Response to Referee #1

General Comments

This manuscript investigates the contribution of sulfuric acid and organic vapours (essentially alpha-pinene oxidation products) on the growth of sub-10 nm size particles as a function of particle size and relative humidity based on laboratory experiments. The investigation appears to be robust and novel enough to be published in a scientific publication. There are a few issues, however, that should be addressed before final acceptance of this work.

Responses and Revisions:

We thank the reviewer for the constructive suggestions and comments concerning our manuscript entitled "Unveiling the organic contribution to the initial particle growth in 3-10 nm size range" [egusphere-2025-4421]. We sincerely appreciate these insightful comments, which have significantly improved both the quality of our manuscript and the methodological rigor of our ongoing research.

We have prepared point-by-point responses to the reviewer's comments below. The original reviewer comments appear in italics. Our responses are presented in blue plain font, while the corresponding revisions in the manuscript appear in blue underlined font.

Scientific issues

1. Comments and suggestions:

Line 17-18: Hydration effects and changes in oxidation products are given as scientific facts for explaining the observations in the abstract. However, when reading the paper, it appears that these explanations, while likely, are speculations rather than facts. I recommend that the authors pay more attention what is interpreted as a scientific fact, a probable explanation, or speculation when discussing the observations.

Responses and Revisions:

We sincerely thank the reviewer for this insightful and constructive comment. The reviewer is correct in pointing out that we should more carefully distinguish between established scientific facts and probable explanations based on our data and literature evidence. We agree that the terms "primarily due to" and "attributable to" in the original manuscript conveyed a degree of certainty that is not fully supported by our direct measurements. We have modified the wording in manuscript to clearly indicate that the proposed mechanisms are based on existing literature and are presented as plausible explanations rather than established facts.

The relevant text in the Abstract has been revised as follows:

"The hygroscopicity of SA decreased 49% as particle size increased (from 0.413 ± 0.011 at 3 nm to 0.209 ± 0.004 at 10 nm) and declined by up to 18% with increasing RH, which may be explained by hydration effects. In contrast, the κ values of OOMs increased with RH by as much as 57%, potentially involving changes in oxidation product."

2. Comments and suggestions:

Lines 59-66: This paragraph lists what will be done/investigated in the paper. The authors should also give either concrete scientific goals of the study or, alternatively, research questions aimed to be answered here.

Responses and Revisions:

We sincerely appreciate the valuable suggestions and comments. As suggested, we have revised the relevant text in our manuscript (Section Introduction):

"In this study, we conducted a series of laboratory nucleation and growth experiments using a custom-built flow tube reactor. SO_2 and α-pinene were employed as gas-phase precursors to generate SA and organics (OOMs, oxygenated organic molecules), respectively. Experiments were performed under purely inorganic, purely organic, and mixed precursor conditions with varying [α-pinene]/[SO_2] ratios, across a wide RH range (20%-80%). We first measured the κ values of 3-10 nm particles formed from the oxidation products through SFCPC. Then our analysis established size-resolved linear relationships between κ and f_{org} for SA-OOMs mixed particles, enabling quantitative determination of organic contributions. Furthermore, we systematically examined the effects of particle size, gas precursor concentration ratio, and humidity on both particle hygroscopicity and organic contribution. Based on these experimental results, this study aims to quantitatively investigate the distinct roles of sulfuric acid and oxygenated organics during nanoparticle growth, and to clarify how environmental conditions modulate the chemical composition and water uptake of sub-10 nm particles."

3. Comments and suggestions:

Lines 249-250: This statement (This behaviour is attributed to …) is given without a proper justification. The authors should add some reasoning(s), or at least speculations.

Responses and Revisions:

We sincerely thank you for this insightful comment. You are right to point out that the statement regarding the attribution of the observed behavior needed further justification. In response to your suggestion, we have revised the manuscript to frame this explanation more appropriately as a plausible mechanism or speculation, which is then supported by the subsequent reasoning and references. We have modified the relevant paragraph in the revised manuscript (Section 3.3):

"We speculate that these behaviours arise from the competing influences of humidity on the physicochemical properties of α-pinene oxidation products and the Kelvin effect. For such small nanoparticles, the partitioning of a molecule into the particulate phase is influenced by both its volatility and the Kelvin effect (Riipinen et al., 2012). Previous molecular measurements in both gas and particle phases have reported increased yields at elevated RH (Poulain et al., 2010). Concurrently, Surdu et al. (2023) observed that α-pinene oxidation products become more volatile under humid conditions. The relative stability of f_{org} in the 3-5 nm particles at low RH condition may thus be explained by a balance between these two competing mechanisms, where the heightened Kelvin effect presents a significant barrier to condensation. For larger particles, the diminished Kelvin effect facilitates the condensation of organic compounds, allowing even more volatile products to contribute to nanoparticle growth. The distinct response patterns, where the enhancement occurred gradually for 3-5 nm particles but sharply for larger particles, suggest that the Kelvin effect plays a more dominant role for the smallest particle growth at lower RH. Overall, increased RH enhances the organic contribution by altering the properties of α-pinene oxidation products, with a more pronounced effect observed for larger particles."

Technical issues

4. Comments and suggestions:

Lines 126-129 and 194-196: Although the procedure of determining the OOM mass fraction is relatively straightforward, the paper would benefit from having an example plot on how this works in practice for the data applied here.

Responses and Revisions:

We thank the reviewer for this constructive suggestion. As suggested, we have now included an example plot in the Supplementary Information (Figure S1) to explicitly illustrate the practical procedure of how to establish size-resolved linear relationship between the hygroscopicity parameter (κ) and the organic mass fraction (f_{org}), and how the f_{org} is retrieved from the measured κ. This figure demonstrates the application of our method in this study, thereby enhancing the clarity of our analytical approach.

Correspondingly, we have revised the relevant descriptions of method in the manuscript:

"In this work, we introduced κ-f_{org} linear relationship into the mixing products from flow tube—a setup designed to simulate atmospheric processes—in order to explore the organic content in the particulate phase. Furthermore, we established size-resolved κ-f_{org} linear relationship to eliminate the mentioned uncertainty. The application of the κ-f_{org} linear relationship relies on the assumption of ideal internal mixing within the particles. Under our experimental conditions, for in situ freshly formed 3-10 nm particles, the characteristic mixing times are short, and organic-inorganic mixtures are likely to remain liquid and well-mixed (Cheng et al., 2015). Therefore, the ideal internal mixing assumption is reasonable. For SA-OOMs mixture, we use the κ values of pure organic (OOMs) and inorganic (SA) experiment groups to represent the hygroscopicity of the organic and inorganic component in the mixture particles, respectively. Although the organic and inorganic components in mixture may not be identical to those in pure organic and inorganic particles of the same size under the same RH due to the potential change of oxidation processes, this simplification is a necessary given the current inability to directly measure the composition and component-specific hygroscopicity of particles in the 3-10 nm size range. To further reduce uncertainties associated with the linear relationship, the κ values of pure organic and inorganic particles were taken from the fitted lines to serve as a reference baseline, as shown in Figure S1. Based on the size-resolved κ-f_{org} linear relationship (colored solid lines) and the measured κ values (grey dashed line) of the SA-OOMs mixture, the corresponding f_{org} values (colored dashed lines) for particles generated in the flow tube reactor were derived using Eq. 1"

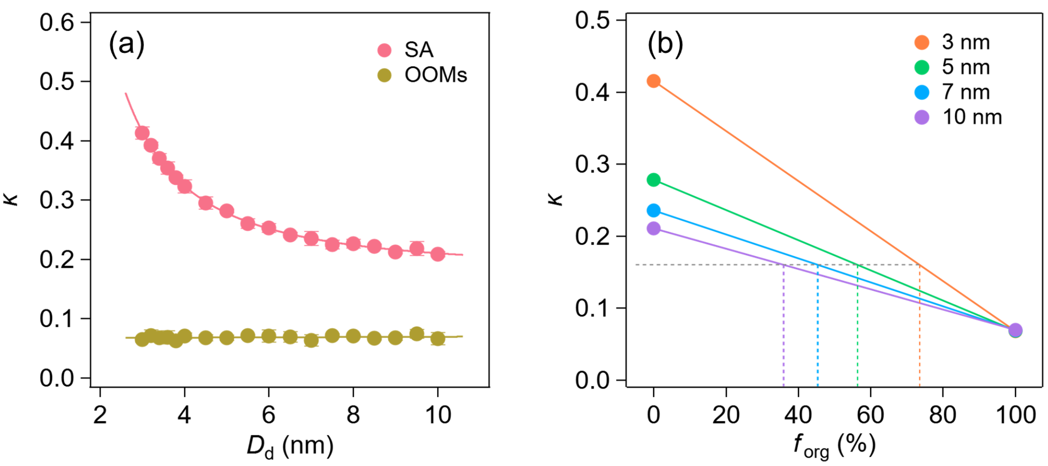

Figure S1. (a) The measured κ values of pure organic (OOMs) and inorganic (SA) under RH=20%. (b) Size-resolved κ-f_{org} linear relationships (solid lines), taking 3, 5, 7, and 10 nm as examples. The grey dashed line represents the measured κ of SA-OOMs particles. The colored dashed lines represent the derived f_{org}.

5. Technical corrections:

Line 169: Differ from --> different from.

The given values in percent on lines 198 and 218 are too accurate. I would recommend using an accuracy of 1% or, in maximum, the accuracy of 0.1%.

Corrected. These comments and suggestions have been rewritten in the revised manuscript.

Refences:

Cheng, Y., Su, H., Koop, T., Mikhailov, E., and Pöschl, U.: Size dependence of phase transitions in aerosol nanoparticles, Nat. Commun., 6, 5923, https://doi.org/10.1038/ncomms6923, 2015.

Poulain, L., Wu, Z., Petters, M. D., Wex, H., Hallbauer, E., Wehner, B., Massling, A., Kreidenweis, S. M., and Stratmann, F.: Towards closing the gap between hygroscopic growth and CCN activation for secondary organic aerosols – Part 3: Influence of the chemical composition on the hygroscopic properties and volatile fractions of aerosols, Atmos. Chem. Phys., 10, 3775–3785, https://doi.org/10.5194/acp-10-3775-2010, 2010.

Riipinen, I., Yli-Juuti, T., Pierce, J. R., Petäjä, T., Worsnop, D. R., Kulmala, M., and Donahue, N. M.: The contribution of organics to atmospheric nanoparticle growth, Nat. Geosci., 5, 453–458, https://doi.org/10.1038/ngeo1499, 2012.

Surdu, M., Lamkaddam, H., Wang, D. S., Bell, D. M., Xiao, M., Lee, C. P., Li, D., Caudillo, L., Marie, G., Scholz, W., Wang, M., Lopez, B., Piedehierro, A. A., Ataei, F., Baalbaki, R., Bertozzi, B., Bogert, P., Brasseur, Z., Dada, L., Duplissy, J., Finkenzeller, H., He, X.-C., Höhler, K., Korhonen, K., Krechmer, J. E., Lehtipalo, K., Mahfouz, N. G. A., Manninen, H. E., Marten, R., Massabò, D., Mauldin, R., Petäjä, T., Pfeifer, J., Philippov, M., Rörup, B., Simon, M., Shen, J., Umo, N. S., Vogel, F., Weber, S. K., Zauner-Wieczorek, M., Volkamer, R., Saathoff, H., Möhler, O., Kirkby, J., Worsnop, D. R., Kulmala, M., Stratmann, F., Hansel, A., Curtius, J., Welti, A., Riva, M., Donahue, N. M., Baltensperger, U., and El Haddad, I.: Molecular understanding of the enhancement in organic aerosol mass at high relative humidity, Environ. Sci. Technol., 57, 2297–2309, https://doi.org/10.1021/acs.est.2c04587, 2023.