Referee #2

This manuscript, titled "Contrasting Inland-Coastal Aerosol Mixing States: An Entropy-Based Metric for CCN Activity", presents a systematic investigation of how aerosol mixing states—specifically, the degree of internal vs. external mixing—affect cloud condensation nuclei (CCN) activity in two contrasting environments: inland (urban Beijing) and coastal (Mace Head, Ireland). This work bridges a critical gap between aerosol microphysics and climate modeling by providing a quantitative framework to incorporate realistic mixing state effects on CCN activity. It underscores the need to move beyond binary mixing assumptions and adopt entropy-based metrics for more accurate climate projections, particularly in diverse and dynamic environments like urban and coastal regions. This paper merits publication after minor revisions. To further strengthen this manuscript, the following questions should be addressed:

Why were these two locations chosen? Are they representative for inland and coastal? If possible, efforts should be made to collect more mixing state data from inland and coastal to support this discussion.

Re: Thank you for your suggestion. The IAP field measurements used in this study were collected during winter and summer as a part of the Atmospheric Pollution and Human Health in a Chinese Megacity (APHH-Beijing) program (Shi et al., 2019). The observation site is located between the Third and Fourth Ring Roads in Beijing, China. It is a typical urban site with significant aerosol population variability, primarily influenced by local anthropogenic sources such as vehicles, cooking emissions, and residential heating. In contrast, the MHD observation and research facility is situated on the west coast of Ireland. Observations indicate that over 60% of air masses at MHD are classified as clean oceanic air masses (O'Dowd et al., 2014), while the remaining 40% are subject to varying degrees of anthropogenic influence. The primary objective of this study is to investigate the heterogeneity of hygroscopicity of aerosol particles in polluted inland and clean coastal regions. For the first time, we apply the mixing state index based on entropy theory to real-world atmospheric conditions to explore its impact on cloud condensation nuclei (CCN) activity. To achieve this, we selected four datasets: IAP winter, IAP summer, MHD winter, and MHD summer.

Indeed, to facilitate a more comprehensive comparison between inland and coastal areas, it is essential to gather additional mixed state datasets. However, most reported mixed state indices currently available are based on χ calculated from chemical composition or standard deviation of the κ-PDF. A detailed dataset of hygroscopicity distribution is crucial for characterizing the heterogeneity of hygroscopicity in mixing state index. Unfortunately, such data are still relatively scarce. Therefore, we have revised the title as: "**Contrasting Aerosol Mixing States at Inland and Coastal Sites: An Entropy-Based Metric for CCN Activity**".

"But the current models lack regional-specific mixing state parameters and usually assume uniform mixing in both environments. This could lead to large uncertainties in predicting CCN concentrations, highlighting the need for site-specific observations." I suggest discussing in detail this substantial uncertainty and its sources.

Re: The sentence has been revised as follows or **Lines 88-102**: "…However, the current models lack regional-specific mixing state parameters and usually assume uniform mixing in both environments. This could lead to large uncertainties in predicting CCN concentrations, highlighting the need for site-specific observations. For example, Ren et al. (2018) found that the impact of aerosol mixing state on CCN activation characteristics ranged from -34% to +16 % in urban atmosphere. Comparison between a fully internal mixture assumption and using the mixing state index from the particle-resolved model, Ching et al. (2017) found the obvious overestimation in CCN concentration estimation. Especially in the regions eg., Amazon Basin, Central Africa and Indonesia, the particles appeared to be more external, errors in CCN concentration would increase up to 100% (Hughes et al., 2018). A detailed exploration of mixing state on CCN concentration in global scale was conducted by Zheng et al. (2021a), and the results showed that the mixing state varied spatially with more externally mixed over the North Atlantic Ocean, off the coasts of Southern Africa, and Australia. Thus, assuming particles with internally-mixed would introduce errors in CCN concentration of 50-100%…"

Does the surrogate choice (κNH = 0.01, κH = 0.6–0.8) fully capture the hygroscopic diversity of organics, especially oxygenated and fresh POA?

Re: Thanks for your suggestion, here the heterogeneity in aerosol hygroscopicity is calculated based on the measurement of κ-PDF, differing from previous reported χ based on the chemical diversity (Ching et al., 2017; Zheng et al., 2021) by grouping two surrogate species (one with BC and POA, the other with inorganic and secondary organic aerosol species). By referred from Yuan et al. 2021, the key assumption is that the aerosol containing aerosol particles is a binary system consisting of the non- and/or less hygroscopic (κ_N of <0.05) and more hygroscopic components (κ_H of 0.5-0.6, referred inorganics), which corresponds to the minimum and maximum hygroscopic parameters. In ambient atmosphere, each aerosol particle in the population contains one or two of the components. As shown in Figure R1 or S1, κ-PDF at IAP can be considered the normalized aerosol number fractions varied with κ between 0 and 0.6. and at MHD atmosphere, κ varied between 0 and 0.8. Thus, considering of the variation in κ_H, calculation assuming κ_H of 0.6 and 0.8 given in Figure S2 and the results show that the mixing state index do not differ significantly from those calculated assuming κ_H of 0.6. So, the calculation assumes κ_H of 0.6 was chosen in our study. The sensitivity of the hygroscopic parameter for the group of the hygroscopic species on the mixing state index χ was done both for the inland and coastal aerosols as seen in the revised text. See follows and **Lines 193-204**:

"…To characterize the heterogeneous distribution of the hygroscopic and non-hygroscopic components in populations (Chen et al., 2022b), we calculated the mixing state index (χ) using the κ-PDF, following the methodology of Yuan et al. (2023). Two surrogate groups in a population of *N* aerosol particles were assumed (Zheng et al., 2021a). One surrogate group consists the non- and/or slightly hygroscopic species with κ_N of <0.05 and another group contains the more hygroscopic species with κ_H of 0.5-0.6 (Yuan et al., 2023, referred inorganics). Ambient particles typically contain one or two of the components and the κ lies between 0 and 0.6 at IAP or 0.8 at MHD as shown

in Figure S1. Taking into account the enhanced hydrophilicity of marine aerosols at MHD site, calculation assuming κ_H values of 0.7 and 0.8 were shown in Fig. S2. While these variations in κ_H introduced a mean uncertainty of 8% in χ values, it did not significantly affect the seasonal or site comparisons ..."

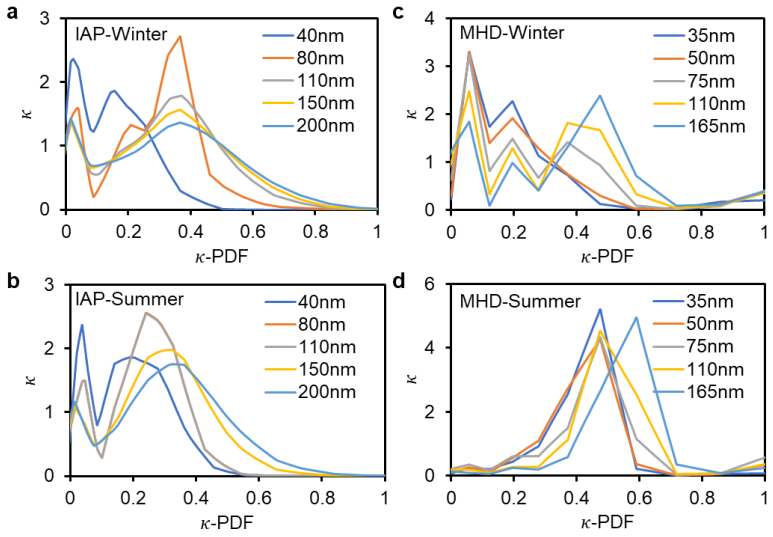

Fig. R1 and Fig. S1 Mean value of the κ–PDF for aerosols of five diameters during winter and summer periods at IAP (a and b) and MHD (c and d) sites.

Do the short campaign windows (≈ 1 month per season) adequately represent inter-annual variability in air-mass type and photochemical intensity?

Re: Although the short campaign windows might not represent inter-annual variability in air-mass type and photochemical intensity well, it provided direct observational evidence that the current model does not consider the spatial differences of mixing states, which leads to a significant overestimation of CCN concentration. In addition, to investigate the potential impact of mixing states on CCN concentration, simultaneous observation of particle size distribution, hygroscopic distribution, chemical composition and CCN is required. The field observations of IAP and MHD sites provide us with the feasibility to explore the spatial differences between inland and coastal mixing states in this study. Of course, it is necessary to conduct long-term observations in the future to investigate the temporal variations of mixing states.

Some statements have been added as follows or See **Line 123-137**: "…The inland atmospheric measurements were conducted for two campaigns from 16 November to 6 December 2016 and 29 May to 13 June 2017 as a part of the Air Pollution and Human Health (APHH) project (Shi et al., 2019), at the Institute of Atmospheric Physics, Chinese Academy of Sciences (IAP, 39.97° N, 116.37° E) in urban Beijing. The campaigns were complemented by the hygroscopicity and CCN observations and were conducive to provide information on the aerosol hygroscopicity affecting urban pollutions. This urban site exhibited highly variable aerosol populations dominated by local anthropogenic sources including vehicular, cooking emissions, and residential heating. Coastal measurements were performed at the Mace Head atmospheric research station (MHD, 53.33° N, 9.90° W) from 1 November 2009 to 30 January 2010, and summer periods from 11 to 31 August 2009 and July 2010, which located on the west

coast of Ireland. Aerosol particles here experience alternating influences from polluted continental and clean marine atmospheres. The map of the sites was shown in Figure 1. More details about the campaigns were given in Fan et al. (2020) and Xu et al. (2021a) …"

Is there evidence of κ-köhler non-ideality that would invalidate the single-parameter κ assumption at high S?

Re: The single-parameter κ assumption may not be valid under high supersaturation (S) conditions due to non-ideal behavior in surface tension and bulk composition. For example, surfactants in aerosol can lower surface tension (Ovadnevaite et al., 2017; Fan et al., 2024), which is not considered in the classical Köhler theory. Additionally, interactions in multi-component aerosol systems can also lead to non-ideal behavior. Experimental studies have shown deviations from the κ assumption under high S conditions. Therefore, more complex models are needed to accurately describe aerosol activation. This study is mainly focused on exploring the possible impact of mixing state on CCN concentration at the supersaturation of ~0.2% as an example, due to the less sensitivity to mixing state at high S (Bhattu et al., 2015).

How about the results if the proposed parameterization being implemented in a sectional or modal aerosol model to quantify the reduction in CCN bias compared to default internal/external mixing assumptions?

Re: Thanks for the suggestion, some statements have been added as follows or See **Line 557-570**:

"…Entropy-based analyses confirm the pivotal role of mixing state in regulating N_{CCN}, especially for externally mixed aerosols: a 0.1 χ increase can enhance N_{CCN} by 39–65%. Current models often oversimplify aerosol mixing states as purely internal or external (Stevens et al., 2019; Bauer et al., 2013), the latter being particularly sensitive to organic matter (Ren et al., 2018; Bhattu et al., 2015). Such simplifications introduce significant biases in N_{CCN} estimation (Riemer et al., 2019; Ching et al., 2019). The χ-D_{cri} parameterization proposed here offers a novel approach to reduce model complexity in representing aerosol hygroscopicity and CCN activation, enabling more accurate simulations of aerosol CCN capacity. It is expected mitigate the underestimation in CCN compared with the complete external mixing assumption, while effectively alleviates the overestimation that arises from applying the complete internal mixing assumption in regions characterized by high external mixing (Zheng et al., 2021a). This advancement improves our understanding of aerosol-cloud interactions (IPCC, 2021; Rosenfeld et al., 2019), critical for refining climate effect assessments."

What is the sensitivity of the Pearson correlation (r = –0.74) to random vs. systematic errors in Dcri?

Re: Here we use simulated data to evaluate the sensitivity of Pearson correlation coefficient to random error ϵ and systematic error δ in D_{cri}. As shown in the **Fig. R2**, the correlation coefficient is not sensitive to systematic errors. Further introducing the random error ϵ (standard deviation σ ranging from 1.5 to 15), as ϵ increases, the correlation coefficient decreases from 0.74 to 0.52, indicating correlation coefficient is more sensitivity to random error in D_{cri}.

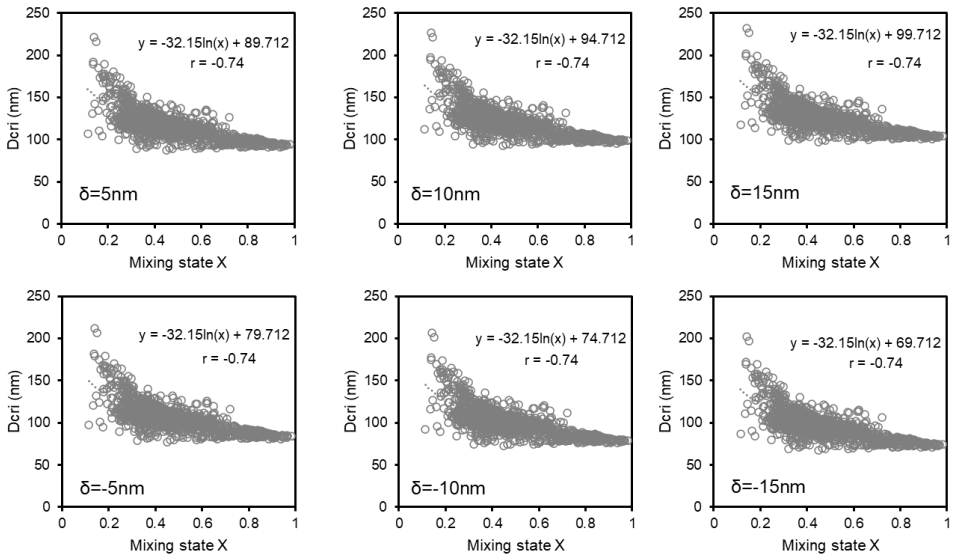

Fig. R2 Dependency of the critical diameter on the χ, with different systematic errors.

The relationship between Dcri and χ is heavily influenced by the chemical composition of particulate matter, as well as factors such as new particle formation, emission sources, and secondary reactions. Consequently, this relationship may exhibit significant variations across different regions. Is it possible for the author to further verify this using the results directly from chemical composition analysis?

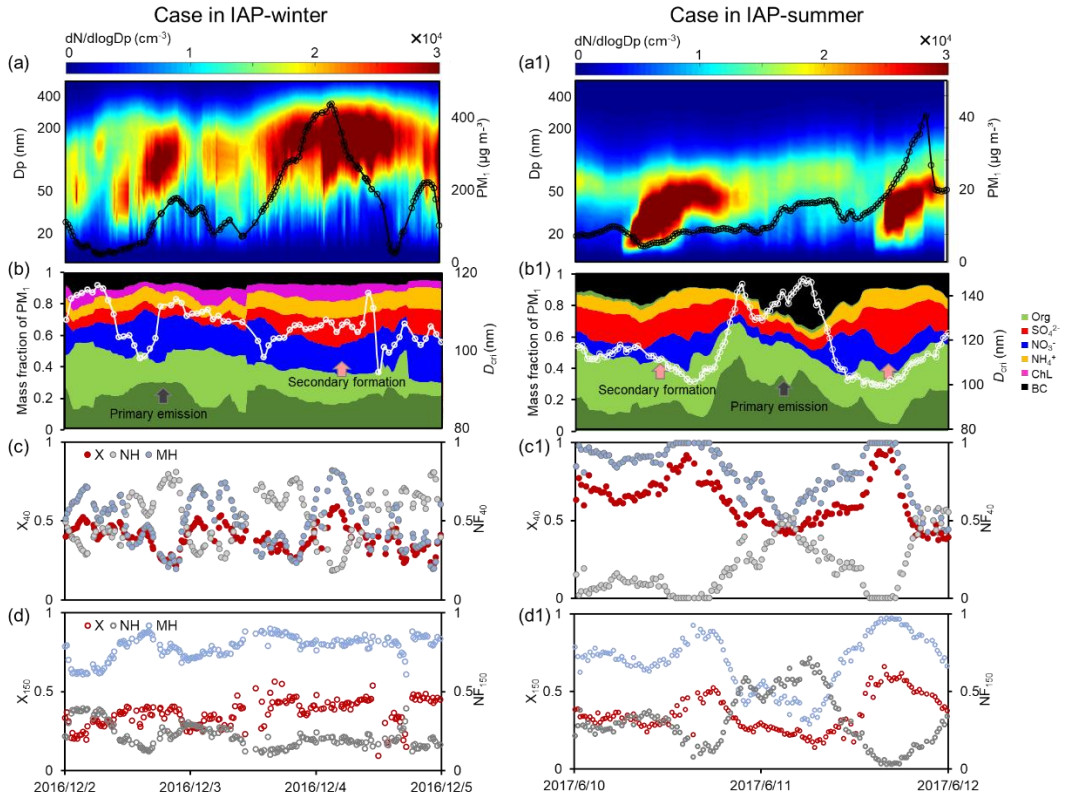

Fig. R3 and Fig. 5 Case in IAP-winter and IAP-summer. Particle number size distribution and PM1 (a), mass fraction of the PM_1 and the critical diameter (b), mixing state index (χ), number fraction of the nearly hydrophobic mode (NH) and more hygroscopic mode (MH) for 40 nm particles (c), χ, NH and MH for 150 nm particles

(d).

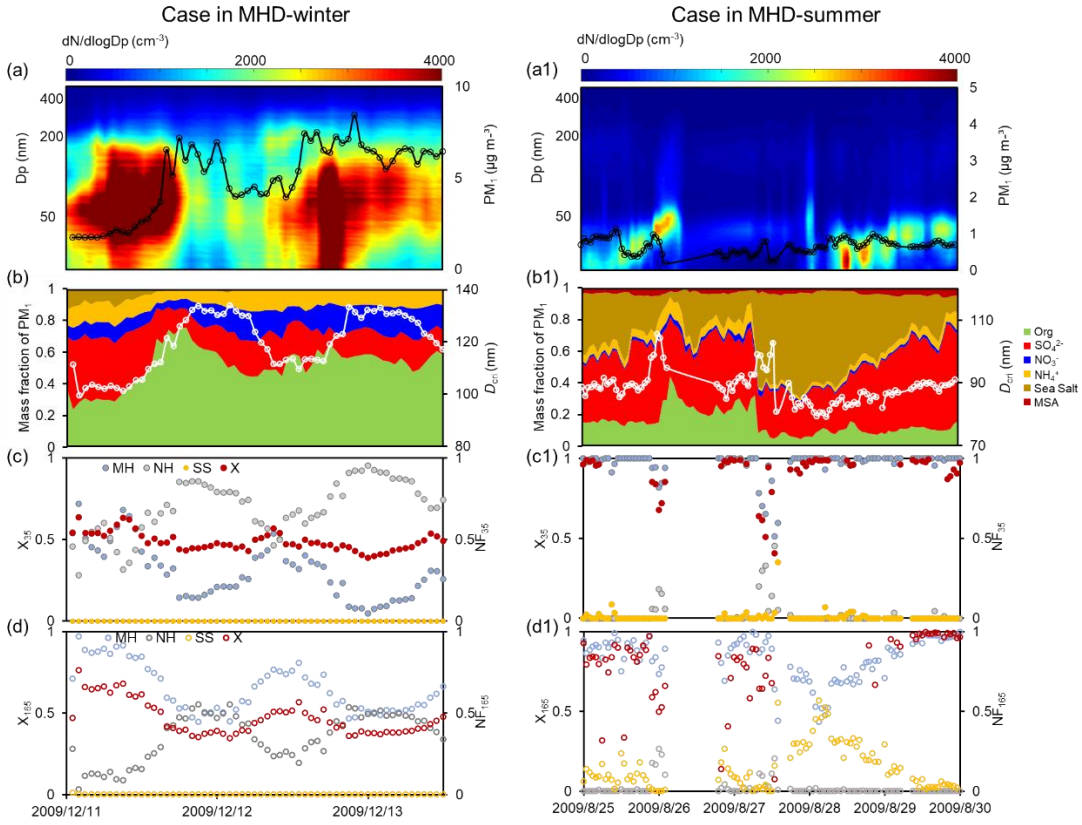

Fig. R4 and Fig. 6 Case in MHD-winter and MHD-summer. Particle number size distribution and PM1 (a), mass fraction of the PM_1 and the critical diameter (b), mixing state index (χ), number fraction of the nearly hydrophobic mode (NH) and more hygroscopic mode (MH) for 35 nm particles (c), χ, NH and MH for 165 nm particles (d).

Re: Thanks for the suggestion, some statements have been added as follows or See **Line 483-496**:

"…As already discussed above, strong impact of primary emission and secondary formation on aerosol mixing state was observed in both sites (Fig. 5 and 6). It also provides even more details on the D_{cri}-χ correlations. For example, the D_{cri} exhibited rapidly increased with the 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 inland atmospheric measurements were conducted for two periods from 16

November to 6 December and 29 May to 13 June" in which year?

Re: Revised and See **Lines 123-127**: "…The inland atmospheric measurements were conducted for two campaigns from 16 November to 6 December 2016 and 29 May to 13 June 2017 as a part of the Air Pollution and Human Health (APHH) project (Shi et al., 2019), at the Institute of Atmospheric Physics, Chinese Academy of Sciences (IAP, 39.97° N, 116.37° E) in urban Beijing ..."

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