ($[SA_2]$ and $J_{1.4}$) supports the significance of SA-DMA collision in NPF."

2.5. Figure 5 does present SA_2 scaled instead. Good: it does show a decently strong temperature dependence (would be helpful to have data in Figure 4 colored by temperature also.) But two things are bothersome in this analysis: the above-mentioned dependence on DMA is washed away and details are scant on the reason behind the

temperature dependence of the simulations (bond strength, and only for the SA.DMA cluster?)

Response:

For the colored data points, we have revised not only Figure 4 (lines 256-258), but also Figure S7 (lines 190-192 in the Supplement) as:

“

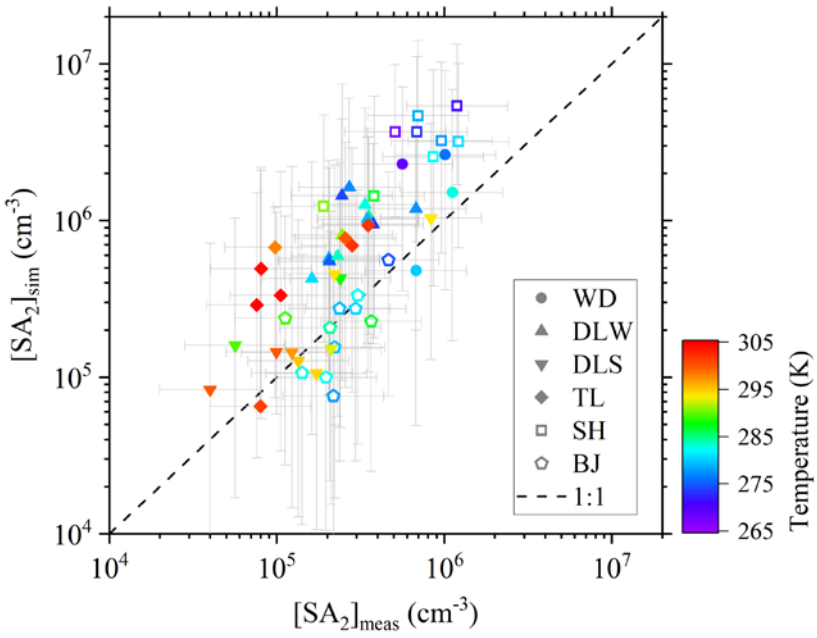

Figure 4: The comparison between $[SA_2]_{meas}$ and $[SA_2]_{sim}$. Horizontal and vertical error bars connected with each symbol indicate the uncertainties of x-axis and y-axis, respectively.”

“

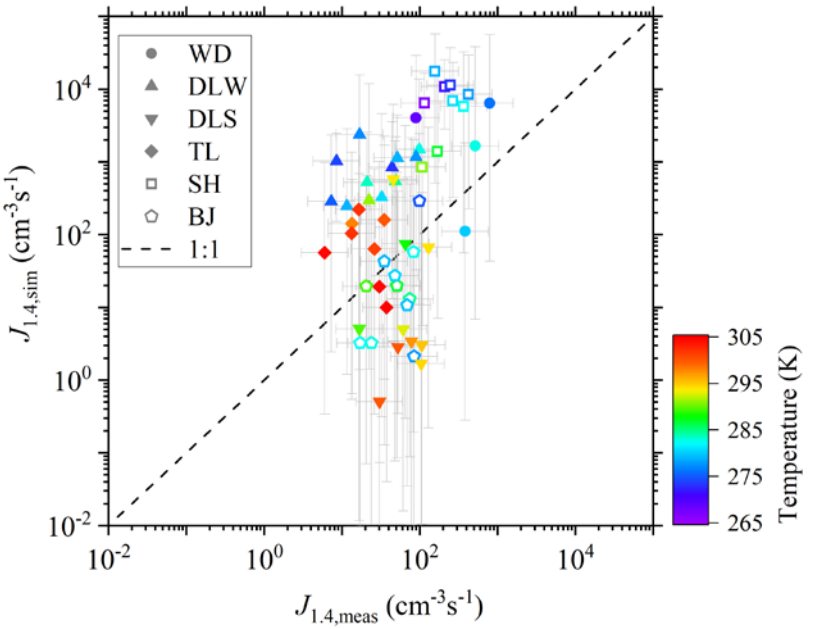

Figure S7: The comparison between $J_{1.4,meas}$ and $J_{1.4,sim}$. Horizontal and vertical error bars connected with each symbol indicate the uncertainties of x-axis and y-axis, respectively.”

For the insufficient analysis of DMA, the response to Comment #2.2 explains this concern. In short, it is undeniable

that DMA plays a critical role in the analysis of nucleation mechanisms. We were concerned that readers might overlook the significance of DMA, so we have elaborated on this aspect more clearly.

For the reason behind the temperature dependence of the simulations, we attribute the main cause to the thermal stability of the clusters, and have revised our manuscript as (lines 83-89 in the Supplement):

"Temperature modulates nucleation processes by altering the evaporation rates of clusters, which were derived from collision coefficients and the cluster formation free energy referenced from the literature (Olenius et al., 2017). Among these clusters, SA_1DMA_1 exhibits the most pronounced temperature dependence, and its net formation represents the dominant pathway through which temperature modulates nucleation processes. Reported values for the Gibbs free energy of formation ($\triangle G$) of SA_1DMA_1 at 298.15 K range from -11.0 to -15.4 kcal mol^{-1} (Olenius et al., 2017; Myllys et al., 2019; Ge et al., 2020; Han et al., 2020). Here, it was set to be -13.5 kcal mol^{-1} at 298.15 K, according to the value from Myllys et al. (2019)."

Moreover, several references to the temperature dependence of simulations were also presented in lines 263-267:

"At the molecular level, it is proposed that SA and DMA form SA_1DMA_1 clusters, which subsequently contributes to SA_2 formation, during nucleation (Olenius et al., 2017; Myllys et al., 2019). While SA_2 with one or two DMA molecules has been demonstrated to already be stable against evaporation (Jen et al., 2014), the formation of SA_1DMA_1 is a temperature-sensitive process that acts as the major rate-limiting step in clustering (Cai et al., 2022b)."

and lines 272-275:

"Theoretically, the evaporation rates of SA trimers and tetramers show limited sensitivity to temperature (Olenius et al., 2017), and their variation can be even neglected in some cluster dynamics models (Cai et al., 2021). Thus, the observed reduction in larger clusters at elevated temperatures is likely constrained by the formation of SA_2."

In addition to the point-by-point responses above, we have performed a thorough revision of the manuscript, thereby ensuring that the support for main conclusions is well presented.

3. Figure 2 also gives good indirect support to the (or a) SA-DMA mechanism but can the SA_3 and SA_4 signals be correlated to neutral cluster concentrations? They are the ones with DMA in them! This would be support of a more direct nature. Also, this figure needs a bit more explanation. What is/are S-O ions? Symbol size meaning diameter or area? Since the plots are relatively clean, a few could be tagged with logSignal values.

Response:

Regarding the first comment, we are not sure about what you specifically meant by "neutral cluster concentrations". We have interpreted it as "the number concentration of sub-3 nm particles" and have plotted a new figure (Figure S3), which showed good correlation between this quantity and both SA_3 and SA_4. The results indicated that these neutral clusters contributed to NPF. We have revised our manuscript as (line 168-171 in the Supplement):

“

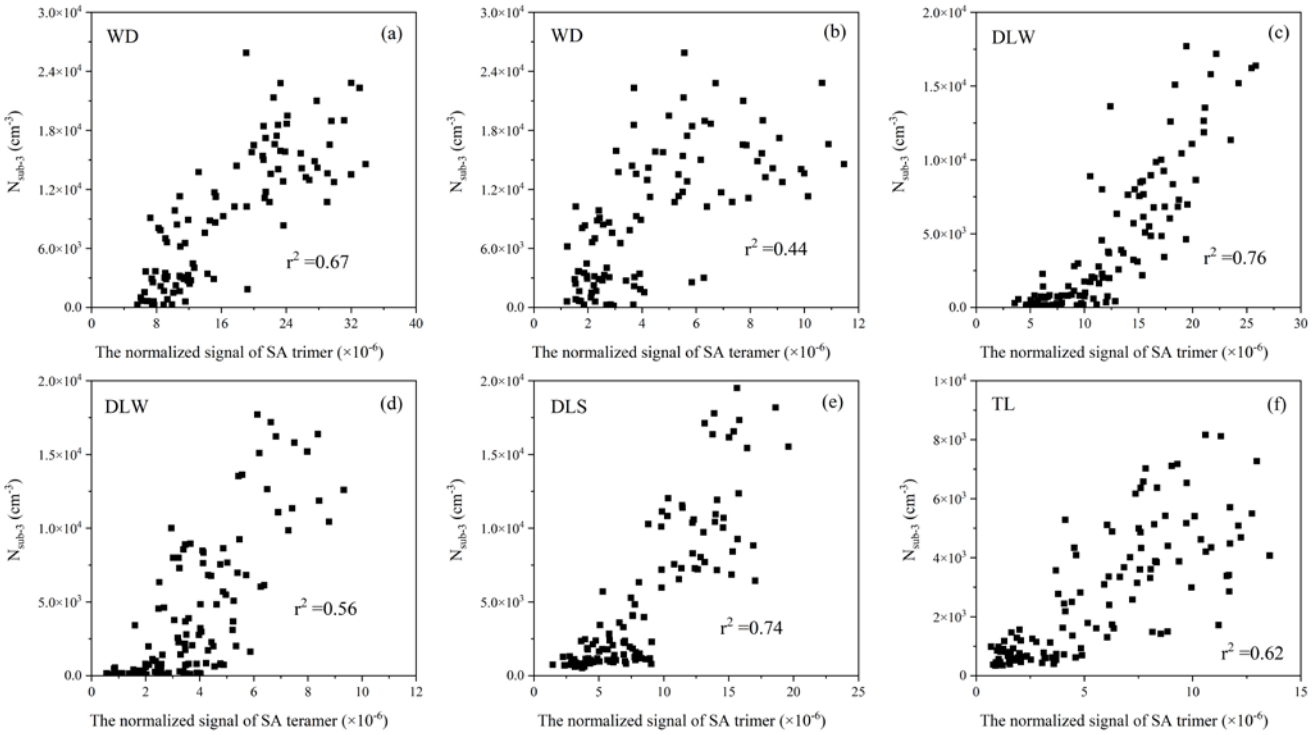

Figure S3: The correlation between the normalized signal of SA clusters and the number concentration of sub-3 nm particles：(a)-(b) January 20th, 2019 at WD; (c)-(d) January 27th, 2023 at DL in winter; (e) May 2nd, 2023 at DL in spring; (f) August 7th, 2023 at TL. Only data recorded between 06:00 and 18:00 were included in the analysis.”

We have also provided a description of this figure (lines 190-193):

“Besides, the normalized signal of SA trimer and tetramer show good correlations (r^2 = 0.44-0.76) with the number concentration of sub-3 nm particles (Figure S3). Such correlations between clusters and newly formed particles were reported in other atmospheric observations (Bianchi et al., 2016; Yan et al., 2021), indicating that these clusters typically signified the molecular clustering processes in NPF events.”

For S-O ions, they are clusters containing only sulfur/oxygen atoms beyond sulfuric acid. we have removed them, as they are not directly relevant to NPF, and retained SA and SA-DMA clusters in the figure. The area of symbol is proportional to cluster signals, and we have also annotated the logarithm of normalized signals in this figure. The revised Figure 2 is shown as (lines 197-204):

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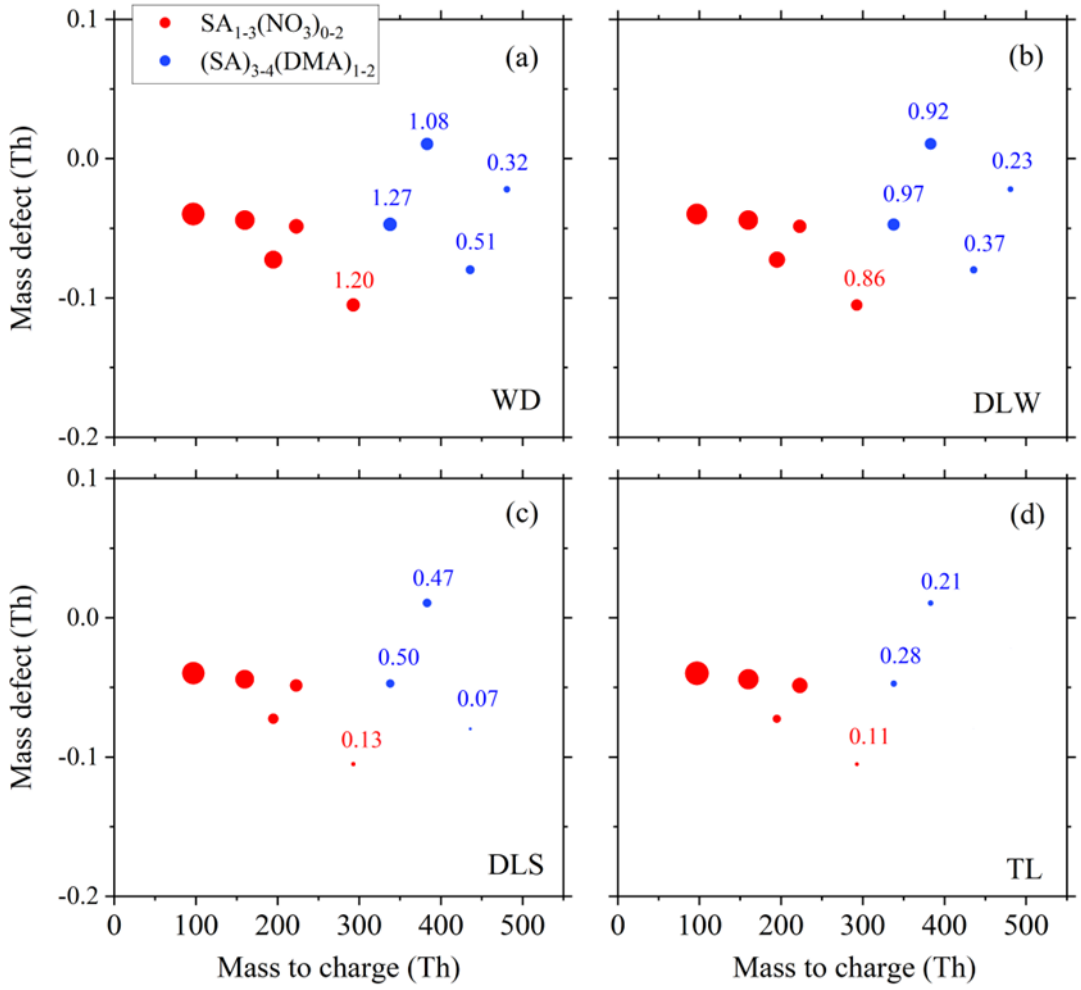

Figure 2: The mass defect of SA molecules and its clusters during four NPF events on (a) January 20th, 2019 at WD (temperature = 275 K; [SA_1] = 1.4×10^7 cm^{-3}; CS =0.055 s^{-1}; [DMA] = 3.4 pptv); (b) January 27th, 2023 at DLW (temperature = 277 K; [SA_1] = 7.3×10^6 cm^{-3}; CS =0.012 s^{-1}; [DMA] = 1.5 pptv); (c) May 2nd, 2023 at DLS (temperature = 295 K; [SA_1] = 9.5×10^6 cm^{-3}; CS =0.014 s^{-1}; [DMA] = 2.9 pptv); (d) August 7th, 2023 at TL (temperature = 304 K; [SA_1] = 2.6×10^7 cm^{-3}; CS =0.023 s^{-1}; [DMA] = 1.8 pptv). Other species detected by CI-LToF-MS were not shown, because they are not directly related to atmospheric nucleation. The area of symbol is proportional to the logarithm of normalized signal. (multiplied by a factor of 1×10^6 before taking the logarithm). The logarithm of values is annotated for larger clusters.”

4. Sentence on line 245 talks about dependence on DMA and mentions Figure S4 but that figure shows no (or even inverse!) difference in [DMA] between events and non-events.

Response:

Regarding the difference in [DMA] between events and non-events, we think you referred to Figure S4 (formerly Figure S2). In fact, the dependence of NPF on [DMA] are not contradictory to the difference in [DMA] between events and non-event. As discussed above (in the response to Comment #2.2), there was a good correlation between [DMA] and CS during NPF periods, and the suppression of NPF by high CS likely masked the enhancing effect of

DMA. We have a new figure (Figure S6), which shows a positive correlation between [DMA] and CS (lines 186-188 in the Supplement):

"

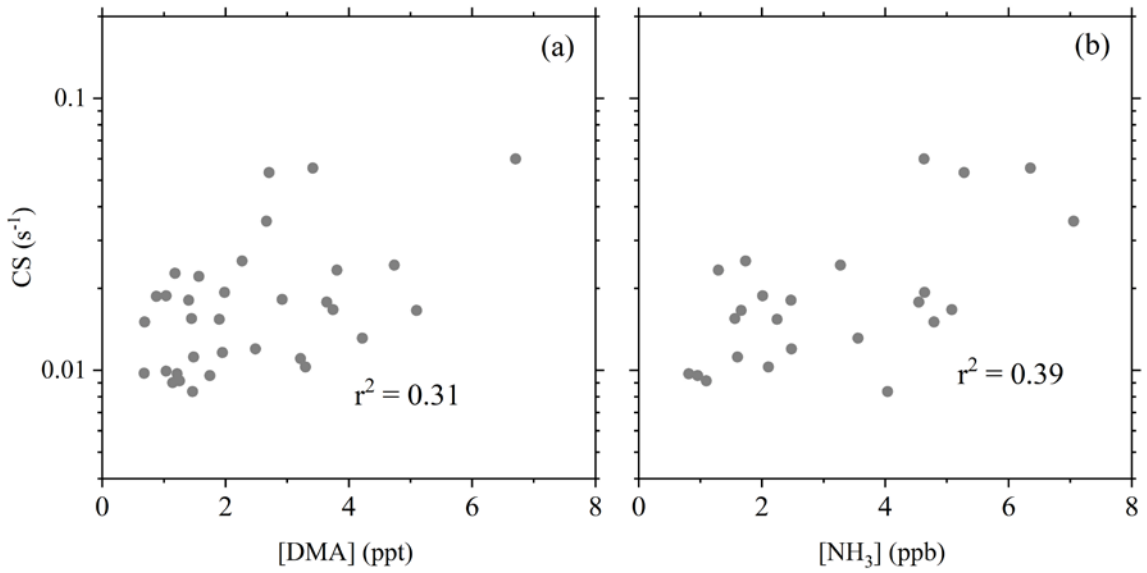

Figure S6: Correlations between the concentrations of basic precursors and CS during NPF periods: (a) [DMA] at WD, DL and TL; (b) [NH_3] at WD and DL. The NPF period is defined as the period with the maximum value of $J_{1.7}$ in each NPF event."

The dependence of NPF on [DMA] becomes discernible when other factors are accounted for, as evidenced in Figure S5 (formerly Figure S4).

5. There are many sentences with strange wording choices e.g. in paragraphs such as lines 59-70, lines 138-150 (also, this scaling procedure leaves the reader a bit uneasy).

Response:

The manuscript has been revised for better expression, logical clarity, and grammatical precision. All major co-authors contributed to this revision.

6. Lines 304-315 in the conclusions are accurate and reflect the indirect nature of the evidence for SA-DMA nucleation but what does this paper add to what is already there? It seems the present day tools are inadequate to directly resolve the question. What should be improved? Looking for some more strongly worded conclusions.

Response:

Thanks for your comments. We have improved the Conclusion section to better highlight our key findings. Using multi-site data from eastern China, our primary contribution lies in demonstrating that the SA-DMA mechanism remains applicable across broader spatial and temperature ranges. Furthermore, we provide atmospheric evidence supporting the role of OOMs in the initial growth of new particles. The revised version is (lines 348-368):

"We studied the mechanism and influencing factors of NPF on a large spatial scale by using observational data at multiple sites in the eastern region of China, including the concentrations of key chemical species, temperature and PSD.

By Comparing with previous studies that investigated atmospheric nucleation mechanism in individual sites, we have showed the applicability of a similar mechanism over a large geographic region. Based on the correlation between [SA_1] and particle formation rate, the identification of key clusters, and comparisons between simulations and measurements, we concluded that nucleating processes, mainly exemplified by SA_2 and $J_{1.4}$, could be largely attributed to SA-DMA collision, although other precursors, such as NH_3 and OOMs, might also participated. However, SA and its clusters were insufficient, at least at DSL and BJ, to explain the initial growth of nucleated particles, while OOMs make great contribution to this process, thereby affecting $J_{1.7}$, which was derived from model-observation comparisons. While previous understanding of the contribution of OOMs to initial particle growth was reflected by chamber studies, our study provides supporting evidence from atmospheric observations. Given the considerable spatial separation among five sites, we infer that within this extensive urban agglomeration, SA and DMA are capable of describing atmospheric nucleation up to 1.4 nm, whereas OOMs are potentially involved in in subsequent growth. This may also apply to other populated and polluted regions, where the NPF mechanism warrants investigation.

As for influencing factors, the occurrence of NPF was governed by [SA_1] and CS, whereas the frequency and intensity of NPF were mainly determined by temperature, which generally exhibited a negative correlation with NPF over a wide temperature range. Compared with previous studies investigating NPF dependence on temperature from a temporal perspective, dependences of cluster concentrations and particle formation rates on temperature were illustrated quantitatively through scaling at five sites, suggesting the differences in nucleation intensity across this region could be explained by variations in temperature under the comparable mechanism. We expect that this finding holds for similar polluted atmospheric environments on large spatial scales worldwide, particularly where significant temperature gradients exist."

This manuscript is based on likely state-of-the-art analytical approaches and the best currently available dataset for nucleation in polluted atmospheres. By applying a scaling approach to account for multiple atmospheric factors, we have provided multiple evidence supporting SA-DMA nucleation. However, as you noted, these pieces of evidence remained indirect. We think that future advances in the direct measurement of nucleating clusters are essential to reach more definitive mechanistic conclusions, which may lead to the unveiling of the contribution from other nucleation precursors. Our discussion of future research directions has been revised as (lines 369-374):

"The case for SA-DMA nucleation presented in this study remains indirect, as it relies on precursors, limited clusters and modeling rather than comprehensive identification of nucleation process. To better resolve atmospheric nucleation mechanisms, future studies are warranted to advance beyond current methods of cluster detection, for instance, by enabling direct measurements of all basic molecules within SA clusters. In the complex urban atmosphere, the potential involvement of other pollutants will require novel direct measurements and analytical techniques, along with more comprehensive modeling, to clarify the roles of additional precursors."

We appreciate you for these constructive comments, which have significantly improved the quality and clarity of our manuscript.