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## **Comment on acp-2022-35**

Christina Williamson (Referee)

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Referee comment on "A sulfuric acid nucleation potential model for the atmosphere" by Jack S. Johnson and Coty N. Jen, Atmos. Chem. Phys. Discuss.,  
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### **Review of "A Sulfuric Acid Nucleation Potential Model for the Atmosphere"**

This manuscript addresses the scientific question of understanding the drivers of new particle formation in different environments. This is important for understanding atmospheric aerosols from the perspective of both climate and air quality. This study has general implications for atmospheric science as the model developed for aerosol nucleation can be applied for different environments around the world, as demonstrated in the study, and is specifically useful for comparing different environments. I therefore consider this study to fit very well within the scope of ACP.

This paper presents a very novel tool, namely a new model for directly quantifying and comparing aerosol nucleation in different environments. The conclusions reached, that the model is useful for categorizing and comparing nucleation in different environments and can inform us about what precursors are involved in the nucleation process, are substantial.

The scientific methods and assumptions are valid and clearly outlined, with a few minor exceptions which I draw out in detailed comments below. The use of both flow-chamber and atmospheric data supports the conclusion that the model can inform us about the involvement of different precursors in nucleation, although some of the conclusions drawn about the unimportance of thermodynamic conditions and the amount of information the model gives us about precursors are not fully supported by the data presented. I have detailed below where this is the case.

Description of experiments and calculations lacks clarity in some areas, and this may hinder reproduction of results by fellow scientists. I have detailed where this occurs in my comments below. In addition, some important information on the method and how the model works has been relegated to the supplementary material, but seems essential

enough to the understanding of the method that they might be better placed in the main text. The manuscript is generally well structured and the language is fluent and precise, except for the final section in the supplementary material, where I struggle to understand the main point as detailed in the specific comments below.

Authors mostly give proper credit to related work, but I have noticed a few missing citations, which I detail below. The title clearly reflects the contents of the paper and the abstract mostly provides a concise and complete summary. An issue I have throughout the study is a conflation between different precursor potency/amounts and thermodynamic conditions. Following more through addressing of this issue in the main manuscript, I believe this point should also be mentioned in the abstract.

This study is an interesting and important contribution to understanding and comparing aerosol nucleation over a variety of conditions. There are some open issues that need resolving/clarifying before publication.

Specifics:

## SECTION 1

Introduction introduces the current state of the art and why there is a need for a new type of nucleation model well.

Line 30 – discussion of sulfuric acid driven nucleation gives the impression that this only occurs in the presence of bases, even though organic acids, oxidized organics, ions and water mentioned later in the same paragraph. This may be a distinction the authors are making between pure binary nucleation (sulfuric acid and water only) and other types of nucleation involving sulfuric acid, but not exclusively. Clarity of the manuscript would be improved by addressing this explicitly.

Line 60 – “most global climate models do not account for sulfuric acid nucleation” – my understanding is the models that include nucleation almost always account for pure binary, but not always nucleation involving additional species. Is this what the authors meant? Clarification and references are required here.

Line 65 – “emissions inventories used in global climate models only contain SO<sub>2</sub> and ammonia” – it would be useful to reference the emissions inventories to which they are referring here. Some inventories do include, for example, emissions of volatile organic compounds in the CEDS emissions database (Hoesly et al., 2018).

Line 67 – “these factors contribute to significant model error in predicting aerosol number concentrations in regions with no dominant nucleation pathway” – This needs supporting evidence. There are a number of existing studies comparing measured number concentrations to observations in diverse regions that should be cited here.

Line 74 – “circumvents the need to deploy a mass spec” – only in the sense of capturing nucleation rates. More care should be taken to present it in this light, after all chemical info is needed also for predicting growth, hygroscopicity, emissions etc.

The method uses concentrations starting at 1 nm. Many atmospheric measurements start at higher diameters only, and measuring down to 1 nm can be extremely challenging in some environments, such as from aircraft. It would be helpful if the authors considered this issue and commented on whether this limits the use of the method in the introduction.

## SECTION 2

How do the calculations of  $B_{\text{eff}}$  detailed in this section apply to different temperatures and RHs? Confining the method to 300 K and 20 % RH seems to limit the global applicability.

It is not clear to me from this section how losses are taken into account. This is somewhat addressed in the supplementary material, but would be better addressed here to give the reader a full understanding of the method. Furthermore, the description of how losses are accounted for in the supplementary is unclear in places, as detailed below.

## SECTION 3

## SECTION 3.1

Flow reactor measurements are made at sulphuric acid concentrations of  $1.4 \times 10^8 \text{ cm}^{-3}$  and ammonia, DMA, MA, TMA concentrations between 0-35 pptv. It would be helpful to have a comment on how these relate to atmospherically relevant concentrations, and what the implications of this are for substantiating the method and the conclusions drawn from the flow reactor data.

Line 110 and Fig 1 –  $[A_1]_0 \sim 1.4 \times 10^8 \text{ cm}^{-3}$ ,  $t_{\text{nuc}} \sim 2 \text{ s}$  – Why are these approximate and what gives the range? Does this uncertainty affect the results in fig 1 at all? Given the scatter in the data in fig 1, uncertainties in  $[B]$  and  $[B_{\text{eff}}]$  appear noticeable on the scale of the graph and so should be shown. This also applies to fig 2.

Line 115 – “short nucleation time when compared to previous experimental studies” – this needs references, unclear which studies are being referred to.

Line 121 – Authors mention that nucleation rates plateau when coagulation rate are larger than predicted by model. Why is the model unable to deal with these coagulation rates? How does it deal with coagulation rates? This was not completely clear to me from the main manuscript and the description in the SM also left me with some questions (see below). Does this present a limit of applicability of the model e.g. can it work in polluted regions? Or plumes from volcanoes or aircraft?

Line 140 “MA, NH<sub>3</sub> and TMA concentrations do not change significantly” – is this assessment justified? NH<sub>3</sub> concentration more than doubles, and TMA goes from nothing to 2 pptv – Other studies e.g. (Kurten et al., 2016) show that nucleation rates can be very sensitive to small concentrations of ammonia? Nucleation rates for TMA alone seems to have a strong response to the TMA concentration changes of less than 6 pptv in fig 1, and seems to have the strongest response at the lowest concentrations, indicating that 0-2 pptv may indeed be significant. In fig 2, the difference in  $J$  for DMA and DMA+73pptv NH<sub>3</sub> is large enough to suggest that the difference of 25 pptv between the 2 and 3 component systems may indeed be significant. The ability of the reader to judge the significance of these concentration changes is also impaired by the lack of error bars.

Line 140 – I’m not sure that the argument that NH<sub>3</sub>-DMA synergistic reaction dominates given small change in  $B_{\text{eff}}$  with addition of MA and TMA is justified. NH<sub>3</sub> concentrations vary a lot between the three systems.

Line 145 – “NPM can determine HOW a complex mixture of compounds enhances SA nucleation” – this seems to be overstating the case. NPM can show that a complex mixture enhances the nucleation, and measure by how much, but cannot point to how (as in the chemical mechanism) this is done as is claimed above – or at least doesn’t with the data

available for the reasons mentioned in the comment on line 140.

Line 150 – The uncertainty mentioned here really needs to be illustrated on the figure somewhere to help the reader see whether or not it impacts the trends.

## SECTION 3.2

Line 175 – I question the claim that temperature and RH effects may not be significant given similar  $B_{\text{effs}}$  in Boulder and Hyytiälä. Since temperature and RH are very different for these two locations, could not the similar  $B_{\text{eff}}$  be because by compensating effects from differing precursors and thermodynamic conditions? This should be highlighted also in the introduction to the NPM as it is important that future users of the NPM fully understand that the model puts these influences together. This does not detract from the usefulness of the model, especially to compare observations where T and RH are known, but does need to be properly acknowledged in analyses such as this. It could be a useful extension of the future work proposed in the next line to measure  $B_{\text{eff}}$  for known  $\text{H}_2\text{SO}_4$  concentrations to also map  $B_{\text{eff}}$  for known  $\text{H}_2\text{SO}_4$  concentrations over a range of atmospherically relevant temperatures and RHs.

Fig 3 - this clear distinction between the different environments is really powerful and such a strong endorsement of the potential power of this mode. It is very interesting also to see how, in contrast to other locations in this study  $B_{\text{eff}}$  in Beijing is mostly controlled by factors other than sulfuric acid concentration.\

Fig 4 – overlap of opaque symbols hides some of the spread of the October and November data.

## CONCLUSION

Line 195 – Again the possible variation of  $B_{\text{eff}}$  due to temperature or RH is ignored. Is this

assumed to be small compare with precursor concentrations? If so, are there data from controlled or measured conditions to illustrate this?

## SUPPLEMENTARY MATERIALS

Line 16 – is it reasonable to set cluster balances up to [N3] equal to zero? What is the justification fort this?

Line 16 – Why does coagulation with larger clusters replace wall loss rates for atmospheric measurements? I understand that of course wall losses now don't exist, but coagulation with pre-existing particles also existed in the flow chamber. Or is this not taken into account in the chamber version? And if not, why not? Previous studies have shown that in chamber conditions self-coagulation can be an important loss impacting the calculation of nucleation rates significantly (Kurten et al., 2015).

Line 18 – coagulation loss rate assumed constant for field campaigns – why was this done? And was it calculated from the measured size distributions? Did these change? And if so, which size distribution measurement was used? More detail needed here for others to be able to reproduce the method on other field campaign data.

## METHODOLOGY TO EVALUATE THE NUCLEATION POTENTIAL MODEL

I find it hard to understand what the main point of this section is.

Line 21 – “first set of bars” unclear – refer to how they are labeled in the figure. This whole sentence is a bit unclear – is the point being made just that there are many particles sized between 1 and 2 nm? If so, this might be clearer with a linear y axis in fig S1 and the text could use some clarifying.

Line 27 – “This inferred size distribution is more compatible with the nucleation model, which accounts for particles up to N8 (larger than 1 nm).” Does this mean that the nucleation potential model does not work for size distributions dominated by smaller

particles/clusters? Isn't this quite a lot of nucleation events and wouldn't that be a major limitation of the model? If that is the case, why is this not highlighted in the main manuscript

The lack of SMPS scans for the flow tube – does this mean there are no size distribution measurements? And if so, how is the coagulation sink accounted for?

## References

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