We thank the reviewer for their valuable comments, which have greatly helped improve our study. In response to these comments, we have carefully revised the manuscript. For clarity, the reviewer's comments are presented in black, our responses are highlighted in blue, and the specific revisions made to the main text are marked in red.

Referee #1

The authors have made some revisions that improve the statements and discussions in the manuscript. However, my main concern regarding the concept and treatment of aerosol mixing state remains unresolved. In their responses to the major comments, the authors repeatedly refer to the meaning of mixing state index and its applications, which is already described in the manuscript and also a known concept for the reviewer, but this does not directly address the core issue raised.

Re: We thank the reviewer for the comments. We attach great importance to the questions you raised and have made in-depth reflections and further revisions regarding the concept and treatment of aerosol mixing state that you are concerned about.

In this study, the mixing state index χ is defined based on the hygroscopicity distribution of aerosols, reflecting the distribution of different hygroscopicity modes within the aerosol population. The changes in χ reflect the variations in aerosol mixing state, which are interrelated with multiple factors such as aerosol hygroscopicity, size distribution, and chemical composition. To clarify our point of view and address your doubts more clearly, we have used the term "**covariation relationship**" in the revised manuscript to specifically describe the relationship between the changes in mixing state and CCN activity. We hope that these supplements and revisions can directly respond to your core issue. Once again, we appreciate your valuable comments, which have played a key role in improving our research and the quality of our paper. Please see our point-to-point response to each comment below.

It should be clearly recognized that the mixing state index is derived from HTDMA measurements at specific particle diameters. Therefore, it quantifies the mixing state of aerosols at those diameters, rather than representing the mixing state of the entire aerosol population. In contrast, the activation ratio (AR) reflects the activation behavior of the entire aerosol population. These two quantities are conceptually different and not directly comparable. The manuscript should explicitly clarify this distinction.

Re: Thank you very much for your comments. This study used the mean values of mixing state index at different diameters to approximate the characteristics of the aerosol population, thereby establishing the covariation relationship with activation ratio. We have clarified this distinction as follows or **Lines 425-434**:

"… Given that CCN activity reflects the characteristics of the entire particle population while χ is calculated from HTDMA measurements at specific particle diameters, this study chooses the N_{CCN}, activation ratio (AR) at supersaturation of 0.2% and the mean χ for accumulation-mode to illustrate the covariation characteristic approximately. This approach is employed to ensure that both variables/parameters reflect the characteristics of the accumulation-mode particle population. The covariations of particle size and chemical composition with the mixing state (χ ranging from 0 to 1 at intervals of 0.1) are illustrated in Figure 7. This figure provides key insights into two fundamental determinants of CCN activity (Dusek et al., 2006) ...”

Furthermore, when discussing the influence of one factor on another, it is necessary to first isolate the effects of other contributing factors. The AR of the entire aerosol population is determined jointly by aerosol size distribution, chemical composition, and mixing state. It is important to keep in mind that when aerosol mixing state is on the basis of known mass concentrations of different aerosol species. Therefore, to rigorously quantify the impact of mixing state, the effects of size distribution and chemical composition must be first controlled or isolated.

Finally, I understand that the authors aim to convey that aerosol mixing state exhibits substantial variability and that an empirical relationship between AR at a given supersaturation (SS) and the mixing state index may exist. If this is the case, the term “covariation relationship” would be more appropriate than “impact”, as the current analysis does not establish causal influence.

Re: Thanks for your comments. As you suggested, the control variable method is effective for exploring the impact of a specific factor. This is analogous to previous CCN closure studies, which typically hold the mixing state information constant to evaluate the relative importance of particle size, composition, and mixing state on CCN activity.

This study mainly emphasizes the evolution of particle size and composition during the mixing aging process (Figures 3 and 7), as well as the evolution of CCN activity. We have revised the term “impact” to “covariation” as you suggested. See ***Section 3.3*** as follows and **Lines 419-551:** “

3.3 Covariation relationships between the Mixing State and CCN Activity

The mixing state of particle populations undergoes dynamic transformations during atmospheric aging, profoundly influencing their CCN activity. Unlike prior CCN closure studies that assumed mixing states based on chemical component fractions (Yang et al., 2012; Padró et al., 2012; Ren et al., 2018), this work employs the hygroscopicity distribution- and entropy-derived mixing state index χ to clarify the covariation relationships between the mixing state and CCN activity. Given that CCN activity reflects the characteristics of the entire particle population while χ is calculated from HTDMA measurements at specific particle diameters, this study chooses the N_{CCN}, activation ratio (AR) at supersaturation of 0.2% and the mean χ for accumulation-mode to illustrate the covariation characteristic approximately. This approach is employed to ensure that both variables/parameters reflect the characteristics of the accumulation-mode particle population. The covariations of particle size and chemical composition with the mixing state (χ, ranging from 0 to 1 at intervals of 0.1) are illustrated in Figure 7. This figure provides key insights into two fundamental determinants of CCN activity (Dusek et al., 2006).

As χ increases, the peak diameter (D_{peak}) of the particle number size distribution (PNSD) shifts toward larger sizes (Fig. 7a and Fig. S8), while peak concentrations occur within the intermediate χ range (0.3–0.6). This trend indicates that CN number concentration (N_{CN}) first increases, driven by primary emissions and new particle formation, then decreases due to mixing and aging processes (Fig. 7b). Notably, new particle formation events frequently occurred in IAP-summer (Fig. S9), corresponding the gradually increase of χ. And the χ for Aitken-mode is significantly larger than the accumulation-mode particles during this period. Thus, N_{CN} exhibits a sustained slight increase as the degree of the internal mixing increases in IAP-summer.

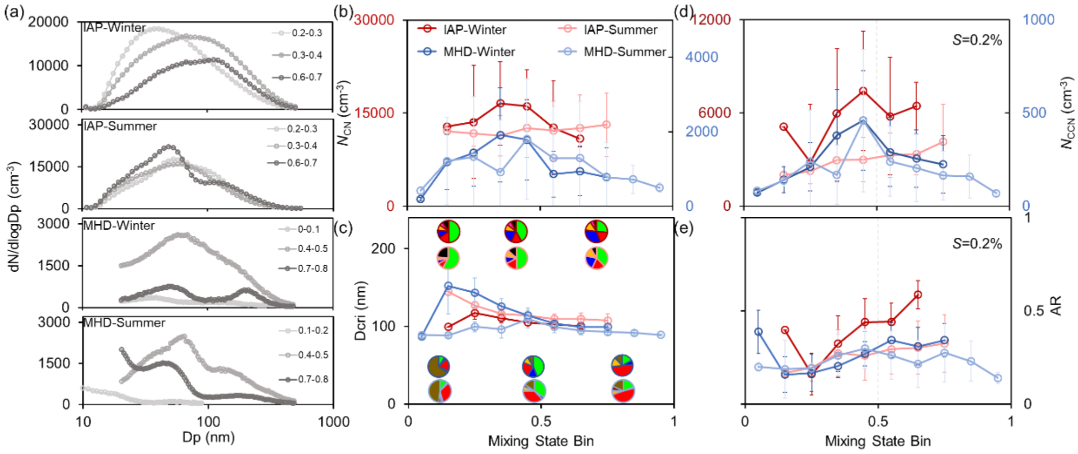


Fig 7. Comparison of the average particle number size distribution (PNSD) in different mixing state index (χ) (a), CN number concentration (N_{CN}) as a function of χ (b), Critical diameter (D_{cri}) at S=0.2% and mass fraction of chemical composition as a function of χ (c), CCN number concentration (N_{CCN}) (d) and activation ratio (AR) at S=0.2% a function of χ (e).

The critical diameter (D_{cri})—defined as the minimum size required for activation at a given supersaturation—depends on aerosol hygroscopicity. In turn, this hygroscopicity is jointly determined by the hygroscopicity of individual soluble components and their mass fractions in the aerosol (Petters and Kreidenweis, 2007). Using measurements at supersaturation of 0.2% as an example, Fig. 7c shows that D_{cri} decreases with increasing highly hygroscopic inorganic components (e.g., sulfate, nitrate) in the inland atmosphere. In contrast, coastal D_{cri} exhibits nonlinear variations with χ: high external mixing (low χ) elevates D_{cri} due to dominant organic components, reducing sea salt particle fractions. As χ increases, the mass fraction of non-sea-salt sulfate (nss-sulfate) rises, enhancing activation potential by decreasing D_{cri}.

The covariation characteristic of CCN activity at 0.2% supersaturation with mixing state index χ reveals distinct inter-atmospheric differences, as shown in Fig. 7d-e. In IAP, N_{CCN} at S=0.2% demonstrates a monotonic increasing trend with χ, attributed to the synergistic effects of rising N_{CN} and decreasing D_{cri} (Fig. S10). By contrast, coastal N_{CCN} follows a pattern analogous to N_{CN}, with peak concentrations shifting toward higher χ values. This highlights the dominant role of particle size effects in enhancing CCN concentrations under marine-influenced conditions (Dusek et al., 2006).

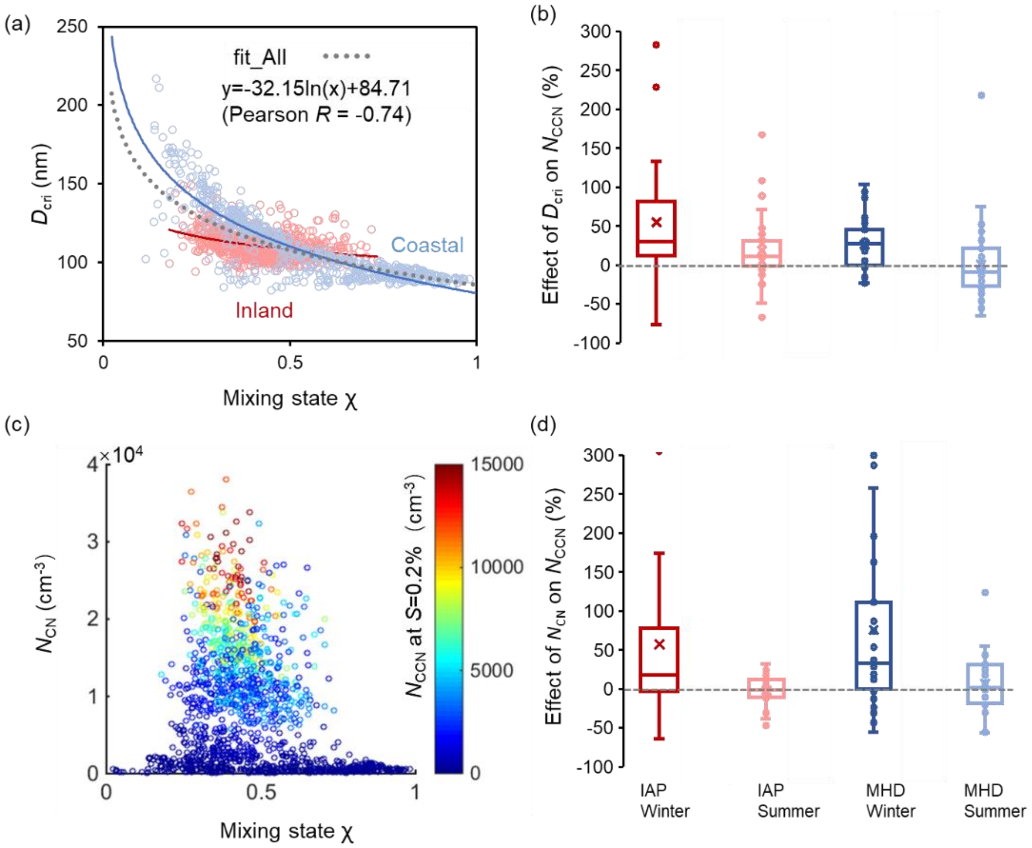


Fig 8. Covariation characteristics of the critical diameter (D_{cri}) with the χ (a), relative change of CCN number concentration (N_{CCN}) at supersaturation $S = 0.2\%$ with the reduction in D_{cri} (b); Covariation characteristics of the CN number concentration (N_{CN}) with the χ, different colors represent the N_{CCN} (c), relative change of N_{CCN} with the change in N_{CN} (d).

Two distinct D_{cri}-χ trends underpin these disparities: one remains stable, driven by the inherent hygroscopicity of sea salt, while the other exhibits steep D_{cri} declines associated with anthropogenic pollution as internal mixing intensifies. These discrepancies are further manifested in the nonlinear D_{cri}-χ relationship. The activation ratio (AR)—quantifying aerosol cloud droplet formation potential at fixed supersaturation—also varies by site (Fig. 7e). Notably, AR shows a marked increase with χ in IAP-winter, likely due to enhanced N_{CCN} from the elevated inorganic fraction under higher mixing states (Fig. 3). Conversely, the inorganic fraction decreases during other sampling periods, dampening AR growth.

Fig. 8 further shows the covariation characteristics of CN concentration, chemical compositions (i.e., D_{cri}) with mixing state across particle populations. D_{cri} exhibits heightened sensitivity to minor fluctuations in the mixing state (χ) when $\chi < 0.5$(Fig. 8a). In contrast, for particles already characterized by internal mixing, further increases in χ (i.e., higher degrees of internal mixing) exert a negligible influence on D_{cri}. This behavioral pattern implies that the D_{cri}-χ relationship could enable a novel parameterization for D_{cri} estimation, a framework that has not yet been reported in the existing literature.

Aerosol observation at MHD site (blue dots) span a broad D_{cri} range (80–220 nm) with χ varying from 0.1 to 1, reflecting alternating influences of highly hygroscopic inorganic salts (sea salt, sulfate) and less-hygroscopic organic matter. In contrast, aerosols—dominated by anthropogenic pollutants—exhibit a narrower D_{cri} range (90–150 nm) at IAP site. Both environments show negative D_{cri}-χ correlations, but with distinct functional forms: MHD aerosols feature an exceptional logarithmic fit ($D_{cri} = -42.98\ln(\chi) +80.36$, $R^2 = 0.75$; Fig. 8a blue line), while IAP aerosols (red line) yield a shallower slope (-12.04). Pooling all data, we derive a generalized parameterization: $D_{cri} = -32.15\ln(\chi) + 84.71$ (Pearson r = -0.74, $R^2 = 0.54$). As discussed above, strong impact of primary emission and secondary formation on aerosol mixing state was observed at both sites (Fig. 5 and 6). One could obtain more details on the D_{cri}-χ correlations. For example, the D_{cri} exhibited rapidly increase with the increase of primary emissions (ie., mass fraction of POA enhanced) during polluted periods. The D_{cri} pattern appeared opposite with that of the mixing state index, especially for the accumulation-mode particles. More pronounced D_{cri}-χ correlations were observed during the new particle formation (Fig. 5a1-d1). The decreasing presence of D_{cri} matched the increasing proportion of SO_4^{2-} and SOA with the χ increased during NPF events. Similar correlations between the critical diameter and mixing state index were also found in the coastal atmosphere, especially for the case of the enhanced anthropogenic organic matter and sea salt production (Fig. 6). This implies that the relationship between the D_{cri} and χ might be disturbed by the variation of emission pollution and secondary formation processes, resulting in spatiotemporal differences. The D_{cri} reduces by 2.2–6.8% with the mixing state increase at a step of 0.1, with the steepest winter decline (Fig. S11).

Changes in N_{CN} with differ starkly between environments: positive effects in polluted inland air (+9%) versus negative effects in coastal regions (-2%). Aerosols in IAP, frequently perturbed by primary emissions and new particle formation, exhibit elevated N_{CN} (peaking at $\chi = 0.2$–0.7), while in MHD N_{CN} remains ~5000 cm^{-3} across all χ. We categorized data into two groups: C1 (particles within specific N_{CN} ranges) evaluates N_{CCN} covariations mainly driven by D_{cri}-χ relationships, while C2 (particles within fixed D_{cri} intervals) assesses N_{CN}-χ effects (Fig. 8b). Relative changes (RC) in D_{cri}, N_{CN}, and N_{CCN} with χ were calculated by comparing successive χ increments (χi+1 vs. χi, i=0,0.1…1) within defined N_{CN} or D_{cri} windows.

Notably, the covariation relationship between the N_{CCN} and mixing state exerts more pronounced for the case of externally mixed aerosols dominated. For example, MHD-winter aerosols (high external mixing; $\chi_{mean}=0.38\pm0.12$) showed RCs in N_{CCN} of 23% (C1) and 72% (C2), whereas MHD-summer aerosols (high internal mixing; $\chi_{mean}=0.69\pm0.19$) exhibited negligible effects (-2.5% in C1, 0.9% in C2). Inland atmospheres, despite smaller seasonal χ variations, showed analogous trends: RCs of N_{CCN} in winter (55% in C1, 57% in C2 for external mixing) exceeded summer values for more internally mixed populations (Fig. 8d). These results confirm that hygroscopic heterogeneity strongly influences N_{CCN} under external mixing, aligning with prior work (Ching et al., 2017).

The covariation characteristics are most pronounced during winter in both environments, attributed to heightened winter D_{cri} sensitivity to χ: a 0.1 χ increase reduces D_{cri} by 5.2% (winter), boosting N_{CCN} by 39%, versus 2.4% D_{cri} reduction (summer) yielding only 6% N_{CCN} enhancement. Concomitantly, winter N_{CN}-χ effects on N_{CCN} reach 65%, far exceeding summer responses.

In contrast to previous evaluation methods that oversimplify mixing states (Ren et al., 2018; Xu et al., 2021b), the entropy-based framework employed in this study explicitly characterizes the covariation between the CCN activity and transitions in the mixing state. Aerosols in IAP-winter are presumably shaped by intense urban pollution sources—including traffic emissions, residential heating, and cooking activities—thereby enriching the externally mixed particle fraction (Fan et al., 2020; Xie et al., 2020). Analogously, aerosols in MHD-winter exhibit dominant external mixing, consisting of near-hydrophobic and hydrophilic particle mixtures (Xu et al., 2021a). As illustrated in Fig. S2, the winter aerosol population exhibits bimodal or multimodal κ–PDF distributions—this pattern indicates a high degree of external mixing, with the aerosols characterized by chemically diverse compositions. Collectively, these results underscore the pivotal role of mixing state heterogeneity in modulating CCN activity across different environments."

Some suggestions are listed below:

(1) The calibration results of HTDMA and CCN should be presented

Re: Thanks for your suggestions. Because the calibration methods for concurrent datasets have been specifically introduced in previous studies (Xu et al., 2021 and Ren et al., 2018), here we added the calibration results of HTDMA and CCN in the Supporting Information, see follows or **Lines 31-39 (SI)**: "

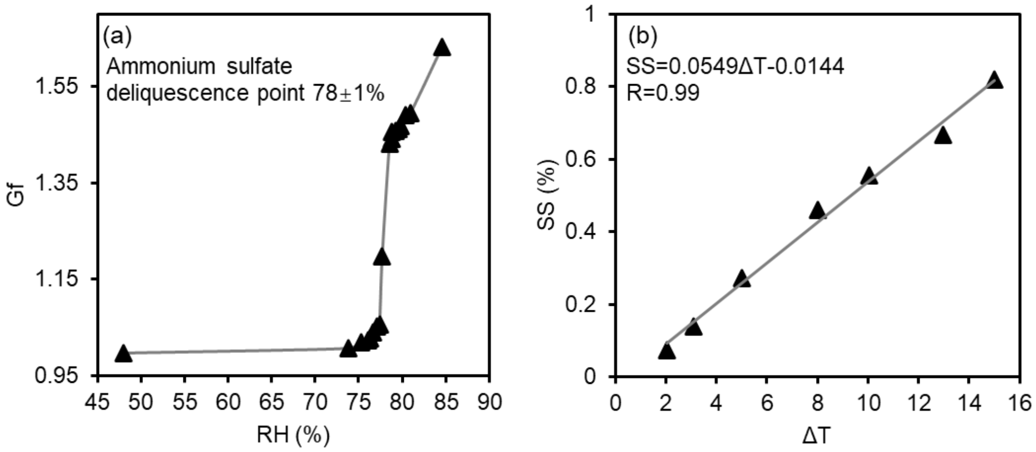


Fig R1 or S1. Example of Calibration results of HTDMA and CCN used in this study, (a) Humid gram of ammonium sulfate for 150-nm particles measured with HTDMA, (b) Variation of supersaturation as function of Delta temperature for ammonium sulfate aerosol.

The HTDMA system was regularly calibrated with ammonium sulfate solution for RH calibration. Fig. S1a gives the calibration result in IAP site as an example. The deliquescence point of ammonium sulfate is 78±1 %, which is consistent with previous studies (Tan et al., 2013). The CCN-100 was calibrated with ammonium sulfate for column supersaturation as suggested by Rose et al. (2008). Fig. S1b shows the supersaturation (SS) levels of the CCNc with longitudinal temperature differences of 2, 3, 5, 8, 10, 13, and 15K. Based on this calibration, five effective SS levels were 0.12, 0.14, 0.23, 0.40, and 0.76 %. Similar calibrations were operated in the measurements at MHD site (Xu et al., 2021)."

(2) Calculation method of critical activation diameter should be presented.

Re: Revised see follows or **Lines 153-167**:

"Here for each particle size, the hygroscopicity parameter κ can be subsequently calculated using κ-Köhler theory (Petters and Kreidenweis, 2007):

$$\kappa = (Gf^3 - 1) \cdot \left[\frac{1}{RH} \exp\left(\frac{4\sigma_{\frac{s}{a}} M_w}{RT\rho_w D_d Gf}\right) - 1\right] \quad (1)$$

where RH is the HTDMA relative humidity (90% set in the instrument), $\sigma_{s/a}$ is the surface tension of pure water (0.072 mN m^{-1}), M_w and ρ_w are the molecular weight and the density of pure water, R is the gas constant, and T is the absolute temperature, D_d is the droplet diameter.

Then, the κ-PDF is obtained and normalized as $\int_0^{\infty} c(\kappa) d\kappa = 1$, where $c(\kappa)$ is normalized as κ-PDF. Further it was used to calculate the particle population heterogeneity (Calculation seen in Section 2.3).

According to the κ-Köhler theory, the critical diameter (D_{cri}) corresponding to the supersaturation can be expressed as:

$$D_{cri} = \sqrt[3]{\frac{4A^3}{27\kappa \ln^2 S}}, \quad A = \frac{4\sigma_{\frac{s}{a}} M_w}{RT\rho_w} \quad (2)$$

where S is the given supersaturation ratio (here 0.2% used in this study), κ is the mean value of the hygroscopicity parameter calculated in Equation (1)."

(3) Change "summer measurements" to "measurements during summer periods", the short campaign could not represent summer.

Re: Revised. See follows or **Lines 34-35**: "… However, measurements during summer periods showed pronounced differences …"

(4) Change usage of words, for example "impacts" to "covariation relationships",

Re: Revised. See follows or

Lines 483-484:

"… Fig. 8 further shows the covariation characteristics of CN concentration, chemical compositions (i.e., D_{cri}) with mixing state across particle populations …"

Lines 534-535:

"… The covariation characteristics are most pronounced during winter in both environments …"

Lines 575-576:

"… Entropy-based analyses further support the covariation relationships between the mixing state and N_{CCN} …"

“Dependency of the critical diameter (Dcri) on the χ” in Figure caption of Fig.8 to “Covariation characteristics of Dcri and χ”. Please also check other places with these suggestions.

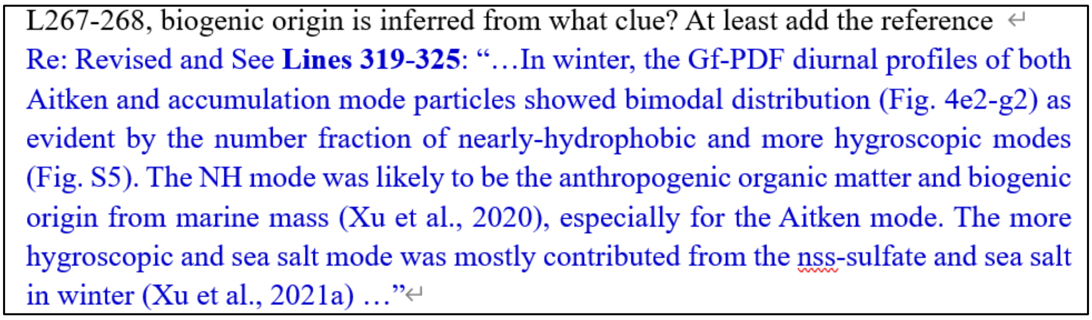
Re: The caption of Fig. 8 has been revised. See follows or **Lines 479-483**:

“Fig 8. Covariation characteristics of the critical diameter (D_{cri}) with the χ (a), relative change of CCN number concentration (N_{CCN}) at supersaturation S = 0.2% with the reduction in D_{cri} (b); Covariation characteristics of the CN number concentration (N_{CN}) with the χ, different colors represent the N_{CCN} (c), relative change of N_{CCN} with the change in N_{CN} (d).”

Suggestions on the response:

Please respond more directly to the question. It is difficult to identify what specific changes have been made to address the points I raised.

Give an example: If you have included the requested information or references, please highlight them clearly. For example, highlight the specific clue or the added reference in the revised manuscript. It is very time-consuming to compare the new version with the previous one without clear indications of the changes.



L267-268, biogenic origin is inferred from what clue? At least add the reference ↵

Re: Revised and See **Lines 319-325**: “…In winter, the Gf-PDF diurnal profiles of both Aitken and accumulation mode particles showed bimodal distribution (Fig. 4e2-g2) as evident by the number fraction of nearly-hydrophobic and more hygroscopic modes (Fig. S5). The NH mode was likely to be the anthropogenic organic matter and biogenic origin from marine mass (Xu et al., 2020), especially for the Aitken mode. The more hygroscopic and sea salt mode was mostly contributed from the nss-sulfate and sea salt in winter (Xu et al., 2021a) …”↵

Re: We apologize that the previous reply may not have highlighted the explanation. The biogenic origin is inferred from **Xu et al., 2020 and 2021a**.

Xu, W., Ovadnevaite, J., Fossum, K. N., Lin, C., Huang, R. J., O'Dowd, C., Ceburnis, D.: Aerosol hygroscopicity and its link to chemical composition in the coastal atmosphere of Mace Head: marine and continental air masses, Atmospheric Chemistry and Physics., 20(6), 3777–3791, https://doi.org/10.5194/acp-20-3777-2020, 2020.

Xu, W., Ovadnevaite, J., Fossum, K. N., Lin, C., Huang, R.-J., O'Dowd, C., Ceburnis, D.: Seasonal trends of aerosol hygroscopicity and mixing state in clean marine and polluted continental air masses over the Northeast Atlantic, Journal of Geophysical Research: Atmospheres., 126, e2020JD033851, https://doi.org/10.1029/2020JD033851, 2021a.

Some expiation has been added in the revised text, see **Lines 326-331**:

“… The NH mode is likely composed of anthropogenic organic matter and biogenic species derived from marine air masses (Xu et al., 2020), with this composition being particularly prominent in the Aitken mode. Additionally, Xu et al. (2021a) observed a higher abundance of the NH-mode in marine polar and Arctic air masses, this further supports the notion that NH particles are likely of biogenic origin, aside from contributions from anthropogenic activities ...”

The detailed explanation about the biogenic origin of the hydrophobic mode was given *in* ***Xu et al., 2020 and 2021a****.*

"A subset of near-hydrophobic (NH) mode particles has been observed in clean marine environment and reported by Xu et al. (2020), but their source remained unclear. Despite being observed in clean marine air masses their source could have been either anthropogenic or biogenic. A thorough discussion of every possibility has been explored by taking advantage of the long-term data set, which is the primary asset of this study."

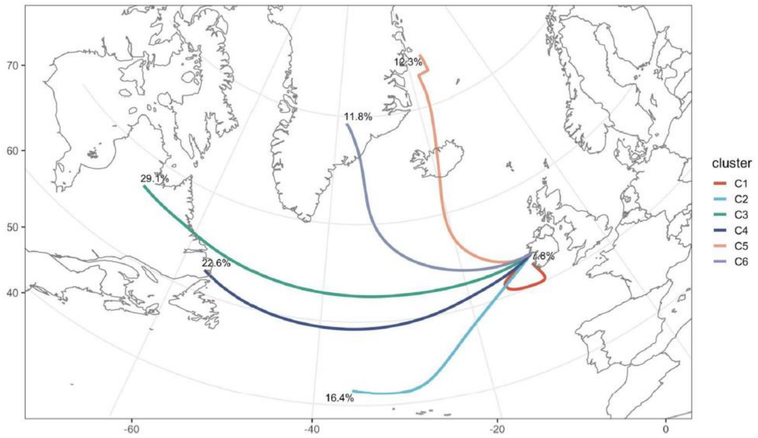


Fig R2. *The representative clusters of clean marine air mass backward trajectories by using k-means clustering technique together with frequency of occurrence during January-March and October-December period when NH particles were abundantly observed: C1: recirculated stagnant air mass; C2: marine Tropical air mass; C3: marine Polar high speed air mass; C4: regular marine polar air mass; C5: marine Arctic air mass and C6: marine Polar/marine Arctic air mass. (****Fig. 10 in Xu et al., 2021****)*

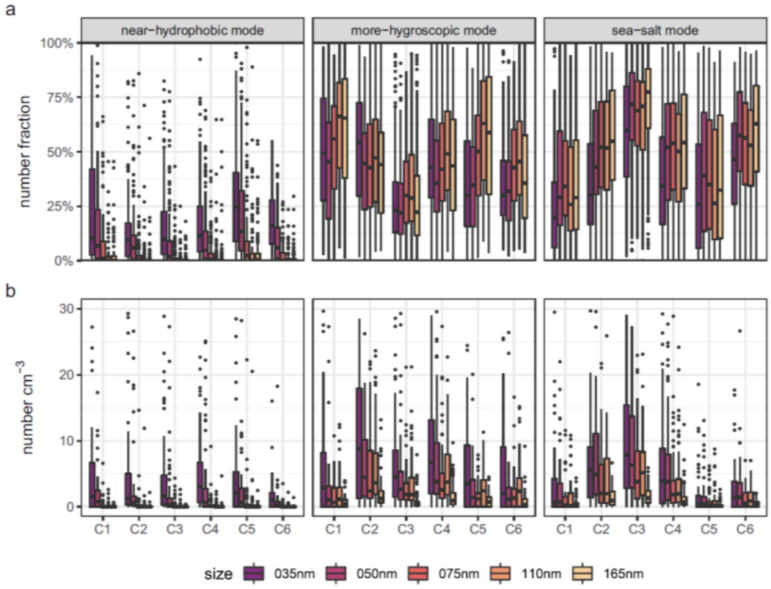


Fig R3. *The boxplot of the (a) number fraction and (b) number concentration of different hygroscopicity modes with lines representing the median, boxes representing 25th to 75th percentiles, and whiskers representing 1.5* interquartile ranges, dots represent outliers in C1-C6 air mass clusters.* ***(Fig. 12 in Xu et al., 2021a)***

And "To summarize, the GF-PDF distribution and the number fraction of each mode in air mass trajectory clusters were consistent with the physicochemical characteristics in previously published studies (Dall'Osto et al., 2010; Ovadnevaite et al., 2014a). Back trajectory clustering revealed that the NH particles were not only observed in stagnant and somewhat anthropogenically impacted air masses, but were rather ubiquitous in all types of clean marine air masses. ***The higher contribution of NH particle in marine polar and Arctic air masses and being minimized in marine tropical air masses suggests that NH particles are more likely of biogenic origin although certain impact of anthropogenically impacted air masses cannot be completely ruled out.*** *Moreover, the shipping routes were much denser under marine tropical air masses region than under marine polar region further supporting the marine origin of the NH particles. However, with the current mainstream measurement techniques, it is impossible to tell the exact chemical nature of Aitken mode NH particles. We, therefore, expect that ongoing efforts should be focused on wintertime/springtime marine aerosols to reveal the source of NH particles and, especially, their production mechanism to corroborate long-term observations in the North Atlantic."*

Finally, feel that many of my comments are not directly addressed.
Re: Thank you very much for your suggestions on the response. We have carefully revised the manuscript in accordance with your core issue raised.