Author responses and changes to Manuscript: egusphere-2025-165

Dear James Brean:

We are very grateful for the constructive comments from you on our manuscript (ID: **egusphere-2025-165**, original title: **Chloric Acid-Driven Nucleation Enhanced by Dimethylamine and Sulfuric acid in the Arctic: Mechanistic Study**. We have studied these comments carefully and have made corresponding revisions which marked in red in the revised manuscript. The all comments and our replies are listed as follows:

<<Comments from Reviewer #RC2>>

Wang and coworkers study the clustering of chloric acid (CA) with sulfuric acid (SA) and dimethylamine (DMA) using quantum chemical methods and cluster dynamics simulations. The cluster configurational space is studies with standard methodologies, relying on the global search algorithm of the ABCluster program and narrowing down the generated configurations in a funneling approach. The final applied level of theory---DLPNO-CCSD(T)/aug-cc-pVTZ// ω B97X-D/6-31++G(d,p)---is up to the current standards, but I miss some justification for the choices. Based on the finding that the CA-DMA cluster formation rate is higher than the CA-SA cluster formation rate, the authors conclude that the CA-DMA clusters must contribute to new particle formation (NPF) in the Arctic. I believe this comparison is quite misleading and do not see evidence in the manuscript that the clusters contribute to NPF in the Arctic.

The manuscript is relatively easy to follow, the calculations are carried out at a respectable level of theory and the cluster systems are of relevance and value to the atmospheric chemistry community. However, especially the abstract and conclusions have misleading statements that leaves the reader with the impression that these clusters are unambiguously important for NPF in the Arctic. I highly urge the authors to clearly state that the CA-DMA clustering system does not appear relevant for Arctic NPF, to ensure that the calculations are not taken at face value and misused. Remember, it is an equally as important finding that CA-DMA does not contribute to NPF. Hence, I fully agree with the community comment by James Brean and believe some major rephrasing is required before I can recommend publication. For instance there are many dubious duplicate sentences and paragraphs.

Detailed comments are given below.

Comments

Line 26: “ Recent studies have shown that CA is prevalent in the Arctic boundary layer.”

I would definitely not call CA prevalent in the Arctic. The only existing measurements are from Tham et al. with values up to ~107 molecules cm-3. I would consider this trace amounts. Perhaps state that trace amounts has been detected in the atmosphere instead.

>>**Response:** Thank you for your nice comment. We have revised the wording to “trace amounts of CA have been detected in the Arctic boundary layer.”

Line 29: “It is expected that CA is involved in the oceanic nucleation process.”

Based on available literature and current knowledge on nucleation in the marine boundary layer, I would not expect CA to contribute. You could say “speculated” to be involved, but definitely not expected.

>>**Response:** Thank you for your nice comment. We have revised the wording to“speculated” .

Line 36: “The cluster formation rate of the CA-DMA cluster system is higher than that of the CA-SA cluster system. The CA-DMA cluster system in the Arctic atmosphere contributes to NPF.”

The fact that X is larger than Y does not tell us anything about their relevance for NPF. You need to look at the absolute cluster formation rate numbers.

It would be much more relevant to compare the systems to cluster systems that are known to contribute to cluster formation. A natural comparison would be the SA-DMA system, where QC data is freely available to directly compare with. I get the impression that this comparison was not made, as it would diminish the relevance of the CA-DMA system, as SA-DMA binds stronger.

>>**Response:** Thank you for your nice comment. We have removed the statement that “The CA-DMA cluster system in the Arctic atmosphere contributes to NPF.” In subsequent sections, we use SA-DMA system as the control group.

Line 47: “New particle formation (NPF) contributes to more than half of the global cloud condensation nuclei, which in turn contributes to cloud formation (Gordon et al., 2017; Takegawa et al., 2020; Williamson et al., 2019; Zhang et al., 2012).”

I believe the recent study by Zhao et al. (https://www.nature.com/articles/s41586-024-07547-1) would be worth mentioning here.

>>**Response:** Thank you for your nice comment. We cite the latest research by Zhao et al. (https://www.nature.com/articles/s41586-024-07547-1).

Line 66: “Chloric acid (CA) has no photoactivity and CA is ubiquitous in the spring in the Arctic, with concentrations estimated to range from 1 × 105 to 7 × 106 molecules cm−3 (Tham et al., 2023).”

Please add a reference to the lack of photoactivity of CA. In addition, I would refrain from calling CA ubiquitous in the Arctic, as there are simply no measurements to back up this statement.

>>**Response:** Thank you for your nice comment. In the study by (Tham et al., 2023), his paper mentions that CA lacks photoactivity. We have deleted that CA is widespread in the Arctic.

Line 87: “Considering its strong nucleation ability(Sipilä et al., 2010; Faloona, 2009), it is likely that SA molecules nucleate in marine regions along with CA.”

Sulfuric acid by itself is a horrible nucleator in the lower atmosphere. It is only in the combination with bases that SA contributes to NPF. I believe this motivates why the

CA-DMA system is interesting to study. It could be an additional source of acids in the marine atmosphere that could contribute. However, in its current formulation this statement is slightly misleading. Please rephrase.

>>**Response:** Thank you for your nice comment. We added in the article that "Sulfuric acid by itself is a horrible nucleator in the lower atmosphere. It is only in the combination with bases that SA contributes to NPF. This precisely demonstrates the value of studying the CA-DMA system—it may serve as an additional source of acidic substances in the marine atmosphere."

Line 90: As this is a purely theoretical study, a literature survey stating the current knowledge about cluster formation from QC calculations would be in its place. What has been studied previously, and which compounds are believed to contribute. For instance, nucleation by iodine species (oxo acids and oxides) is a hot topic at the moment. In addition, there are many QC studies on clustering of sulfuric acid, methane sulfonic acid and bases. Finally, it should be mentioned that CA cluster formation has been studied previously by Engsvang et al. (https://pubs.acs.org/doi/abs/10.1021/acs.estlett.3c00902) where it was concluded that CA did not contribute.

>>**Response:** Thank you for your nice comment. The nucleation of iodine species (oxyacids and oxides) is a current hot topic(Li et al., 2024; Ning et al., 2024). Additionally, extensive quantum chemical studies have been conducted on the clustering phenomena of sulfuric acid, methanesulfonic acid, and alkali

compounds(Wu et al., 2023). Engsvang et al.(Engsvang et al., 2024) has investigated the formation mechanism of CA clusters, concluding that CA did not contribute.

Line 94: “The temperatures used in this study are within the temperature range of the atmospheric boundary layer in the ordinary range(Miřijovský and Langhammer, 2015).”

Please add the temperatures studied to this statement.

>>**Response:** Thank you for your nice comment. We have supplemented that the specific temperature value studied is 238, 258 and 278K.

Line 96: “The concentration of CA was estimated to be in the range of 1.0 × 106 − 1.0 × 108 molecules cm−3 based on measured data.”

Line 68 states that Tham et al measured 1.0 × 105 − 7.0 × 107. Why not use this range? It is perfectly fine to use a higher concentration if you clearly state that this is higher than measured and used for testing/prediction purposes.

>>**Response:** Thank you for your nice comment. The concentration of CA used is higher than the measured value and is intended solely for testing/prediction purposes.

Line 101 – Computational details: I am missing some justification to the application of the methods:

What previous work is the funnelling approach based on?

Why use PM7?

Why was the ωB97X-D functional chosen for the study?

How to justify that the small 6-31++G(d,p) basis set is adequate for modelling these systems.

Is the DLPNO-CCSD(T)/aug-cc-pVTZ level good enough for calculating the single point energies.

There are numerous benchmarks on cluster formation to justify these choices. Without referring to benchmarks it just appear as arbitrary choices.

>>**Response:** Thank you for your nice comment. We have cited a substantial body of literature to demonstrate the validity of the methodology employed(Li et al., 2024; Ning et al., 2024; Wu et al., 2023).

Line 104: Only the CA-SA and CA-DMA clusters are studied. This implies that the simulated cluster formation rates are from two isolated systems. To fully capture the dynamics of the system the mixed CA-SA-DMA clusters should be studied. This aspect should be commented upon in the manuscript.

By now the SA-DMA system is generally seen as the appropriate benchmark to compare simulated NPF rate to, as it has, both experimentally and theoretically, been shown to be important for NPF. Hence, I highly suggest that the authors compare their simulations to the SA-DMA system, as this is a much more meaningful comparison. The QC data is freely available at the same level of theory in the literature. In this manner the authors can state how large a fraction of CA-DMA that would be expected compared to SA-DMA. It is no shame that the CA-DMA rates are lower, as it is valuable to quantify by how much.

>>**Response:** Thank you for your nice comment. In section of Conclusion, we suggest in the paper that future research could explore mixed CA-SA-DMA clusters. Yes, we

will compare the nucleation rates of CA-DMA cluster systems and SA-DMA cluster systems in the paper. Comparative studies indicate that the cluster formation rate of SA-DMA clusters exceeds that of CA-DMA clusters by more than seven orders of magnitude (Zhang et al., 2022). Under temperature and concentration parameters relevant to Arctic environments, the CA-DMA system could be incapable of forming cluster structures. Despite the negative outcome, this represents a significant advancement in advancing research on nucleation mechanisms in marine and Arctic regions.

Line 117: “The free energy of formation (ΔG) of individual clusters is calculated at different temperatures 238, 258, and 278 K.”

Line 119: “The ΔG of individual clusters is calculated at different temperatures. ”

These two sentences are essentially stating the same. How did both end up in the manuscript?

>>**Response:** Thank you for your nice comment. We have removed Line 119.

Line 123: Remove “time-evolving”

>>**Response:** Thank you for your nice comment. We have removed “time-evolving”.

Line 125: “ there is good agreement between the conclusions of the ACDC simulations and the experimental results obtained using the birth and death equations (Almeida et al., 2013; Lu et al., 2020; Kürten et al., 2018).”

I do not understand what you mean by “good agreement between conclusions” here.

Conclusions on what? Please rephrase.

>>**Response:** Thank you for your nice comment. We have changed content to “ACDC simulation conclusions are obtained based on the birth and death equation.”

Line 129: “The (CA)5(DMA)5 clusters are set as boundary clusters (see Supporting Information (SI) for details).”

I do not understand why the 5-5 cluster was chosen as the boundary cluster. This would imply that only cluster collisions (1-1 clusters or larger) would lead to a flux out of the system. Were monomer collisions allowed to contribute to the flux out? In figure 6 it looks like the flux out is by CA collisions, leading to the (CA)5(DMA)4 cluster. Please elaborate.

>>**Response:** Thank you for your nice comment. We have designated the $(CA)_5(DMA)_4$ cluster as the boundary cluster and made corresponding modifications in the supplementary materials.

Line 131: “The concentration ranges of [CA], [SA] and [DMA] were set to 106 − 108, cm−3, 106 −108 cm−3 and 0.1−100 ppt, respectively.”

The choice of concentration ranges and at what regions these are relevant should be further discussed. For instance, on line 77 the authors state:

“Widely dispersed DMA has an atmospheric concentration of 0.4 − 10 pptv over the ocean and plays a key role in marine NPF (Van Pinxteren et al., 2019).”

Hence, 100 ppt of DMA is likely unrealistic in the Arctic and over the oceans.

>>**Response:** Thank you for your nice comment. Widely dispersed DMA has an atmospheric concentration of 0.4 − 10 pptv over the ocean and plays a key role in

marine NPF(Van Pinxteren et al., 2019). DMA at concentrations up to 100 ppt is primarily used for prediction.

Line 136-144 and Line 145-152: These two paragraphs appear to be reformulations of each other. I am a bit puzzled on how both have made it to the manuscript. Please remove one of them.

>>**Response:** Thank you for your nice comment. We have removed the content of Line 145-152.

Line 140 – Figure 1: I believe it would be worth commenting on how the obtained cluster structures compare with the literature. How does the cluster structures studied here compare to the clusters studied by Engsvang et al?

>>**Response:** Thank you for your nice comment. Yes, we compared clusters studied by Engsvang et al. It is worth noting that the most stable cluster structure of CA-DMA we obtained exhibits similarities to the findings of Engsvang et al(Engsvang et al., 2024). CA-DMA clusters are primarily stabilized by hydrogen bonds.

Line 169: “The ΔG values of $(CA)1(SA)4$ and pure SA clusters are lower than the corresponding ΔG values of the corresponding CA-DMA system.”

These clusters do not contribute to the growth paths of the systems. Hence, I do not see how this sentence contributes to the discussion. I suggest the authors remove the statement.

>>**Response:** Thank you for your nice comment. We have deleted this sentence.

Line 174-175: Some minuses are missing in front of some values here.

>>**Response:** Thank you for your nice comment. We have added the minuses.

Line 174: “The ΔG values of (CA)1−4 clusters are 10.08 − 28.16 kcal mol−1 higher than those of the corresponding (CA)1−4(DMA)1 clusters, suggesting that pure CA clusters may grow by collision with DMA.”

As the pure CA clusters would never form in the first place, I do not believe you can state this. You could state that DMA stabilizes the CA clusters. Please rephrase.

>>**Response:** Thank you for your nice comment. We have revised to “DMA stabilizes the CA clusters”.

Line 177: “As the size of CA-DMA clusters increases, the clusters gradually form a cage-symmetric structure.”

This statement appears a bit out of place. What is the implication of forming cage-symmetric structures?

>>**Response:** Thank you for your nice comment. We have revised to “DMA stabilizes the CA clusters”. We have deleted this sentence.

Line 185-187: “The smaller value of $\Sigma\gamma$ means that the stability of CA-DMA clusters is higher and the clusters shrink further. ”

Line 187-188: “The smaller value of $\Sigma\gamma$ implies the higher stability of CA-DMA clusters and further contraction of the clusters.”

Again these two sentences are just reformulations of each other … Please remove one. With that being said, I do not understand what the authors mean by “shrinking/contracting” in this context. A low total evaporation rate would mean that the clusters do not fragment in the atmosphere.

>>**Response:** Thank you for your nice comment. We have deleted this sentence.

Line 188: “… CA molecules and the number of DMA molecules …” -> “… CA and DMA molecules …”

Section 3.2: In this section the authors find that even at the high end of realistic concentrations (CA = 107 and DMA = 10 ppt) the clusters do not form at 278 K. Hence, the authors lower the temperature to 258 K and 238 K to suppress evaporation and see higher NPF rates. It should be very clearly stated in the this section under which exact conditions this will be relevant. Considering temperature and concentrations relevant to the Arctic would lead to essentially zero clusters being formed from the CA-DMA system. The authors should more transparently present this finding. Again, while negative, this is also an important result, that still further our understanding of marine and Arctic NPF.

>>**Response:** Thank you for your nice comment. We drew the relevant conclusions in Section 3.3. Under temperature and concentration parameters relevant to Arctic environments, the CA-DMA system could be incapable of forming cluster structures. Despite the negative outcome, this represents a significant advancement in advancing research on nucleation mechanisms in marine and Arctic regions.

Line 270: “The cluster formation rates of the pure CA-PA and CA-SA nucleation systems are relatively low, and the contribution of DMA to CA nucleation is stronger than that of SA.”

What is PA here?

>>**Response:** Thank you for your nice comment. Here, PA refers to perchloric acid. We calculated the nucleation of chloric acid and perchloric acid in the supplementary materials.

Line 271: “The CA-DMA nucleation system contributes to the NPF at low Arctic temperatures.”

I do not believe that the presented data allows for this conclusion. You need to make this argument from the absolute NPF rates, not by comparing the relative rates between CA-SA and CA-DMA.

>>**Response:** Thank you for your nice comment. We have deleted this sentence.

Line 272: “Clusters with the same number of CA and DMA molecules ((CA)1(DMA)1, (CA)2(DMA)2, (CA)3(DMA)3, and (CA)4(DMA)4 clusters) play a key role in the growth path of CA-DMA clusters.”

This is a very common finding in acid-base clustering systems. Please elaborate on that this is consistent with the existing literature, so it is not conceived as an entirely new finding.

>>**Response:** Thank you for your nice comment. This conclusion is consistent with the existing literature.

Line 276: “The study clarifies the role of CA in the marine NPF and reveals the mechanism of DMA acting as a key enhancer to CA-based NPF through intermolecular interactions.”

I believe the word “reveals” is a bit exaggerating here. From SA it is well-known that bases enhance NPF. Hence, I would tone down this as a novel finding. It is expected.

>>**Response:** Thank you for your nice comment. We have deleted the word “reveals”.

Line 278: “The results suggest that CA-DMA synergistic nucleation in the Arctic atmosphere is an under-recognized source of NPF …”

With the presented data, I do not believe this is a valid statement. In addition, in the context of cluster formation, synergy is usually used in three or more component systems. Please rephrase.

>>**Response:** Thank you for your nice comment. We have deleted the sentence“The results suggest that CA-DMA synergistic nucleation in the Arctic atmosphere is an under-recognized source of NPF, which provides a theoretical basis for improving regional climate models (e.g., cloud condensation nucleation prediction) and assessing the Arctic aerosol-climate feedback effect.” CA-DMA cluster did not contribute. This study is important for a deeper understanding of Arctic atmospheric nucleation. The current simulations do not take into account charge effects, the involvement of water molecules, and the influence of complex atmospheric matrices (e.g., organic matter). In the future, it is necessary to validate the simulation results with field observations and extend it to multi-component (e.g., IA/SA/DMA mixing or CA-SA-DMA clusters) nucleation systems in order to quantify the contribution of chlorine-containing substances to the global NPF in a more comprehensive way.

Engsvang, M., Knattrup, Y., Kubecka, J., and Elm, J.: Chlorine Oxyacids Potentially Contribute to Arctic Aerosol Formation, Environmental Science & Technology Letters, 11, 101-105, 2024.

Fang, Y.-G., Wei, L., Francisco, J. S., Zhu, C., and Fang, W.-H.: Mechanistic Insights into Chloric Acid Production by Hydrolysis of Chlorine Trioxide at an Air–Water Interface, Journal of the American Chemical Society, 146, 21052-21060, 2024.

Li, J., Ning, A., Liu, L., and Zhang, X.: Atmospheric Bases-Enhanced Iodic Acid Nucleation: Altitude-Dependent Characteristics and Molecular Mechanisms, Environmental Science & Technology, 58, 16962-16973, 2024.

Ning, A., Shen, J., Zhao, B., Wang, S., Cai, R., Jiang, J., Yan, C., Fu, X., Zhang, Y., and Li, J.: Overlooked significance of iodic acid in new particle formation in the continental atmosphere, Proceedings of the National Academy of Sciences, 121, e2404595121, 2024.

Tham, Y. J., Sarnela, N., Iyer, S., Li, Q., Angot, H., Quéléver, L. L., Beck, I., Laurila, T., Beck, L. J., and Boyer, M.: Widespread detection of chlorine oxyacids in the Arctic atmosphere, Nature Communications, 14, 1769, 2023.

Wu, N., Ning, A., Liu, L., Zu, H., Liang, D., and Zhang, X.: Methanesulfonic acid and iodous acid nucleation: a novel mechanism for marine aerosols, Physical Chemistry Chemical Physics, 25, 16745-16752, 2023.

Sincerely

Prof. Qingzhu Zhang

Environment Research Institute

Shandong University

Qingdao 266237

P. R. China