Referee #3

This study examines the divergent relationships between aerosol mixing states and CCN activity at inland and coastal sites, by combining field measurements of hygroscopicity distribution with an entropy-based algorithm. Prior to consideration for acceptance, the following issues in the manuscript must be addressed.

Re: We thank the reviewer for the valuable comments, which have greatly helped improve our study. In response to these comments, we have carefully revised the manuscript.

1. The critical diameter (Dcri) of particles is closely related to the chemical composition of that size range. While the mixing state index can reflect the heterogeneity among particles, it does not capture chemical composition. Therefore, the inherent rationale for parameterizing the relationship between Dcri and the mixing state index requires further discussion.

Re: Thank you for highlighting this important conceptual issue. First, the mixing state directly reflects the degree of particle aging, which subsequently influences particle composition and size. Therefore, although the mixing state is not directly related to the critical diameter (D_{cri}), it can indirectly affect D_{cri} by serving as an indicator of particle aging. Furthermore, the mixing state captures the range of hygroscopicity (κ) variations that stem directly from compositional heterogeneity. When particles are externally mixed, they exhibit different κ values within the same size range due to variations in individual particle compositions. Specifically, lower χ values correspond to broader hygroscopicity distributions, rendering D_{cri} more sensitive to such distributions and thereby producing a larger D_{cri} variation range.

See follows or **Lines 483-502**:

"… The mixing state directly reflects the degree of particle aging, which subsequently influences the particle composition and size. Fig. 8 further examines the covariation characteristics of CN concentration, chemical compositions (i.e., D_{cri}) with mixing state across particle populations. The mixing state index quantifies the variance in hygroscopic distribution that emerges directly from compositional heterogeneity. Thus, it can indirectly affect D_{cri} by serving as an indicator of particle aging. The critical diameter (D_{cri}) is intrinsically sensitive to the hygroscopic distribution—wherein broader hygroscopic spectra (corresponding to lower χ) engender more extensive D_{cri} ranges. As shown in Fig. 8a, the D_{cri} exhibits heightened sensitivity to minor χ fluctuations in the mixing state (χ) when $\chi < 0.5$. This significant decrease in D_{cri} with increasing χ further confirms the potential effect of aging degree on critical particle diameter. 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}. Particularly when $\chi > 0.7$, the variation in D_{cri} with χ is within 20%. This behavior pattern reflects the influence of hygroscopic heterogeneity on critical diameter and might enable a novel parameterization for D_{cri} estimation. This behavior pattern implies that the D_{cri}-χ relationship could enable a novel parameterization for D_{cri} estimation when the aerosol particles are not highly aged or when the internal mixing degree of aerosol particles is relatively low, serving as a novel framework for integrating mixing state effects on CCN activity in atmospheric models …"

2. As shown in Figure 8, the relationship between the mixing state index and Dcri is strongly environment-dependent. This is evident from the differences in the fitting results for IAP and MACE HEAD, respectively. It raises the question of whether the fitted equation is highly limited and significantly influenced by environmental conditions, thus potentially not generalizable globally. This point should be further discussed as well.

Re: Thanks for the comments, yet the parameterization is not globally generalizable, but it provides the mechanistically-grounded framework that can be adapted across regimes. Some discussion regarding the environment-dependent nature of the D_{cri} -χ relationship has been added. See follows or **Lines 503-529**:

"… 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, observation at IAP site that is dominated by anthropogenic aerosols exhibit a narrower D_{cri} range (90–150 nm). Both environments show negative D_{cri} -χ correlations, but with distinct functional forms. For instance, MHD aerosols feature an exceptional logarithmic fit ($D_{cri} = -42.98\ln(\chi) + 80.36$, Pearson r = -0.87, $R^2 = 0.75$; Fig. 8a blue line), while IAP aerosols (red line) yield a shallower slope (-12.04) and Pearson r of -0.4. This quantifies that D_{cri} sensitivity to χ is 3.6 times steeper in MHD environments. This behavior pattern implies that the D_{cri}-χ relationship could enable a novel framework for D_{cri} estimation. The slope reflects the compositional diversity of the regime, steeper slopes occur where small χ variations correspond to large compositional shifts (e.g., sea salt in coastal site). As discussed above, strong impact of primary emission and secondary formation on aerosol mixing state was observed in 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) …"

3. The mixing state characteristics may not be a critical factor influencing the critical diameter—except under extreme externally or internally mixed conditions. Some of the data in Figure 8 also reflect this. I think the conclusion could be framed more effectively by specifying "under what range of the mixing state index its impact on activation assessment is significant," which might offer greater practical value than the current parameterized formula.

Re: Thanks for the comments, the conclusion has been framed as follows or See **Lines**

40-45:

"… Both environments show the negative correlations between the critical diameter (D_{cri}) and χ but with distinct decrement rates for coastal vs. inland aerosols. Specially, D_{cri} exhibits heightened sensitivity to fluctuations in χ when $\chi < 0.5$. This offers a practical approach to estimate D_{cri} from χ when the particles are not highly aged. Further analysis reveals that N_{CCN} exhibits heightened sensitivity to fluctuations in χ at low values…"

Lines 583-592:

"… As χ increases, CN number concentrations (N_{CN}) first rise—driven by primary emissions and new particle formation—then decline due to condensation and coagulation during aging. The critical diameter (D_{cri}) exhibits heightened sensitivity to minor χ fluctuations when $\chi < 0.5$. 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}. Additionally, both environments show negative D_{cri} -χ correlations, but with distinct functional forms. We propose a practical approach for estimating D_{cri} from χ, applicable when the aerosol particles are not highly aged or when the internal mixing degree of aerosol particles is relatively low, serving as a novel framework for integrating mixing state effects on CCN activity in atmospheric models …"

4. Why does the Mace Head site, being a coastal location, show significant primary emission influence?

Re: The primary emissions at the MHD site are predominantly of marine origin, which is fundamentally different from the continental primary organic sources at the IAP site. As indicated by previous studies, marine aerosols contain substantial amounts of organic matter, sourced from the scavenging of surface-active organic substances or other biogenic materials through bubble bursting (primary organic aerosol, POA), as well as the oxidation of marine volatile organic compounds (VOCs) such as dimethyl sulfide (DMS), aliphatic amines, isoprene, and monoterpenes (secondary organic aerosol, SOA) (O'Dowd et al., 2004; Chen et al., 2025). Recent studies have also shown that the POA fraction can reach up to 51% during periods of high biological activity at the MHD site (Chen et al., 2025). We note that while elevated OA fractions in winter at MHD may be associated with biomass emissions, these air masses might undergo substantial atmospheric aging during transport to the coastal site.

5. The units for the surface tension of water need to be verified for correctness.

Re: The unit for the surface tension of water has been verified as "J m^{-2}".

References

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O'Dowd, C., Facchini, M. C., Cavalli, F., et al.: Biogenically driven organic contribution to marine aerosol, Nature, 431, 676–680, https://doi.org/10.1038/nature02959, 2004.

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