Response to the Comments of Referees

Journal: Atmospheric Chemistry and Physics
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Title: Analysis of new particle nucleation events and comparisons to simulations of particle number concentrations based on GEOS-Chem/APM in Beijing, China
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We thank the reviewers and editor for providing helpful comments to improve the manuscript. We have revised the manuscript according to the comments and suggestions of the referees.
The referee's comments are reproduced (black) along with our replies (blue). All the authors have read the revised manuscript and agreed with the submission in its revised form.

< Anonymous Referee #1 >

Comment: This study reanalyzed an NPF dataset reported in previous literature and explored possible nucleation mechanisms by contrasting measurements to simulations. It is interesting to see an attempt to reproduce urban NPF events with a global chemistry transport model. The topic of this study fits the scope of Atmospheric Chemistry and Physics. I recommend the authors take advantage of the review process to improve the manuscript substantially, such that it can meet the quality for publication.

We thank the referee for the positive comments on our manuscript. The manuscript has been carefully revised according to the referee's comments and suggestions.

Major comments
Comment 1: The TIMN scheme was found to be able to "overall well simulate the total and sub-3 nm particle number concentrations and nucleation rates in Beijing", with significantly higher values than BHN, BIHN, and THN. However, the nucleation rates in Fig. 10 seem to be lower than typical values in polluted megacities. For instance, the formation rates of freshly nucleated particles were usually higher than 10 cm-3 s-1 in Shanghai (Yao et al., 2018) and Beijing (Yan et al., 10.1029/2020GL091944).

The relatively coarse spatial resolution in a global model implies that the model produces a regional mean nucleation rate compared to the observation. Thus, it is difficult to perfectly reproduce the nucleation rate characteristics over urban areas. Nevertheless, we agree with the reviewer that nucleation rates measured in urban areas can be higher than 10 cm^{-3} s^{-1} (Yao et al., 2018; Yan et al., 2021) and this has been pointed out in the revised manuscript. The possible reasons for higher nucleation rates in urban areas are discussed in replies to the comments below.

Since the rate of ion-mediated nucleation may be limited by the ion production rate, as

well as the high sink, does this indicate that ion-mediated nucleation may not able to produce those high formation rates?

Yes. There are six parameters controlling nucleation rates for TIMN (J_{TIMN}): sulfuric acid vapor concentration ([H_2SO_4]), ammonia gas concentration ([NH_3]), temperature (T), relative humidity (RH), ionization rate (Q), and surface area of pre-existing particles (S) (Yu et al., 2020). Therefore, on the ground, the ion nucleation rates could be limited by ion production rates and cannot produce nucleation rates higher than Q. Compared to J_{TIMN}, there is one fewer controlling parameter for nucleation rates for THN (J_{THN}) (no Q dependence) so that J_{THN} can be very high on the ground under certain conditions. Depending on the definition, THN may be treated as a part of TIMN in the ternary nucleation system (Yu et al., 2020). Nevertheless, we acknowledge that it is possible other nucleation mechanisms such as H_2SO_4-amine and H_2SO_4-organics nucleations may also simultaneously contribute to nucleation in polluted urban areas, which needs further study in the future.

Besides, it will be more convincing to show the measured particle formation rate in Fig. 10.

We have added the measured particle nucleation rates reported in Cai et al. (2017) to Figure R1.

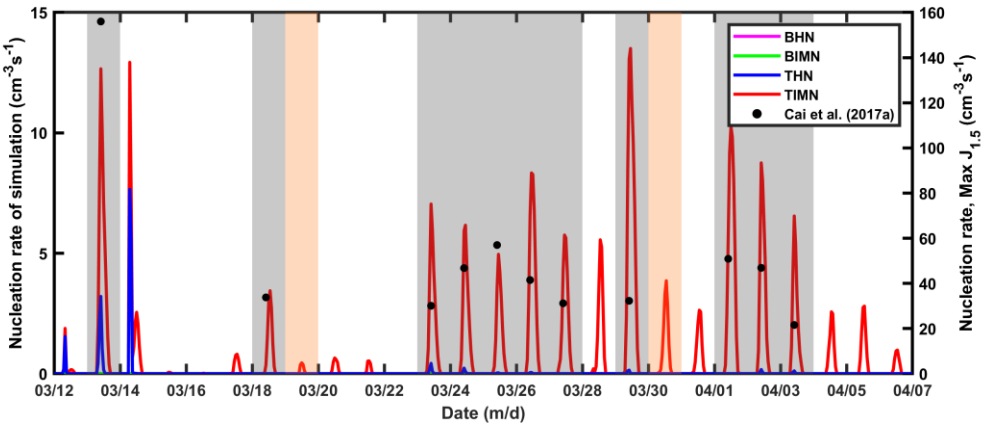

Figure R1. Time series of nucleation rates simulated on the basis of BHN, BIMN, THN, and TIMN schemes during the measurement period and the measured particle nucleation rates of 1.5 nm particles (Max $J_{1.5}$) reported in Cai et al. (2017). The identified NPF days and undefined days are shadowed by grey and orange background, respectively.

These sentences have been added to the revised manuscript.

Comment 2: There might be a large room for improvement in the manuscript when addressing the current knowledge of NPF in terms of both nucleation mechanisms and their roles in the atmosphere. Some important advances in the last decade are missing from discussions.

Thanks for your suggestions. We have added more important findings to the introduction and discussion in the revised manuscript.

There are quite many places where the discussions are confusing and some are even at the risk of self-contradictory. Two examples are given below and some are given in minor comments, and I encourage the authors to improve the manuscript thoroughly.

Thanks for the suggestions and corrections, we have revised the manuscript accordingly (see our revised manuscript and response to minor comments).

Amines can be a key base for sulfuric acid nucleation in polluted megacities for their much higher efficiency in stabilizing clusters than ammonia and ions, as has been discussed in Yao et al. (2018) and many other studies. The authors have cited Yao et al. (2018) but why not address the roles of amines in the simulation?

We agree that amine can be a key base for sulfuric acid nucleation in polluted megacities. Recent measurements in urban Shanghai found that dimethylamine (DMA, $(CH_3)_2NH$) is perhaps the dominating base to stabilize H_2SO_4 clusters (Yao et al., 2018). Cai et al. (2021) found that H_2SO_4-amine nucleation can explain the observed high nucleation rate under the high coagulation sink. It's a good suggestion to address the roles of amines in the simulation. However, there is probably a long way to go before using the model to address the role of amines in nucleation for the following reasons. Firstly, the parameterization of sulfuric acid-amine nucleation scheme is not yet mature enough and a lot of validations against observations need to be done. Secondly, there is quite limited information on amine sources and thus all current emission inventories, to our knowledge, do not contain the inventories for amines. Therefore, it is not possible currently to carry out such simulations.
We have added more discussions to the revised manuscript.

Is it possible that sulfuric acid-amine nucleation can produce a comparable or higher nucleation rate than TIMN?

Yes, if concentrations of amines are high enough, sulfuric acid-amine nucleation can produce a comparable or higher nucleation rate than TIMN.

The authors stated that LVOCs play an important role in NPF, which is plausibly true and consistent with previous findings in Beijing. However, it is also stated that "TIMN scheme has a good simulation performance on the growth, condensation, coagulation and other processes after the nucleation process." Have the LVOCs been accounted for in TIMN? If not, does this indicates either a negligible contribution from LVOCs or a bias in the simulation results?

The TIMN does not include the contribution of nucleation involving LVOCs although

the contribution of LVOCs to growth is considered in the APM model. The growth of nucleated particles through the condensation of sulfuric acid vapor and equilibrium uptake of nitrate, ammonium, and secondary organic aerosol (SOA) is explicitly simulated, along with the scavenging of secondary particles by primary particles (dust, black carbon, organic carbon, and sea salt) (Yu and Luo, 2009). Yu (2011) has further developed the APM module to explicitly calculate the co-condensation of sulfuric acid and low-volatility secondary organic gases (LV-SOGs) or LVOCs on secondary particles and primary particles. The aerosol simulation considered the successive oxidation aging of the oxidation products of various VOCs (Yu, 2011). It should be noted that APM model contains the organics-mediated nucleation scheme (Yu et al., 2017) but it is not considered in the present study.

Sorry for the confusing statement. The difference in the growth process is due to different nucleation rates in the lookup tables of each scheme. It was inappropriate to state that "TIMN scheme has a good simulation performance on the growth, condensation, coagulation and other processes after the nucleation process." We have revised the model description chapter of the manuscript and explained the growth of nucleated particles in the model.

Comment 3: Most of the findings in the measurement part have been discussed in previous literature, which can also be seen from the discussions in the main text. The authors may need to clearly show the advances of this study compared to previous studies, including but not limited to the source of the dataset used in this study (Cai et al., 2017). Shortening the discussions, figures, and conclusions based on the measurement results can be an alternative way, and this will help emphasize the results based on simulations.

Thanks for the suggestions. For the measurements-based results, our revised manuscript mainly focused on the analysis of solar radiation and meteorological conditions favorable for NPF, and already shortened the discussions and deleted Figure 3.

Minor comments

Comment 4: Lines 55-56. This sentence is confusing because whether ions, specifically, charged particles measured by NAIS herein, grow faster than neutral particles or not is not directly relevant to the formation of the critical nucleus.

Thanks for your suggestions. This sentence has been deleted.

Comment 5: Lines 60-64. The mechanism proposed by Wu et al. (2020) is not a nucleation mechanism. It will be better to address it elsewhere, e.g., in lines 230-240.

Done as suggested.

Comment 6: Line 213, "7 % higher". It can be questionable to conclude the importance

of temperature on NPF based on a 7 % difference.

This sentence has been deleted.

Comment 7: Lines 296-297. Better to explain why and how a nucleation scheme can simulate the processes after nucleation.

The growth of nucleated particles through the condensation of sulfuric acid vapor and equilibrium uptake of nitrate, ammonium, and secondary organic aerosol (SOA) is explicitly simulated, along with the scavenging of secondary particles by primary particles (dust, black carbon, organic carbon, and sea salt) (Yu and Luo, 2009).
We have revised the model description chapter of the manuscript and explained the growth of nucleated particles in the model.

Sorry for the confusion. It was inappropriate to state that "TIMN scheme has a good simulation performance on the growth, condensation, coagulation and other processes after the nucleation process." This sentence has been deleted.

Technical comments

Comment 8: Lines 40-41. It is worth double-checking whether Huang et al. (2020) and Li et al. (2021) concluded that "new particles derived from NPF played a significant role in the formation of haze".

Corrected.

Comment 9: Line 130. Better to use steady-state or quasi-steady-state. NPF cannot reach an equilibrium.

Corrected.

Comment 10: Line 138, "banana shape". This is perhaps not necessary since NPF events in urban environments may not be banana-type events.

This sentence has been deleted.

Comment 11: Line 342. Please use "TIMN scheme" instead of "TIMN nucleation scheme", as N is for nucleation.

Corrected.

Reference

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