Response to Referee #4

General Comments
The authors investigate the influence mechanisms of sulfuric acid and oxygenated organic molecules on particle growth under varying particle sizes and RH conditions using a custom-built scanning flow condensation particle counter (SFCPC) to measure size-resolved hygroscopicity parameters and organic mass fractions in 3 – 10 nm particles. It further elucidates how the contribution of organic components evolves with particle size, particularly highlighting that increased RH significantly enhances the role of organics in the growth of 5 – 10 nm particles. This finding holds important value for understanding atmospheric new particle formation and growth mechanisms.

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.

1. Comments and suggestions:
The authors treat the a-pinene and SO2 as the gas precursors, however, the true components participating particle nucleation should be OOM and H2SO4, which I guess that you did not measure in the current experiment setup. But still, I am wondering that does the [a-pinene]/[SO2] ratio could represent the ambient atmospheric condition?

Responses and Revisions:

We thank the reviewer for raising this important point regarding the atmospheric relevance of our experimental design. We fully agree that atmospheric nucleation is directly driven by the oxidized products (OOMs and H_2SO_4). In our experiments, α-pinene and SO_2 were used as gas-phase precursors and were oxidized via O_3 + H_2O + UV light to generate the components that participating in particle nucleation and subsequent growth.

Regarding the representativeness of the [α-pinene]/[SO_2] ratio (0.1-1), we would like to clarify our rationale by combining reported atmospheric field observations and

laboratory experiments. The ambient SO_2 concentrations in urban China typically range from 2 to 40 ppbv (Yang et al., 2017; Zhang et al., 2021), while α-pinene levels in forested regions are generally on the order of a few ppbv or below (Li et al., 2023; Magand et al., 2025). However, in laboratory experiments, a wide range of concentration ratios is often employed to systematically investigate relevant processes. For instance, Lehtipalo et al. (2018) explored multi-component new particle formation using ratios spanning over two orders of magnitude (0.5-5 ppbv SO_2 and 530-590 ppbv monoterpenes). In our study, the [α-pinene]/[SO_2] ratio was set between 0.1 and 1. This range aligns with ratios used in other laboratory studies, such as Xu et al. (2021), who investigated the role of SO_2 in biogenic secondary organic aerosol formation with SO_2 at 107-112 ppb and γ-terpinene at 102 ppb, and Zhao et al. (2018), who studied the effects of SO_2 on α-pinene photooxidation using ~20 ppb α-pinene and ~15 ppb SO_2.

Our selection of this concentration ratio was based on both atmospheric observations and previous experimental literature. The data obtained under this ratio—including hygroscopicity, organic fraction, and the dependence on particle size and RH—provide valuable insights that can serve as a reference for understanding atmospheric new particle formation and subsequent growth.

2. Comments and suggestions:

Table 1 and Line 185: The authors claimed that the observed increase in κ values at higher RH may be attributed to the production of components with stronger hygroscopicity, it there any direct evidence? What is the product in different RH condition and how to explain their influence on hygroscopicity?

Responses and Revisions:

We thank the reviewer for raising this important point. We acknowledge that our current study did not obtain molecular-level chemical composition data; therefore, we lack direct experimental evidence identifying the specific, more hygroscopic compounds produced at different RH levels in our system.

However, our interpretation is supported by consistent findings from prior literature on analogous α-pinene oxidation systems, which offer both product identification and mechanistic explanations. Yuan et al. (2017) found that at elevated RH, higher κ values were observed for secondary organic aerosol (SOA) formed from α-pinene ozonolysis. Through ion chromatography analysis, they directly detected increased levels of formate in the particle phase under humid conditions, linking the elevated κ to the presence of specific, more hygroscopic products. Poulain et al. (2010) reported that under humid conditions, the product composition shifted towards compounds containing more oxygenated functional groups, specifically identifying

multifunctional carboxylic acids (e.g., pinonic acid). The formation of such highly oxygenated compounds in the presence of water vapor aligns with the understood chemistry involving stabilized Criegee intermediates. The influence of these products on hygroscopicity could be explained by the fundamental relationship between molecular functionality and κ. Han et al. (2022) demonstrated that the hygroscopicity of organic compounds varies widely with functional groups and κ increased with the functionality in the following order: ($-CH_3$ or $-NH_2$) < ($-OH$) < ($-COOH$ or C=C or C=O). where the carboxylic acid groups are particularly hygroscopic.

Therefore, although we did not directly measure the molecular composition in our experiments, the collective evidence from these studies allows us to reasonably conclude that the observed increase in κ at higher RH is likely due to the production of more oxygenated compounds, such as multifunctional carboxylic acids. Their higher intrinsic hygroscopicity, as established by structure-activity relationships, would elevate the overall particle hygroscopicity. We have revised the manuscript text (Section 3.1) to clarify this reasoning and its basis in the literature:

"Contrasting with the negligible size dependence, the measured κ values of OOMs exhibited a pronounced increase with RH, rising by 57% from 20% to 80% RH. This finding aligns with Razafindrambinina et al. (2022), who reported higher κ values for laboratory-generated α-pinene oxidation products under humid conditions ($\kappa = 0.191$ at 75-80% RH) compared to dry conditions ($\kappa = 0.130$ at RH < 10%). Similarly, Luo et al. (2024) observed that the molecular composition of α-pinene oxidation products evolves with increasing RH. While direct molecular-level speciation from our measurements is unavailable, previous studies on α-pinene oxidation systems provide an explanatory framework. The work of Yuan et al. (2017) suggests that in the presence of water vapor, particles formation may promote the generation of more stable Criegee intermediates, leading to the production of more hygroscopic materials in monoterpene systems. This is supported by evidence of increased formation of oxygenated functional groups, such as multifunctional carboxylic acids, under humid conditions (Poulain et al., 2010). The hygroscopicity of such compounds is intrinsically higher, as the κ increases with the functionality in the following order: ($-CH3$ or $-NH2$) < ($-OH$) < ($-COOH$ or C=C or C=O) (Han et al., 2022). Consequently, the observed increase in κ values at higher RH in this study is attributed to the likely formation of more hygroscopic components."

3. Comments and suggestions:

Figure 5: It seems that the 3-5 nm particles are more affected by RH compared with larger size, why?

Responses and Revisions:

We apologize for any lack of clarity in our original manuscript that may have led to this interpretation. Upon re-examining our results, we believe the observed trends are not due to the 3-5 nm particles being more affected by RH in an absolute sense, but rather due to the competing influences of the Kelvin effect and the RH-induced changes in the properties of α-pinene oxidation products (increased yields and volatility).

For the larger particles (5-7 nm and 7-10 nm), the Kelvin effect is diminished. Therefore, the primary influence of increased RH is to enhance the contribution of organics by altering the physicochemical properties of the α-pinene oxidation products. This leads to the sharp increase in f_{org} observed at 40% RH, which then stabilizes at higher RH as these effects reach a balance. In contrast, for the smaller 3-5 nm particles, the stronger Kelvin effect presents an energy barrier for condensation of organic vapors. This barrier effectively counteracts the RH-induced enhancement at low to moderate RH. Only when RH increases further dose the driving force for condensation become strong enough to overcome this barrier, leading to the observed increase in f_{org}. Thus, the gradual increase in f_{org} for 3-5 nm particles is a manifestation of this delicate balance between two competing mechanisms, highlighting a distinct size-dependent response mechanism to RH, rather than indicating a greater overall sensitivity for the smallest particles.

This interpretation is our inference based on the observed experimental results and supported by the cited literature. To avoid any misunderstanding, we have revised the relevant paragraph in the manuscript (Section 3.3) to articulate this mechanism more clearly:

"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."

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