Answers to the First Reviewer's Comments

Parameterization of particle formation rates in distinct atmospheric environments

Xinyang Li et al., 2025

The line numbers in bold refer to indicating the changes made in the manuscript to be further uploaded.

 L217-218: I think the correction for hygroscopic growth was necessary for the intercomparisons. The CS and CoagS terms may vary substantially depending on the RH and the aerosol chemical compositions.

Reply:

We appreciate the reviewer highlighting the concern of the hygroscopic correction on CS and CoagS. The goal of not implementing the hygroscopic correction is mainly to harmonize the data composition and the later model analysis.

We will add the following text in section 2.3.3 to support the decision of excluding the hygroscopic correction on CS and CoagS.

Additional text from L218 (Now L224-236):

"There are several ways to determine the hygroscopic growth factors in CS and CoagS calculations. Laakso et al., (2004) developed parameterizations for Hyytiälä solely based on the meteorological conditions and the aerosol composition in Hyytiälä, which results in the inapplicability of that method to other sites. In the Supplementary of Baalbaki et al., (2021), Figure S4 shows the CS with hygroscopic correction is about 1.1 – 1.3 times higher than dry CS, which would result in an overestimation on CS for the case in Cyprus. Petters and Kreidenweis (2007) introduced the single hygroscopicity parameter κ (kappa), which can be derived from Humidified Tandem Differential Mobility Analyzer (HTDMA) or cloud condensation nuclei counter measurements or based on aerosol chemical composition obtained from instruments such as the Aerosol Chemical Speciation Monitor (ACSM) or Aerosol Mass Spectrometers (AMS). In other locations, since organics are typically the dominant component of aerosol mass in continental areas or marine polluted areas (Chen et al., 2022) and are less hygroscopic than inorganics, one can expect an underestimation of CS similar to the one reported in Baalbaki et al., (2021). As a result, we omitted the hygroscopic growth impact for the chosen measurement sites to harmonize the data composition and the later model analysis."

Furthermore, since we have RH in our parameterization combined with CS without a hygroscopicity correction, the increased sink due to hygroscopic growth of particle is transferred from CS to RH in our parameterization. We modified the text in section 3.1 into the following form in L242 (Now L260-269):

"For example, CS is a measure of a sink for anthropogenic vapors in a megacity (Wang et al., 2011) and for biogenic vapors in a clean boreal forest (Dada et al., 2017; Tuovinen et al., 2020), as well as a sink for growing sub-5 nm clusters and particles (Kulmala et al., 2017). When combined with H_2SO_4 as an input variable, the evidently important sink effect of a pre-existing particle population on the ambient H_2SO_4 concentration is implicitly transferred from CS to H_2SO_4 in our parameterization. Indirectly, CS may also be associated with 1) either emissions or sinks of vapors other than H_2SO_4 participation in NPF or particle growth, and 2) primary particle emissions from traffic, which would influence particle formation rates estimated from observations using eq. 1. Furthermore, since we omit the influence of hygroscopic growth of particles on CS, a fraction of real sink effect of CS is implicitly transformed to the variable RH in our parameterization."

2) L248: It is understandable not to include HOMs and NH₃ in the parameterization due to the lack of data. However, it is more important to know how the exclusion of these compounds would impact the performance of these models. How sensitive are these models to the H₂SO₄ data, especially when H₂SO₄ proxies are used, which may lead to substantial uncertainty in H₂SO₄ input data?

Reply:

We agree that adding HOM and NH_3 could potentially enhance the model performance further. For HOM, our first consideration was that the definition of HOM varies from environment to environment depending on the primary emission types and oxidizing compounds. It leads to challenges in generalizing the molecular mass range of HOM for global model parameterization. Here we can provide the comparison result of model trainings with and without adding HOM data (same measurement period as H_2SO_4) from Hyytiälä. From Figure 1 below it can be seen that HOM is not improving the model, but quite the opposite as seen from the decreased Pearson *r* values. Therefore, we stayed with the most significant vapor H_2SO_4 .



Figure 1. Model training with the functioning forms of $J_5 = k_{\text{test}}[H_2SO_4]$ (left), and $J_5 = k_{\text{test}}[H_2SO_4]$ [HOM] (right) using Hyytiälä data.

For NH₃, it is indeed a very significant component in particle nucleation processes in many environments. Though we cannot provide test examples due to the unavailable NH₃ data in any of the chosen sites, we will explain our concerns here. NH₃ is emitted primarily from agriculture lands. In our case, the only agriculture-relevant environment is Agia Marina in Cyprus, where the vapor types are typically mixed among H_2SO_4 , organic vapors, NH₃ and marine vapors. In addition, Cyprus data is short-term compared to other sites included (except for Budapest) in this study. Therefore, we speculate the effect of NH₃ is minor in our model training.

Both H_2SO_4 models for Hyytiälä and Beijing in Dada et al., (2020) have their slopes extremely close to 1 on testing dataset, which granted advantages to the models to be applied on a broader scale. According to our testing results (Table 3), the Pearson *r* differs little using the measured H_2SO_4 or H_2SO_4 proxy data in Hyytiälä. The difference in Beijing Pearson *r* between using the measured and proxy H_2SO_4 is possibly due to the data availability in the testing dataset. The measured H_2SO_4 in Beijing testing dataset ranges from May 2018 to April 2019 (almost one year), while the proxy data covers March to April 2019 (only in spring).

3) L356: Strictly speaking, NPFs were often associated with Low RH conditions, which does not necessarily mean that low RH favors NPFs. These two phenomena may concur due to the same underlying cause. For instance, stronger solar irradiation can lead to higher ambient temperature and, thus, lower RH. However, the real factor in intensifying NPF could be the increased atmospheric photooxidation capacity that led to more production of NPF gas precursors.

Reply:

In section 3.1.1, we mentioned the relation between global radiation and RH, and we agree with your suggestion and will modify the text accordingly:

Current text in the current manuscript, from L355-357:

"which confirmed the strong relationship of the low RH favoring NPF occurrence for the boreal forest environmental conditions (Dada et al., 2018; Hamed et al., 2011)"

Text modified from L355-357 (Now L383-386):

"which demonstrates a potential favoring of NPF under low RH conditions, likely associated with increased global radiation for the boreal forest environment (Dada et al., 2018; Hamed et al., 2011) and lower sinks for vapors and growing sub-5 nm particles (see section 3.1)."

- 4) L357: It is a bit strange that the higher SA and lower CS in Värriö would lead to a lower frequency of NPF.
- 5) L373: There is still no direct evidence that meteorology will significantly impact NPF in Beijing. The CS term was indeed playing a critical role in regulating NPF in Beijing.
- 6) L374-375: How did background aerosols sustain NPF? Did not the loss to preexisting aerosols compete with the formation of sub-5 nm particles? The high levels of background SO₂, VOCs, and their oxidation products may be responsible for the intense NPFs in Beijing.

Reply to comments 4, 5 and 6 together:

The lack of other stabilizing agents in Värriö (e.g. NH_3 , amines, VOCs, etc.) may result in the low contribution of H_2SO_4 even when H_2SO_4 concentration is higher than that in Hyytiälä. For that, we would need measurement of the stabilizing gases to investigate further. Another speculation of the low NPF frequency in Värriö is that the organic vapor pathway may compete with the H_2SO_4 pathway at 5 nm particles, leaving high H_2SO_4 concentration seemingly less effective. As a result, we believe the statements given above are potentially the reasons for such NPF phenomena in Värriö. We will add the modifications in the manuscript accordingly.

We sincerely thank the reviewer for the critical and important comment on the meteorological impact on NPF in Beijing and appreciate that the reviewer pointed out an imprecisely addressed statement on CS in the text.

We have modified the text in the current manuscript in L370 (Now L399-405) into the following form:

"As expected, the testing result showed dramatic underestimations for Beijing using model 1 with only H_2SO_4 concentrations considered (Fig. 3(d1)), whereas models 2 (Fig. 3(d2)) and 3 (Fig. 3(d3)) yielded clearly enhanced J_5 predictions, with relatively minor differences between models 2 and 3. These features are consistent with the fact that in addition to H_2SO_4 , also other vapors are import to NPF and sub-5 nm particle growth in Beijing, and demonstrate that RH and CS in our parameterization together determine in a complicated way the sources and sinks of these vapors, the survival probability of sub-5 nm particles, and the potential emissions of sub-10 nm primary particles from traffic."

We also added clarifications to Sect. 4.1 in L349 (Now L377-379):

"It is notable that with the combined data sets, the condensation sink receives a positive exponent in models 3 and 4 (k_{CS} = 0.56 and 0.67, respectively), likely due to its association with concentrations of other condensable vapors than H₂SO₄ and traffic emissions."

... in the conclusions in L465 (Now L506-511):

"The particle formation schemes involve the main precursor vapor H_2SO_4 , relative humidity (RH) and condensation sink (CS). Due to the small number of parameters and the diversity of environments included to generate the schemes, the roles of RH and CS are not only related to their potential direct impact on J_5 , but also to sources and sinks of vapors other than H_2SO_4 contributing to formation and growth of sub-5 nm particles and to potential emissions of sub-10 nm particles, e.g., from traffic."

...and additional texts in L490 (Now L535-537):

"Some caution should be maintained when utilizing these models for environments with very low RH and/or high CS, especially if the high CS is related to primary particle emissions, as the associations between these model parameters and J_5 are complicated and multifaceted."

...and in the abstract (L24-26):

"However, the dependencies between *J*, condensation sink, and relative humidity are affected by their interlinked relations to sources and sinks of other condensable vapors than sulfuric acid and the potential traffic emissions to the observed size range."

Additionally, we have replaced the wordings possibly interpreted to mean (direct) impacts of meteorology and vapor loss with expressions more clearly mentioning relative humidity and condensation sink as model parameters (**L466**).

7) L411: These results strongly suggested that precursors other than H₂SO₄ should be considered for these models to work appropriately in marine environments.

Reply:

We appreciate the reviewer for the insightful comment on the precursors in regards of marine environment in the parameterization. Indeed, iodine-driven nucleation can be more responsible than H_2SO_4 -driven nucleation in marine environment during NPF events. However, iodine related vapors are confined within marine environment (Sipilä et al., 2010). When we do the parameterization for a single environment, we will consider thoroughly the key components in the local NPF characteristics. When parameterizing global environments, we aim for the models to be as representative and simple as possible to cover the most common NPF mechanism for the majority of environments. In addition, SO_2 is also transported globally and oxidized in the atmosphere above the marine regions, providing that its role as a precursor vapor in marine NPF mechanisms cannot be neglected. Naturally, we strongly recommend conducting the *J* parameterizations in marine environments following the environment-specific NPF mechanism.

8) L426: The Manacapuru case may be very special. The RH was very high year-round, and thus, J_5 became insensitive to variations in RH and the corresponding aerosol hygroscopic growth, which may be treated as a constant. This may explain the better slope (1.02) found in model 1 simulation (Fig. 3h1).

Reply:

We would like to thank the reviewer for clarifying the RH impact on the NPF mechanism in Manacapuru. Manacapuru is a very interesting environment for our parameterization precisely because of the near insensitivity of RH on J_5 as compared to other locations. This is an observation acknowledging that RH likely doesn't play a dominant role in controlling NPF events in Manacapuru.

We will modify the text in L426-429:

"These current findings provide evidence for H_2SO_4 being an effective enough precursor for the particle formation at 5 nm, as well as the RH stabilization effect on H_2SO_4 in the atmosphere of Manacapuru. So far, model 4 with a focus on the H_2SO_4 concentrations along with meteorology and vapor loss impacts manages to predict J_5 for biogenic vapor dominated environment like Manacapuru."

Text modified in L426-429 (now L466-470):

"These current findings provide evidence for H_2SO_4 being an effective enough precursor for the particle formation at 5 nm in the atmosphere of Manacapuru (model 1, Fig 3(h1)). However, the RH stabilization effect on H_2SO_4 is not exerted necessarily, as RH remains at high values at around 89 ±13 % despite whether it is measured during wet season or dry season (Myers et al., 2022). With these observations, model 1 with a focus on the H_2SO_4 concentrations manages to predict J_5 well for biogenic vapor dominated environment like Manacapuru."

9) These J-models were developed to predict NPF rates globally, but they did not consider nucleation mechanisms involving iodine oxoacids (IO). Since ~70% of the Earth's surface is seawater, how would this affect the application of these J-models by omitting IO-related NPF mechanisms?

Reply:

We sincerely thank the reviewer for the critical comment on the choice of precursor in our global parameterization models. We believe part of our answers in point 7 can explain this question as well. Besides the global circulation of SO₂ and their oxidation product H₂SO₄ over the marine regions, iodine products play a crucial role in marine NPF events. The iodine measurements take place usually at certain marine site, while they are usually not measured for inland regions, such as Hyytiälä, Värriö, Budapest, etc. It brings difficulties to obtain measured iodine oxidation products for the chosen locations in this study. However, we would strongly recommend including iodine related products when conducting *J* parameterization specifically for marine regions.

We add the following text to support our statement at L490 (now L538):

"While the parameterizations presented in this study offer an improvement over previous approaches, further development is needed to incorporate vapors important for NPF, such as iodine oxoacids, particularly in marine environments.".

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