Modelling gaseous and particulate secondary compounds formation during atmospheric degradation of 2-amino-2-methyl-1-propanol (AMP) (EGUSPHERE-2025-4472 | Research article)

Discussion - 2

We thank the reviewers for their questions and comments on our work and appreciate the time spent to review our manuscript. In the text below, the questions raised appear in brown, followed by our responses and the modifications made to the paper. The sentences added are in blue and the sentences removed are in red .

1 Reply to anonymous referee #1's comments

- Manuscript egusphere-2025-4427 by D. Ladet et al. investigates the mechanism of particle formation related to amines by modelling of a chamber photo-oxidation experiment on AMP, a benchmark amine for carbon capture and storage. In addition to the evaluation of modelled AMP oxidation products in the gas phase against measurements, the formation of particulate organic compounds is compared to measurements by CHARON for the respective size range. Total particle number, the mean particle diameter and particle size distributions measured by SMPS are further used to evaluate the simulated particle formation. The effect of different molecular clusters of type NAnAMPm from reactions of nitric acid and AMP is analyzed in two different simulations of the experiment. While exploring new mechanisms for secondary particle formation involving molecular cluster is appreciated, it needs to be emphasized better what is new about modelling in this study, since the same experiment, albeit only gas-phase products, was already modeled by Tan et al. (2021). This involves a clear outline of the new capabilities and aspects, as well as the limitations of the presented modelling. However, it may be argued that simulation of an additional experiment could lead to the need for further adjustments of the rate coefficients for cluster formation. Several omissions and imprecise statements in the current manuscript impede the complete evaluation. The authors should clarify and accommodate the following questions and concerns, before I can recommend publication of this work.

We have revised the Abstract, Introduction and Conclusion to clarify the novelty of the present study relative to Tan et al. (2021). While that study focused on AMP gas-phase oxidation, our work extends the modelling to particle formation by coupling gas-particle partitioning, nucleation, condensation, coagulation, and particle-size evolution. The main new contribution is the introduction of low-volatility NA_nAMP_m clusters, based on mechanisms proposed for chemically similar compounds, to connect AMP-nitric-acid chemistry with particle nucleation and growth. The model is evaluated not only

against gas-phase products, but also against particulate AMP and nitrate, total particle number, mean diameter, and particle size distributions. The comparison of NA_2AMP_2 and NA_1AMP_2 representations further shows that reproducing particle number and size does not necessarily ensure a correct particulate composition. We agree that the molecular-cluster mechanism is not uniquely demonstrated by the available measurements. It should be regarded as a chemically plausible and operational representation, rather than a definitive identification of the nucleating clusters. We now state this limitation more explicitly in the Conlusion and emphasize that additional chamber experiments will be required to further constrain the cluster-formation rate coefficients.
The following sentences were added to the abstract:

> Building on a previous gas-phase modelling study of the same chamber experiment, we extend the chemical mechanism to represent gas-particle partitioning, nucleation, particle growth, and the evolution of the particle size distribution.
>
> These pathways involve NA_nAMP_m molecular clusters and are derived from mechanisms proposed for chemically similar compounds.
>
> Although the molecular composition of the nucleating clusters cannot be uniquely determined from the available measurements, the proposed mechanism provides a chemically plausible and operational representation of AMP-related particle formation.

The following sentences were added to the introduction:

> The gas-phase oxidation chemistry of this experiment was previously modelled by Tan et al. (2021). The present study builds on that work by introducing the processes required to represent particle formation and evolution, including gas-particle partitioning, nucleation, condensation, coagulation, and the evolution of the particle size distribution. The SSH-aerosol box model (Sartelet et al., 2026) is used to couple these processes with the AMP gas-phase chemical mechanism.
>
> The general objective of this work is to represent the distribution of AMP and nitric acid (NA) between the gas and particulate phases and to reproduce consistently the measured particle mass, number concentration, chemical composition, and size distribution. The main new modelling development is the introduction of low-volatility NA_nAMP_m clusters that connect AMP-nitric-acid chemistry to particle nucleation and growth. The proposed reaction pathways are based on mechanisms reported for chemically similar compounds and are evaluated here for AMP. Two alternative cluster representations, NA_2AMP_2 and NA_1AMP_2, are investigated to assess how cluster stoichiometry affects the simulated particle number, size distribution, and particulate AMP-to-nitrate ratio.

The following sentences were added to the conclusion:

> The molecular composition of the nucleating clusters is not measured directly and therefore cannot be uniquely identified from the chamber observations. The proposed mechanism should consequently be regarded as a chemically plausible and operational representation

rather than a definitive molecular description of AMP nucleation. Validation against additional chamber experiments will be needed to further constrain the cluster-formation rate coefficients.

- 1.) Introduction: Please check the citations within the introduction. The order of multiple citations seems arbitrary (example: P2, L32). In case of citing several sources in one row, they should be either in alphabetical order or by year, depending on the journal's formatting guidelines.

The references are now cited in the order of publication, and the revisions have been made throughout the entire document.

- 2.) Experimental context: rephrase first sentence on experiment (P3, L72-74). Tan et al. (2021) have modeled the same experiment (June 15, 2015). It needs to be stated why this experiment was chosen here and what information is missing in the simulation shown in Tan et al. (2021). Their work also presents five other photo-oxidation experiments, why have these not been simulated here?

The work of Tan et al. (2021) include a series of five experiments. Therefore, the present study focuses on the experiment for which complete datasets were available. It would have been very interesting to reproduce the different experiments given the diversity of the experimental conditions, but this was not possible due to the unavailability of this data.

P3 L69: This experiment was selected because it focuses on AMP and includes measurements of amines in the gas and particulate phases, as well as detailed information on particle number and mass. Furthermore, the experiment conducted by Tan et al. (2021) shows that up to 20-60 % of aminium nitrates can form.

As previously mentioned, additional clarifications have been added regarding what information is missing in the simulation shown in Tan et al. (2021):

P3 L73: The gas-phase oxidation chemistry of this experiment was previously modelled by Tan et al. (2021). The present study builds on that work by introducing the processes required to represent particle formation and evolution, including gas-particle partitioning, nucleation, condensation, coagulation, and the evolution of the particle size distribution. The SSH-aerosol box model (Sartelet et al., 2026) is used to couple these processes with the AMP gas-phase chemical mechanism.

We change in section 2.1:

P4 L91: ~~The experiment on which this~~ This work is based ~~comes from~~ on the experiments and modelling results obtained by Tan et al. (2021). The selected experiment was chosen because it provides the most complete dataset for the present modelling study.

- 3.) Are time stamps given as local time or UTC (e.g., 07:48:00 on P3, L82)? This must be indicated at all instances throughout the manuscript, including the figure plots.

Timestamps are given in UTC, changes have been made throughout the document and in the figure captions. The changes were made as follows:

> P4 L103:The experiment was carried out on June 15, 2015. The chamber canopy was opened at 07:48:00 (UTC) and about 10 minutes later, a flow of 0.3 µL/min of isopropyl nitrite (IPN) was injected to maintain high levels of hydroxyl radicals. The end of this experiment corresponds to the closing of the chamber canopy at 10:00:00 (UTC).

and in the caption of all Figures as follow for example for the caption of Figure 1:

> Temporal evolution of particle metrics: (a) total number of particles and (b) number concentration per size section. Time is given in UTC, 'Start OH injection' corresponds to emissions of HO_2 and NO producing OH as explained in section 2.3.3.

- 4.) NA2AMP2 clusters (P7, L167-168): can you elaborate a bit more on "subject to a mechanistic representation" of the physical processes governing aerosol evolution? Maybe it should be stated somewhere that the initial aerosol is assumed to consist completely of NA2AMP2, as Figure 4b indicates. Is this assumption consistent in simulation 1 and 2?

The expression "mechanistic representation of the physical processes governing aerosol evolution" refers to an explicit description of the processes controlling the evolution of aerosol particles mass and size within the model, including nucleation, coagulation, condensation and evaporation. This approach differs from empirical parametrizations that describe aerosol growth based on simplified empirical relationships. We have completed the sentence to be more explicit on this point:

> P8 L196: "... the compounds are all subject to a mechanistic representation of the physical processes governing aerosol evolution. The model explicitly represents mechanisms such as condensation, evaporation, and coagulation, described on the basis of thermodynamic and kinetic principles.

Concerning the initial aerosol, in fact, we have only indicated this in Figure 4b. It is now added in section 2.3.1:

> P10 L261:We assume that the aminium nitrates present in the initial conditions are in the form NA_2AMP_2 for both simulations.

The initial aerosol population is assumed to consist of aminium nitrate particles, in accordance with the observations reported by Tan et al. (2021). Therefore, these initial particles are represented as NA_2AMP_2 clusters. This choice is based on the volatility properties of the considered species: NA_2AMP_2 is sufficiently stable to represent an aminium nitrate particulate phase. For simulation 2, the same initial conditions were maintained to ensure a consistent comparison between the two simulations. However, the exact composition at the start of the experiment has a limited impact on the evolution, as its role consists primarily on providing a surface for condensing compounds.

- 5.) P4, L178: unfortunately, in contrast to what is stated here, the kinetic coefficients of R1 to R4 are not provided in Table 7.

Tab. 1: Kinetic rate constants in $cm^3.molecules^{-1}.s^{-1}$ for bimolecular reactions and in s^{-1} for unimolecular reactions, K_1 the scaling factor for NA_2AMP_2 nucleation, K_2 the scaling factor for NA_1AMP_2 nucleation.

Reaction	Simulation 1	Simulation 2
~~R9~~ R1	0.8×10^{-12}	8.0×10^{-14}
~~R10~~ R2	0.1×10^{1}	0.1×10^{1}
~~R11~~ R3	1.9×10^{-14}	9.0×10^{-14}
~~R12~~ R4	1.0×10^{-4}	1.0×10^{-4}
~~R13~~ R5	—	1.5×10^{-14}
~~R14~~ R6	—	1.0×10^{-3}
K_1	5.0×10^{-7}	1.0×10^{-7}
K_2	—	1.0×10^{-9}

We do indeed apologise for this error, which significantly obscures the meaning. The kinetic rate constants provided in Table 7 are those for reaction numbers R1 to R6, not R9 to R14.

- 6.) Simulation setup: at this point (before the simulation setup section) a clearly formulated section must be inserted that outlines the procedure of rate coefficient adjustments for simulation 1 and simulation 2 as comprehensible as possible. Answering the questions: what was the basis of adjusting rate constants before simulation 1 and what was the basis for adjustment of simulation 2. Were adjustments for simulation 2 decided in the beginning or after simulation 1 was performed?

The second part of section 2.2, entitled "Modelling methodology", has been extensively revised in order to clarify the intent and the modelling choices made. We would like to emphasize that the objective of this work is to understand the processes involved in the formation of aminium nitrates. The kinetic coefficients were adjusted with the aim of finding orders of magnitude rather than precise values. This intent is now explicitly mentioned :

> P9 L232: The kinetic rates of cluster formation and their nucleation rates were adjusted with the aim of identifying the appropriate order of magnitude rather than determining exact kinetic values.

The end of this section is now divided into two parts. The first one (P8 L180) describes the various reactions and transformations taken into account in the two modelling configurations. The second one (P9 L231) gathers the methodology applied, the modelling choices made and the reasons for them.

- 7.) Figure 9 shows measured and simulated temporal concentration profiles of AMP oxidation products. Tan et al. (2021) have the same figure in their publication (Figure 9 therein). IPP in their simulation is not overpredicted. Please discuss the discrepancy based on differences in their gas-phase reaction mechanism for AMP.

We would like to emphasize that using the same set of chemical reactions for amine chemistry and kinetic coefficients as Tan et al. (2021) in SSH-aerosol does not lead to identical results. This is

related to the modelling framework. In the MESMER approach used by Tan et al. (2021), the OH concentration profile is constrained from the measured AMP evolution, whereas in SSH-aerosol OH formation is explicitly simulated and coupled with the multiphase processes. In addition, SSH-aerosol includes gas-particle partitioning and aerosol dynamics, which can influence the evolution of gas-phase species. Furthermore, the two models rely on different mechanistic descriptions of chemical processes, which can lead to differences in simulated concentration profiles even when the same chemical reaction is used. Therefore, in our work some kinetic coefficients were adjusted within the uncertainty ranges reported in the literature, as also done in previous modelling studies, to account for these uncertainties and improve the representation of the experimental observations.
A discussion on the profile of IPP has been added to the article as follow:

> P16 L354: However, the AMPal and P2IMI profiles remain well represented and are included in the measurement error bars~~contrary to~~. With regard to the IPP profile, ~~where~~ the simulation overestimates concentrations even though the IPP branching ratio is identical to that of the simulation by Tan et al. (2021), as is the kinetics of IPP oxidation by OH. The simulation performed with SSH-aerosol models OH formation, unlike the simulation proposed by Tan et al. (2021) with MESMER, where the OH profile used is diagnosed from the measured AMP profile. This could explain a discrepancy in the profiles, as the degradation and formation of IPP is directly related to OH. Furthermore, the SSH-aerosol and MESMER models can, as here, simulate on the basis of the same chemical mechanism, but with different levels of kinetic description. The explicit treatment of internal energy in MESMER can lead to differences in the concentration profiles of certain species..

- 8.) Formation of AMP-nitramine (AMPNO2) (P15/16): The conversion of 138% of reacted AMP to AMPNO2 (P16, L336) must be an error. I suggest comparing the modelled AMPNO2 yield against Braten et al. (2008) who suggest an AMP-nitramine yield of 0.4% of AMP reacted per ppbV NO2 (cited from Tan et al., 2021).

We thank the reviewer for pointing out this error. The value reported in the manuscript was incorrect and should be 18 %, not 138 %. This value represents the fraction of AMP reacted with OH that are converted into $AMPNO_2$ at the end of the simulation. It is obtained from the simulated fate of AMP molecules undergoing OH oxidation under the specific experimental conditions considered. It should therefore not be interpreted as the $AMPNO_2$ yield relative to the total reacted AMP, nor as the $AMPNO_2$ formation yield per ppbV of NO_2 as reported by Bråten et al. (2008). We have clarified this point in the manuscript and corrected the value.

> P17 L388: These values represents the fraction of AMP reacted with OH that are converted into AMPNO2 or AMPNO at the end of the simulation. It is obtained from the simulated fate of AMP molecules undergoing OH oxidation under the specific experimental conditions considered.

- 9.) Discuss the possibility of uptake of AMPNO2 to particles and heterogeneous surface reactions on particles.

Uptake of semi-volatile compounds onto particles may only be significant when there is no initial particle mass, i.e. in very clean environments, which are extremely rare. Hence it is not taken into account in the SSH-aerosol software. We have added a discussion on heterogeneous surface reactions in section 3.2:

> P17 L378: In addition, Tan et al. (2021) present mass spectrometer results suggesting the production of nitramine on particles. Their work on particle filters also corroborated this observation with the results of their GC×GC-NCD analyses of nitramines and other organic nitrogen compounds in the particulate phase. However, these observations do not allow us to take into account the formation of nitramines and heterogeneous reactions due to the complexity of these processes and the lack of available data required to characterize and parameterize them (Shen et al., 2023). Other studies also highlight the possible contributions of heterogeneous reactions in the partitioning of several amino compounds, like imines, but present them as complex and multifactorial (Qiu and Zhang, 2013; Tan et al., 2020, 2021; Shen et al., 2023) .

- 10.) Despite simulation 1, which employs the low-volatility dimer NA2AMP2, tends to overestimate the nitrate mass, there are several reasons why simulation 1 should be preferred over simulation 2. What speaks against simulation 2 is that production of PAMP stops earlier than in simulation 1 (Figure 9) even though there is still sunlight to produce HNO3 (measured NO2 is still increasing). Also, I believe that measurements of the total particle number and the particle size distribution have a higher accuracy than the mass-based concentration measurements. Therefore, matching the size-resolved particle numbers is a stronger criterion for evaluation of the simulations than the more uncertain mass component measurements. Simulation 2 performs worse in comparison to SMPS size distribution than simulation 1. Furthermore, the mean diameter (Fig. 10a) in simulation 2 shows a sharp drop 15 minutes before this is observed by the SMPS measurement, indicating that the nitrate aerosol has too high volatility in this simulation.

The reviewer's comments have been taken into account, and the following additions have been made to the manuscript:

> P22 L446: Simulation 1 provides a better representation of the temporal evolution of the mean diameter and particle size distribution compared with the SMPS observations. The earlier decrease in mean diameter obtained with simulation 2 suggests a more volatile particulate phase, leading to faster repartitioning of aminium nitrate compounds between the gas and particle phases. Therefore, simulation 2 should be considered as an exploratory sensitivity case investigating the influence of a different NA/AMP ratio in the molecular clusters, rather than an improved representation of the mechanism despite the improvement obtained for particulate nitrate mass concentration.

> P21 L438: Simulation 2, as previously mentioned, is more complex to optimize. Indeed the additional cluster formation and evaporation pathways increase the number of degrees of freedom and the complexity of the parameter space, making the identification of optimal parameters more challenging.

We would like to reiterate in this response, as we did in response to question (6), that simulation 2 aims to explore the possibilities with the participation of clusters with a ratio of 1:2 for NA and AMP. We agree that simulation 1 gives better results . Furthermore, poorer results are possibly due to the complexity of the system, which includes three additional kinetics (taking nucleation into account), making optimization more complex even when using screening.

- 11.) In addition to comparing the two simulations, it would be helpful to see the simulated particle formation for gradually changing the volatility of the molecular clusters, as a test of sensitivity towards the assumed or derived saturation vapor pressures.

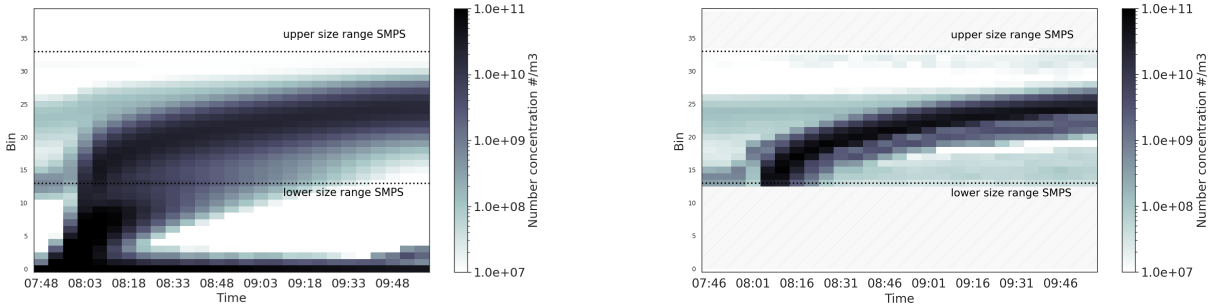
We acknowledge that the saturation vapor pressure of molecular clusters represents a major source of uncertainty in the proposed mechanism. However, no experimental data are currently available for AMP–nitric acid clusters, and the value used in this study is based on molecular modelling results obtained for chemically similar compounds.
A systematic sensitivity analysis of cluster volatility would also require the reoptimization of the associated kinetic coefficients, as evaporation, gas-particle partitioning, and nucleation processes are strongly coupled. Such an analysis is therefore beyond the scope of the present study but should be addressed in future work, together with additional constraints from molecular modelling and chamber experiments.

- 12.) It seems that the reaction numbers (R9-R14) in Table 7 are not the ones that were intended for this table. I had rather expected a table with the rate coefficients of R1 to R6. Table 3 already provides rate coefficients for the chamber-specific reactions R10-R13 and particle loss (is that R14?). Reaction R9 denotes the reaction HO2+NO, which according to the NIST database is 8.91E-12 cm3/molecule s at 298 K (Atkinson, 2004) and certainly not uncertain by two orders of magnitude. At least the reasoning for changing rate constants of R9-R14 in simulation 2 needs to be justified.

Indeed, the coefficients in Table 7 are those for reactions R1 to R6; we have corrected this. None of the reactions relating to deposits are modified between simulations. We would also like to note that reactions R8 and R9 are not included in the chemical diagram but are modeled by the direct emission of HO_2 and NO, which also remains unchanged between the two simulations. This confusion is due to our error in numbering the reactions.

- 13.) The broadening of the modelled number size distribution during growth indicates numerical diffusion. It is stated that increasing the number of size bins does not provide a better representation (P22, L403-405). Nevertheless, the possibility of numerical diffusion needs to be discussed, and the effect of changing the size representation on the width of the modelled size distribution should be documented in a supplement.

The initial formulation of our comment on the number of bins was ambiguous, and we would like to clarify it. Increasing the number of size classes reduces numerical diffusion and improves particle distribution during a simulation. However, between our 40-bin and 80-bin simulations, we did not observe a significant improvement in the particle size distribution over time. We have clarified this point in the article and added a comparison of the curves for the two size distributions in the appendix. We have added the following clarifications:



(a) (b)

Fig. 1: Modelled data and comparison to measurements: particle number concentration and size distribution over time (a) for SSH modelling on 40 bins, and (b) for SMPS data on 40 bins for simulation 1. Time in UTC.

P23 L465: In addition, tests were carried out on the number of bins used, and the results between 40 and 80 ~~bins remained similar. Increasing the granulometric discretization did not provide a better representation of particle distribution.~~bins remained fairly similar. Increasing the particle size discretization did not significantly improve the representation of particle distribution compared to measurements. The simulation and SMPS data projected over 40 bins are presented in the Appendix B. Nevertheless, numerical diffusion is a phenomenon to be considered, as it can impact simulations of this type, particularly when the number of bins is low.

- 14.) Conclusions: atmospheric implications of the suggested formation of molecular nitric acid – AMP clusters in competition to nucleation of amines with sulfuric acid should be more quantitative. For the typical ranges of atmospheric mixing ratios of dimethyl amine (DMA) and sulfuric acid in the background boundary layer, which mixing ratios of AMP and nitric acid would be required to preferentially form NA2AMP2 clusters? The formation of aminium nitrate particles would probably be relevant only in the close vicinity of a capture plant. Such conclusions would obviously also depend on the assumed volatility of the nitric acid – AMP clusters. Another nucleation route may be acid-base reactions with methanesulfonic acid (MSA) when carbon capture is used in coastal environments (Perraud et al., 2024), which should be discussed in the implications section.

A quantitative estimation of the formation of AMP-nitric acid clusters in competition with the formation of AMP-sulfuric acid clusters would require a direct comparison. However, the atmospheric relevance of AMP-nitric acid clustering is expected to depend strongly on environmental conditions and precursor concentrations. Such a pathway may become particularly relevant in the vicinity of amine-based carbon capture facilities, where local AMP concentrations can be significantly enhanced. This would require a consistent description of the different mechanisms, particularly for nucleation with sulfuric acid, under identical atmospheric and operational conditions. This type of comparison could be interesting to carry out within the framework of an atmospheric dispersion model that allows the

formation of particles to be evaluated under realistic conditions. Under typical background boundary layer conditions, nucleation pathways involving sulfuric acid and efficient bases such as dimethylamine are expected to remain highly competitive due to the low volatility of the resulting clusters.
As the objective of this work focuses on studying the processes involved in the formation of aminium nitrate particles, this analysis exceeds the scope of the study but provides an interesting perspective for this work.
Following the reviewer comment, we have made the following changes in the conclusion :

> However, in the case of the atmosphere, amines can also undergo acid-base reactions ~~with sulfuric acid. A similar method, certainly with a higher proportion of nucleation compared to what has been implemented for nitric acid, will have to be implemented.~~with other acids such as sulfuric acid (SA) or methanesulfonic acid (MSA). The relevance of the different particle formation pathways depends strongly on environmental conditions, precursor concentrations, and the thermodynamic properties of the molecular clusters involved. A quantitative comparison of nucleation pathways involving different acids (NA, SA, MSA) using a chemistry-transport modeling approach is a perspective of this work to assess an evaluation under realistic conditions.

- Technical corrections:
  Abstract, L12: add "chamber" before "experiment".
  P3, L77: instead of "Measures of concentrations in the particulate phase", it would be better to write "Measurements of the chemical composition in the particulate phase."
  Figure 1: plot (a) "start OH injection". I assume that OH radicals are not directly injected. What is injected to start OH production? This needs to be fixed in all plots, for example Fig. 5 and Fig. 6.
  Equation (1): "P8L" should not appear in this equation.
  P10, L229: add "is" between "it" and "out".
  P10, L236: replace "setup" by "conditions".
  Figure 5: figure caption should mention the blue shaded area. Does it indicate the measurement uncertainty of NO2?
  P16, L323: Replace "ith" by "being".
  Figure 8 and Figure 9: indicate in the figure captions that Fig. 8 refers to simulation 1 and Fig. 9 refers to simulation 2.
  Figure 12: swap figure part a and b to be consistent with Figure 11.

These comments have been taken into account and changes have been made in the relevant sections.

2 Reply to anonymous referee #2's comments

- Overall evaluation: I agree with reviewer No. 2 that the accuracy and reliability of this AMP mechanism is a major concern.

The proposed mechanism is supported by both established acid-base chemistry and the simultaneous reproduction of a broad set of independent gas and particle-phase observations. Aminium-nitrate

formation is a well-documented pathway for atmospheric amines, and theoretical studies of related amine-nitric-acid systems support the progressive stabilization of clusters containing multiple acid and base molecules. The mechanism is therefore not solely empirical, even though some parameters must be estimated in the absence of AMP-specific molecular data. In the present representation, the clusters are treated as semivolatile or extremely low-volatility gas-phase species that undergo dynamic condensation, evaporation, nucleation, coagulation, and size-resolved aerosol evolution, rather than being transferred directly and irreversibly to the particle phase. The resulting mechanism reproduces gaseous AMP and its major oxidation products, particulate AMP and nitrate, total aerosol mass, particle number, mean diameter, and the temporal evolution of the particle-size distribution. In addition, sensitivity simulations demonstrate that nucleation and coagulation are required to reproduce the observed particle-number evolution. The simultaneous agreement across these complementary observables provides substantial support for the physical consistency and reliability of the mechanism under the investigated experimental conditions. The remaining uncertainties mainly concern the precise values of AMP-specific cluster volatilities and kinetic coefficients, rather than the relevance of the proposed AMP-nitric-acid clustering pathway itself.

In the conclusion section, the sentences lines 410-412 were removed:

> ~~A multiphase chemistry of AMP has been developed and evaluated through the SSH-aerosol model by comparison with a controlled atmosphere experiment. Future deployment of amine scrubbing carbon capture processes will require knowledge to best assess the impacts of atmospheric emissions on people and the environment.~~

and replaced by:

> A comprehensive multiphase chemical mechanism for AMP has been developed, implemented in SSH-aerosol, and successfully evaluated against observations from a controlled-atmosphere experiment. The mechanism provides a physically consistent representation of the gas-phase oxidation of AMP and the formation, partitioning, nucleation, and growth of particulate aminium nitrate. Its ability to reproduce complementary gas and particle-phase observables supports its reliability under the experimental conditions investigated. Such a modelling framework is needed to assess the atmospheric fate and potential environmental and health impacts of AMP emissions associated with the future deployment of amine-based carbon-capture technologies.

and the following paragraph was added:

> In contrast to simplified approaches that directly and irreversibly convert gaseous AMP and nitric acid into particulate matter, the present parameterization explicitly accounts for cluster volatility, gas-particle partitioning, nucleation, condensation, evaporation, coagulation, and size-resolved particle evolution. The resulting framework therefore constitutes a robust basis for simulating AMP aerosol formation and for extending the evaluation of AMP emissions from chamber conditions to atmospheric applications.

- (1) Line 192: The formula of nucleation rate, J could not be well justified.

The nucleation rate was represented using the commonly employed power-law formulation for low-volatility organic nucleation:

$$J = K \times [\mathrm{NA_2AMP_2}]^2 \quad (1)$$

The quadratic dependence assumes that the rate-limiting step is the bimolecular association of two gas-phase NA_2AMP_2 clusters to form an embryo sufficiently stable to enter the smallest particle-size section. According to mass-action kinetics, the collision frequency of two identical clusters is proportional to $[NA_2AMP_2]^2$. The very low saturation vapour pressure assigned to NA_2AMP_2 supports the assumption of limited evaporation following association. The fitted coefficient K should therefore be regarded as an effective nucleation coefficient that incorporates the collision frequency, cluster stabilization and survival to the modelled nucleation size. This formulation is semi-empirical, as explicit molecular-cluster kinetics are not available for the AMP-nitric-acid system.

In the paper, the initial justification of our modelling choice (line 193-195)

> ~~In the absence of an established mechanistic law, we propose choosing a quadratic dependence based on a bimolecular process hypothesis, which ensures realistic sensitivity of the nucleation rate with respect to concentrations.~~

was developed and replaced by

> The quadratic dependence assumes that the rate-limiting step is the bimolecular association of two gas-phase NA_2AMP_2 clusters to form an embryo sufficiently stable to enter the smallest particle-size section. According to mass-action kinetics, the collision frequency of two identical clusters is proportional to $[NA_2AMP_2]^2$. The very low saturation vapour pressure assigned to NA_2AMP_2 supports the assumption of limited evaporation following association. The fitted coefficient K should therefore be regarded as an effective nucleation coefficient that incorporates the collision frequency, cluster stabilization and survival to the modelled nucleation size.

- (2) Line 269: the wall loss rate constant of NO2, O3, HNO3, and AMP was reduced to 1e-5 to keep consistent with particle loss. This setting could not be justified either. It is very likely that HNO3 is deposited to the wall much faster than O3.

The reviewer's interpretation does not correspond to the wall-loss treatment implemented in the model. The wall-loss rate constants are species-specific and were not all set to $1\times10-5\ s^{-1}$. As stated in section 2.3.4, the various wall loss rates used for gaseous species (except AMP) were selected in accordance with a previous study cited in our text (Bloss et al., 2005). Table 3 sets out the numerical values used. The constants used for NO_2, O_3 and HNO_3 are 1.5×10^{-5}, 3.8×10^{-6}, and $8.2\times10^{-5}\ s^{-1}$ respectively, following the characterization of the EUPHORE chamber by Bloss et al. (2005). These three values were not modified. In particular, the HNO_3 wall-loss rate is approximately 22 times higher than that of O_3, in agreement with the reviewer's expectation that HNO_3 is removed much more efficiently by

the chamber walls than O_3. Only the AMP wall-loss coefficient was adjusted, from the apparent value of 4×10^{-5} s^{-1} estimated by Tan et al. (2021) to 1×10^{-5} s^{-1}. Tan et al. derived their coefficient from the apparent first-order decay of gas-phase AMP. In the present model, AMP loss through gas-phase chemistry and gas-to-particle transfer is represented explicitly. Applying the full apparent decay coefficient as an additional wall-only sink therefore resulted in excessive total removal of AMP.
We have corrected the units in the caption of Table 3: all the listed wall-loss coefficients are first-order coefficients expressed in s^{-1}. We have apologize for the unit error that could have lead to ambiguity.

The following sentences were added to the paper:

> Only the AMP wall-loss coefficient was adjusted, from the apparent value of 4×10^{-5} s^{-1} estimated by Tan et al. (2021) to 1×10^{-5} s^{-1}. Tan et al. derived their coefficient from the apparent first-order decay of gas-phase AMP. In the present model, AMP loss through gas-phase chemistry and gas-to-particle transfer is represented explicitly. Applying the full apparent decay coefficient as an additional wall-only sink therefore resulted in excessive total removal of AMP.

- (3) Different rate constants (R9 R14) and scaling factors (K1 and K2) were used in simulations 1 and 2 (Table 7) without proper reasons. Usually, the same rate constant should be kept consistent among different modeling scenarios.

First, we apologise for the entirely avoidable error in Table 7, which makes the discussion confusing. The kinetic rates provided in this table are those for reactions R1 to R6, not R9 to R14. These reactions represent the formation and evaporation rates of the different clusters. The scaling factors are used to quantify the nucleation rates.
Given that the two proposed versions of the mechanism do not represent the same production pathways, and that the same observations are used to empirically adjust the various parameters, while these observations do not provide sufficient constraints to uniquely determine their values, it is not surprising that the two versions do not yield the same results. Consequently, the fitted parameters do not represent independent experimental kinetic constants, but effective parameters associated with each model representation. Simulation 2 should therefore not be considered as an optimization of simulation 1, but rather as an alternative representation of the particle formation mechanism, introducing an additional hypothesis regarding the molecular composition of the nucleating clusters.
We fully agree with the reviewer this is naturally a proof that the values chosen to quantify these different processes are certainly not definitive and that we need additional observation to better constraint the proposed mechanism.
The following paragraph was added to the conclusion:

> The molecular composition of the nucleating clusters is not measured directly and therefore cannot be uniquely identified from the chamber observations. The proposed mechanism should consequently be regarded as a chemically plausible and operational representation rather than a definitive molecular description of AMP nucleation. Validation against additional chamber experiments will be needed to further constrain the cluster-formation rate coefficients.

- Since the chamber experiments discussed here come from another paper and this work relies heavily on the box model, the above concerns regarding the box model are critical. So, I could not recommend its publication in ACP.

We disagree that the use of a published chamber experiment and of a box-model diminishes the scientific contribution of this study. The novelty of the present work lies in exploiting the full potential of an existing, comprehensive experimental dataset to develop and evaluate a new multiphase chemical framework for AMP. The original study by Tan et al. (2021) primarily investigated the OH-initiated gas-phase degradation of AMP. In contrast, the present study extends this work by introducing a mechanistic representation of AMP–nitric-acid cluster formation, dynamic gas–particle partitioning, nucleation, condensation and evaporation, coagulation, and size-resolved particle evolution. These developments are intended ultimately for implementation in chemistry-transport models and constitute the central scientific contribution of the manuscript.
The chamber experiment of Tan et al. (2021) provides a particularly suitable dataset for this development because it includes complementary measurements of gas-phase AMP and oxidation products, particulate AMP and nitrate, total aerosol mass, particle number concentration, and particle-size distributions. Reusing such a comprehensive and well-characterized dataset allows the new mechanism to be evaluated against substantially more information than would be available from many individual chamber experiments. The measurements are not reproduced or reinterpreted as a new experimental contribution; they are used transparently as an observational benchmark for a distinct modelling objective. The use of the SSH-aerosol box-model configuration is also deliberate and appropriate for this stage of mechanism development. A controlled chamber simulation allows chemical and aerosol-dynamical processes to be isolated from atmospheric transport, emissions variability, mixing, and meteorological uncertainties. This provides a more direct test of the proposed multiphase chemistry than immediate implementation in a three-dimensional model, where errors arising from several processes could compensate for one another. Evaluation in a box model under controlled conditions is therefore a relevant first step before application of the mechanism in a chemistry-transport model.
Moreover, the mechanism is not evaluated against a single fitted quantity. It is constrained by the simultaneous representation of gas-phase species, particulate composition, aerosol mass, particle number, mean diameter, and the temporal evolution of the size distribution.
We hope that the corrections and clarifications made in response to the reviewers' suggestions and comments will enable the second reviewer to reconsider their opinion of our manuscript.
We have revised the manuscript extensively in response to the reviewer's methodological concerns. In particular, we have clarified the species-specific treatment of gaseous wall losses, the independent treatment of particle wall loss, the physical interpretation of the quadratic nucleation parameterization. We have stated the limitation of the mechanism more explicitly in the Conclusion and emphasized for instance that additional chamber experiments will be required to further constrain the cluster-formation rate coefficients. We therefore believe that the revised manuscript provides a substantial and relevant contribution to understanding and modelling the atmospheric fate of AMP emissions.

Other minor comments for authors' reference:

- The introduction part should briefly describe currently known degradation mechanism(s) of AMP, if any.

P3 L77: The atmospheric degradation mechanisms of AMP have mainly been investigated in the gas phase. Existing studies have characterized its reaction with OH radicals, the main oxidation pathways, and several gaseous degradation products. The formation of particles containing aminium nitrates has also been experimentally observed; however, the detailed mechanisms describing their formation and subsequent chemical evolution have not yet been established. (Tan et al., 2021; Li et al., 2020; Carter, 2008)

- Line 64: the meaning of "SSH" should be clearly introduced since this is the first time "SSH" appears.

"SSH-aerosol" is the name chosen for the model that represents the physicochemical transformations undergone by aerosols (particles with the surrounding gas). As described in Sartelet et al. (2026), the model is based on the merge of three state-of-the-art models:

- SCRAM: The Size-Composition Resolved Aerosol Model, for aerosol dynamics
- SOAP: The Secondary Organic Aerosol Processor, for organic aerosol dynamics
- H2O: The Hydrophilic/Hydrophobic Organics, for gaseous chemistry.

The name "SSH-aerosol" is therefore simply derived from the initials of the names of these three models and has no specific meaning beyond this simple choice.

- Line 75: "aProton" looks like a typo.

Indeed, many thanks.

- Line 80: several examples of uncalibrated compounds should be given.

Examples were added.

The measuring instruments also have an estimated uncertainty of 25 % for uncalibrated compounds (e.g. the radical $CH_3(CHO)CNH_2$ later noted AMPal or the imine $(CH_3)_2C{=}NH$ later noted P2IMI) and 10 % for calibrated compounds (e.g. AMP).

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