Responses to Editor's Comments on Manuscript acp-2023-15
A parameterization of sulfuric acid-dimethylamine nucleation and its application in three-dimensional modeling

We are grateful for the editor's comments and these comments have helped us to improve the manuscript. Please find our point-to-point responses below. Comments are shown as blue italic text and the revised texts are shown as "quoted underlined text". In the revised manuscript, the changes are highlighted. The line numbers in the response refer to the revised manuscript without tracked changes.

Referee 1:

Suggested Revision to the Title:
Add "Dynamic" since loss processes are an important element of this new parameterization.
  "A Dynamic Parameterization of Sulfuric Acid-Dimethylamine…"
Or
  "A Dynamics-Based Parameterization of Sulfuric Acid-Dimethylamine…"
Response: Thanks for the comment. We have changed the title to "A Dynamic Parameterization …".

Suggested Revisions to the Abstract:
Reword first sentence to better link NPF and source of particles, and replace "diverse" to more strongly state that SA has been linked to NPF in all studied environments: Sulfuric acid (SA) is a governing gaseous precursor for atmospheric new particle formation (NPF), a major source of ultrafine particles, in environments studied around the world.
Replace "atmosphere" with "atmospheres" to indicate more than one urban atmosphere; change throughout manuscript when describing urban atmospheres generally: "polluted urban atmospheres with a high condensational sink" Replace "they" with "these loss processes" to more concisely refer to the loss and not the general representation of the contribution of these clusters to NPF: Coagulation scavenging and cluster evaporation are dominant sink processes of SAamine clusters in urban atmospheres, yet these loss processes are not quantitatively included in the present parameterizations of SA-amine nucleation.
Reconsider "would be able to reproduce" (line 29) and "would improve the performance" (line 36). When the statement has been demonstrated, it is recommended to state this more conclusively. When the statement has not been demonstrated, it is recommended to state this more hypothetically. For example: Compared with previous SA-DMA nucleation parameterizations, this new parameterization was able to reproduce the dependences of particle formation rates on temperature and CS. Representing these processes is thus likely to improve model performance in particle source apportionment and quantification of aerosol effects on air quality, human health, and climate.
It is recommended to revisit the use of "would" throughout the manuscript. It suggests speculation rather than observation or deduction. For example (from section 2.1):

Based on previous studies, under atmospheric conditions, variations of precursor concentrations, temperature and CS and do not result in large deviations to the main pathway. Simulations under different [SA], [DMA], and temperatures have shown that the main pathway was similar under the different conditions studied (Olenius et al., 2013). The effect of CS on nucleation pathway is dependent on the relative relationship between the CS and the evaporation rate of a certain cluster. For most clusters out of the specified pathway, the evaporation rates are much higher than the typical CS range in urban atmospheres (Ortega et al., 2012), therefore such clusters would not dominate the nucleation pathway no matter how low or high the CS is. Thus in this study, the variation of the dominant pathway under different conditions was ignored.
Use past tense when referring to the results; replace "majorly" with "significantly":
Simulation results showed good consistency with the observations in the occurrence of NPF events and particle number size distributions in wintertime Beijing, and represented a significant improvement compared to that using parameterization without coagulation scavenging. Quantitative analysis showed that SA-DMA nucleation contributes significantly to nucleation rates and aerosol population during the 3-D simulations in Beijing (>99% and >60%, respectively).

Response: We have revised the expressions as the editor suggested.

Lines 22-38 in the revised manuscript:" Sulfuric acid (SA) is a governing gaseous precursor for atmospheric new particle formation (NPF), a major source of global ultrafine particles, in environments studied around the world. In polluted urban atmospheres with high condensation sink (CS), the formation of stable SA-amine clusters, such as SA-DMA clusters, usually initializes intense NPF events. Coagulation scavenging and cluster evaporation are dominant sink processes of SA-amine clusters in urban atmospheres, yet these loss processes are not quantitatively included in the present parameterizations of SA-amine nucleation. We herein report a parameterization of SA-DMA nucleation based on cluster dynamic simulations and quantum chemistry calculations, with certain simplifications to greatly reduce the computational costs. Compared with previous SA-DMA nucleation parameterizations, this new parameterization was able to reproduce the dependences of particle formation rates on temperature and CS. We then incorporated it in a three-dimensional chemical transport model to simulate the evolution of particle number size distributions. Simulation results showed good consistency with the observations in the occurrence of NPF events and particle number size distributions in wintertime Beijing, and represented a significant improvement compared to that using parameterization without coagulation scavenging. Quantitative analysis shows that SA-DMA nucleation contributes significantly to nucleation rates and aerosol population during the 3-D simulations in Beijing (>99% and >60%, respectively). These results broaden the understanding of NPF in urban atmospheres and stress the necessity of including the effects of coagulation scavenging and cluster stability in simulating SA-DMA nucleation in three-dimensional simulations. Representing these processes is thus likely to improve model performance in particle source apportionment and quantification of aerosol effects on air quality, human health, and climate."

Suggested Revisions to the Conclusions:

Reorganization so that the contributions are summarized in the beginning, findings/results in the middle, and implications are at the end.

This study presents a dynamics-based SA-DMA nucleation parameterization for application in 3-D chemical transport models. Compared to the more widely-used semi-empirical power-law fitting parameterizations, this new parameterization is based on the key pathway of SA-DMA cluster formation and includes representations of the coagulation scavenging effect and cluster stability. Pseudo-steady state assumptions were applied to reduce computational time and were validated according to the short characteristic equilibrium time and through comparisons with cluster dynamic simulations and the kinetic model. Relative to simulating SA-DMA nucleation with cluster dynamic simulations or the kinetic model, application of this new parameterization in 3-D chemical transport models greatly reduces the computational costs. We incorporated this new parameterization as well as the sources and sinks of DMA into the WRF-Chem/R2D-VBS model. Using the updated model, we simulated the DMA concentrations and PNSDs in Beijing during December 2018 and January 2019. Comparisons were made between 3-D model simulations and ambient measurements.

Good consistency was achieved in simulating the precursor concentrations, which validated the source-sink simulation of SA and DMA. Our quantitative analysis showed that compared to other nucleation mechanisms, SA-DMA nucleation contributed to >99% of particle formation rates and >60% of particle number concentrations during the simulation period in urban Beijing. Although uncertainties exist due to the excess rapid growth in the 3-D simulations, SA-DMA nucleation should be a dominant source of aerosol particles due to the dominant contribution to new particle formation rates.

Further, the 3-D simulations with the new SA-DMA parameterization predicted the CS-dependent NPF occurrence in urban Beijing and quantitatively reproduced the particle size distributions. These results demonstrated that incorporating the SA-DMA nucleation parameterization, including the effects of coagulation scavenging and cluster stabilities, with 3-D chemical transport models can significantly improve the simulation of NPF and the particle size distributions.

Our results demonstrated that 3-D simulations with a new SA-DMA parameterization could reproduce the CS-dependent particle formation rates and NPF occurrence observed in Beijing. Given that CS varies widely between NPF days and non-NPF days in urban atmospheres (Xiao et al., 2015; Wu et al., 2007; Deng et al., 2021), compared to semi-empirical power-law functions, this parameterization of particle formation rates is likely more effective in predicting the NPF occurrence in urban atmospheres. Additionally, the particle formation rates from other nucleation mechanisms should also be suppressed by high CS, which needs further exploration and parameterizations. Our methodology of applying pseudo-steady-state assumptions to kinetic models could be important in reducing computational costs of other SA-amine nucleation systems. For instance, quantum chemistry calculations indicate that other basic molecules like trimethylamine and diamines (Jen et al., 2016; 443 Jen et al., 2014a), might also form relative stable clusters with SA molecules, hence the methodology of parameterizations in this study could be extended for them, or the basic molecules could also be treated as equivalent DMA

concentrations. The improvements in model simulations of particle size distributions are important for improving simulations of cloud condensation nuclei and the climate effects of aerosols and NPF events. The improvements also provide more evidence for quantitatively evaluating the environmental and health effect of ultrafine particles.

I have modified and included this sentence at the end, but I am not sure what it means: The improved simulations of particle size distributions also provide more evidence for quantitatively evaluate the environmental and health effect of ultrafine particles. The fact that NPF is important in urban environments does support evaluating the environmental and health effects of ultrafine particles, but I'm not sure how this relates to a new model parameterization. The measurements themselves demonstrate that such particles/events exist. Maybe you are suggesting that if we have more accurate model simulations, we can more readily use particle size distributions as a metric since we won't have to rely on measurements.

Response: We have revised the expressions as the editor suggested.

Lines 416-447 in the revised manuscript:" This study presents a dynamic-based SA-DMA nucleation parameterization for application in 3-D chemical transport models. Compared to the more widely-used semi-empirical power-law fitting parameterizations, this new parameterization is based on the key pathway of SA-DMA cluster formation and includes representations of the coagulation scavenging effect and cluster stability. Pseudo-steady-state assumptions were applied to reduced computational time and were validated according to the short characteristic equilibrium time and through comparisons with the cluster dynamic simulations and the kinetic model. Relative to simulating the SA-DMA nucleation with cluster dynamic simulations or the kinetic model, application of this new parameterization in 3-D chemical transport models greatly reduces the computational costs. We incorporated this new parameterization as well as the sources and sinks of DMA into the WRF-Chem/R2D-VBS model. Using the updated model, we simulated the DMA concentrations and PNSDs in Beijing during December 2018 and January 2019. Comparisons were made between 3-D model simulations and ambient measurements.

Good consistency was achieved in simulating the precursor concentrations, which validated the source-sink simulation of SA and DMA. Our quantitative analysis showed that compared to other nucleation mechanisms, SA-DMA nucleation contributed to >99% of particle formation rates and >60% of particle number concentrations during the simulation period in urban Beijing. Although the uncertainties exist due to the excess rapid growth in the 3-D simulations, SA-DMA nucleation should be a dominant sources of aerosol populations due to the dominant contribution to new particle formation rates. Further, the 3-D simulations with the new parameterization predicted the CS-dependent NPF occurrence in urban Beijing and quantitatively reproduced the particle size distributions. These results demonstrated that incorporating the SA-DMA nucleation parameterization, including the effect of coagulation scavenging and cluster stabilities, with 3-D chemical transport models can significantly improve the simulation of NPF and the particle size distributions.

Our results demonstrated that 3-D simulations with a new SA-DMA parameterization could reproduce the CS-dependent particle formation rates and NPF occurrence

observed in Beijing. Given that CS varies widely between NPF days and non-NPF days in urban atmospheres (Xiao et al., 2015; Wu et al., 2007; Deng et al., 2021), compared to semi-empirical power-law functions, this parameterization of particle formation rates is likely more effective in predicting the NPF occurrence in urban atmospheres. Additionally, the particle formation rates from other nucleation mechanisms should also be suppressed by high CS, which needs further exploration and parameterizations. Our methodology of applying pseudo-steady-state assumptions to kinetic models could be important in reducing computational costs of other SA-amine nucleation systems. For instance, quantum chemistry calculations indicate that other basic molecules like trimethylamine and diamines (Jen et al., 2016; Jen et al., 2014a), might also form relative stable clusters with SA molecules, hence the methodology of parameterizations in this study could be extended for them, or the basic molecules could also be treated as equivalent DMA concentrations. The improvements in model simulations of particle size distributions are important for improving simulations of cloud condensation nuclei and the climate effects of aerosols and NPF events. The improvements also provide more evidence for quantitatively evaluating the environmental and health effect of newly-formed particles.."

Suggestion to move this to the methods section:
Although some studies have revealed that SA-DMA nucleation could also be enhanced by adding other molecules in certain conditions, quantitative analysis of these effects in relevant atmospheric conditions is still lacking, thus in this study, we set up this parameterization only based on SA-DMA binary nucleation

Response: We have revised the expressions as the editor suggested.
Lines 119-121 in the revised manuscript:" Although some studies have revealed that SA-DMA nucleation could also be enhanced by adding other molecules in certain conditions, quantitative analysis of these effects in relevant atmospheric conditions is still lacking, thus in this study, we set up this parameterization only based on SA-DMA binary nucleation."