Responses to Reviewer #1 Comments

General comments:

This manuscript systematically evaluates the feasibility and applicability of the YZ method proposed by Yuan and Zhao (2023) for retrieving the aerosol mixing state index (χ) from H-TDMA data, using PartMC-MOSAIC simulations. The results show that the YZ method is a promising approach for investigating aerosol mixing states in urban environments. Importantly, this work offers a valuable insight into the assessment of χ without direct reliance on expensive and limited single-particle mass spectrometry or electron microscopy observations and will be useful for improving our understanding of aerosol mixing states and their evolution, as well as for discussing their implications for radiative forcing and aerosol activation. In this respect, the work is both valuable and encouraging. Overall, this manuscript is generally well written and logically structured. I recommend publication after the minor revisions, as outlined below:

> We appreciate the reviewer for dedicating their time to review our paper and for the constructive and encouraging feedback. We have revised the manuscript to clarify the validation library, justify the discussion of sea-salt-containing aerosols, and expand the discussion of the atmospheric implications of χ. The line numbers referenced below correspond to the revised clean manuscript.

Specific Comments:

1. The scenario library employed for validation in the PartMC-MOSAIC simulation appears to be largely representative of urban environments and does not include primary sea-salt emissions. Likewise, the YZ method was originally developed on the basis of urban H-TDMA observations to infer aerosol hygroscopic mixing state. In this context, the close agreement between the χ values derived from the simulations and those retrieved by the YZ method already lends support to the validity of the underlying binary assumption. In Sect. 5.3, the authors further discuss the limitations of the YZ method in the presence of sea-salt aerosols, mainly through conceptual and theoretical arguments. I am not fully convinced that sea-salt-containing aerosols constitute the most appropriate example for illustrating the limitations of the YZ method. Sea-salt are typically coarse particles and relatively short-lived, and they may therefore mix less extensively with other components than fine-mode urban aerosols. As a result, χ may not be the most informative metric for characterizing their mixing state, even at coastal sites. This interpretation also appears broadly consistent with the authors' own χ calculations for the four regions using the YZ method. Since χ was developed primarily to describe the hygroscopicity of multi-modal continental aerosols, I suggest that the discussion in Sect. 5.3 be reframed more carefully, with a clearer justification for if sea salt should be added here to discuss the limitation of the YZ method.

> We appreciate this comment and agree that the scope of the validation library and the motivation for discussing sea salt needed to be clarified. The PartMC-MOSAIC validation library used here is primarily representative of continental anthropogenic aerosol populations and does not include primary sea-salt emissions. Therefore, the model-based evaluation should not be interpreted as a validation of the YZ method for marine-aerosol-dominated populations.
>
> We have revised Section 5.3 to make clear that sea salt is not presented as the central application case for the YZ method, nor as a component represented in the validation library. Instead, it is used as an example of a broader end-member limitation of the binary hygroscopicity framework. For continental aerosol, the prescribed more-hygroscopic end member represents typical inorganic salts such as sulfate, nitrate, and ammonium. In marine-influenced environments, however, submicron sea-salt particles may be present and may have hygroscopicities that extend beyond this prescribed continental end-member range. In that case, the binary mapping from κ to LH–MH composition becomes less unique, and the retrieved χ^{YZ} may become sensitive to the assumed end-member values.
>
> To avoid overinterpreting the sea-salt example, we reframed the discussion in Section 5.3 as an end-member sensitivity/limitation rather than as a realistic marine aerosol simulation. We now explicitly state that the $\kappa_{\mathrm{MH}} = 1.28$ test is a diagnostic sensitivity test performed on the same PartMC aerosol populations, not a validation of the method for sea-salt-containing aerosol. We also state that applications at

coastal sites should be interpreted cautiously when marine aerosol influence is substantial and independent measurements are not available to constrain the abundance and particle-level mixing state of sea salt.

2. One key element of the YZ method is the specification of the κ values assigned to the two components in the binary system. In the present manuscript, the authors extend the original parameter settings from κ_{LH} =0.01 and κ_{MH} =0.60 to κ_{LH} =0 and κ_{MH} =0.65. In the real atmosphere, however, the κ value of the more hygroscopic component may vary over a certain range, depending in particular on the abundance of each inorganic salt. Could the authors include a sensitivity analysis to quantify how uncertainties in κ MH propagate into the retrieved χ? For example, if κ_{MH} varies from 0.60 to 0.65, or even to 0.70, how large would the resulting deviation in χ be? Would such changes increase or decrease the discrepancy between the YZ retrieval and the PartMC-MOSAIC results? Addressing this point would provide a useful practical reference for other researchers when selecting appropriate parameter bounds for the analysis of actual H-TDMA observations.

Thank you for the suggestion. We have added a sensitivity analysis in which the YZ retrieval is repeated using κ_{MH} = 0.60, 0.65, and 0.70, while keeping all other aspects of the retrieval unchanged. The resulting comparison is shown in Figure S1.

The results show that the retrieved χ^{YZ} is sensitive to the assumed more-hygroscopic end member in the expected direction. Decreasing κ_{MH} from 0.65 to 0.60 tends to shift particles with high hygroscopicity closer to the pure-MH end member and therefore lowers the retrieved χ^{YZ}, leading to an underestimation relative to χ^{PMC}. Increasing κ_{MH} to 0.70 has the opposite effect: particles with a given κ are interpreted as containing a smaller MH fraction and a larger LH fraction, which increases the inferred per-particle diversity and tends to overestimate χ^{YZ}. Across the tested values, the correlations remain high, but the mean absolute error increases when κ_{MH} differs from the baseline value of 0.65. Specifically, the MAE increases from 1.6%–2.4% for the baseline κ_{MH} = 0.65 case to 7.2%–11.8% for κ_{MH} = 0.60 and 10.5%–17.3% for κ_{MH} = 0.70, depending on particle diameter. This confirms that the choice of κ_{MH} is important for minimizing systematic bias, while also showing that the retrieval remains qualitatively robust for plausible continental inorganic-salt hygroscopicities.

We made the following changes:

- L175–185: The retrieval framework assumes a representative hygroscopicity for the inorganic-salt component. To assess the sensitivity of the retrieval to this assumption, we repeated the analysis using κ_{MH} values of 0.60, 0.65, and 0.70 (Figure S1). The sensitivity arises because the inferred MH volume fraction in each κ bin depends directly on the assumed end-member values through Eq. (1). For a given particle hygroscopicity, decreasing κ_{MH} increases the inferred P_{MH} and shifts particles with hygroscopicities near the MH end member closer to pure-MH composition, leading to a systematic underestimation of χ. In contrast, increasing κ_{MH} decreases the inferred P_{MH}, causing particles that would otherwise be assigned closer to the pure-MH end member to be interpreted as mixtures of LH and MH components, resulting in a systematic overestimation of χ. Across particle diameters, the MAE increases from 1.6%–2.4% for the baseline κ_{MH} = 0.65 case to 7.2%–11.8% for κ_{MH} = 0.60 and 10.5%–17.3% for κ_{MH} = 0.70 (Figure S1). Nevertheless, strong correlations are maintained across all tested values, indicating that the retrieval is robust to reasonable uncertainty in the representative hygroscopicity assigned to inorganic salts, although accurate specification of κ_{MH} is important for minimizing systematic bias.

3. Sect. 4.4 and Fig. 4 clearly demonstrate that aerosol populations may share a similar bulk mean hygroscopicity while exhibiting substantially different mixing states. This is important and the manuscript would benefit from a somewhat fuller discussion about the impacts of χ on aerosol radiation forcing and cloud droplet activation.

Thank you for the suggestion. We have expanded the discussion of the atmospheric implications of hygroscopicity-based mixing state. Specifically, we clarify that aerosol populations with similar bulk hygroscopicity but different χ values may exhibit different cloud activation behavior because hygroscopic

material is distributed differently among particles. This can affect CCN number concentrations and, consequently, aerosol indirect radiative effects. We focus this added discussion on cloud droplet activation, which is the implication most directly connected to the κ-based mixing-state comparison in Section 4.4.

We made the following changes:

- L226–234: "The distinction between aerosol populations with identical κ_{mean} but different mixing states may have important implications for aerosol-cloud interactions. Activation of a particle depends on whether its hygroscopicity is sufficient to lower its critical supersaturation below the ambient supersaturation (Petters and Kreidenweis, 2007). In an externally mixed population (lower χ), a substantial fraction of particles are dominated by less hygroscopic species, such as black carbon or primary organic aerosol, yielding high critical supersaturations that may exceed the maximum supersaturation reached in clouds. These particles are therefore unlikely to activate as cloud condensation nuclei (CCN). In contrast, a more internally mixed population (higher χ) with the same κ_{mean} distributes hygroscopic material more uniformly across all particles, lowering the critical supersaturation for a larger fraction of the population and increasing the number of CCN-active particles. As a result, aerosol populations with similar κ_{mean} but different χ values may exert different indirect radiative effects."

Minor Comments:

1. Line 9: The term 'true mixing state' may be somewhat misleading. On the one hand, it may be interpreted as referring to the actual atmospheric mixing state; on the other hand, it may inadvertently imply that the YZ method-derived result is "untrue". I suggest replacing it with a more neutral and precise term.

Thank you for pointing this out. We have replaced this phrase with more precise wording, "particle-resolved reference mixing state index".

We made the following changes:

- L9–10: Replaced "true mixing state index" with "particle-resolved reference mixing state index" in the Abstract.
- L153/L155/L170: Replaced similar wording with "reference mixing state".

2. Line 150: It would be helpful if the authors could provide the κ-PDF diagnosed from the model output.

Thank you for the suggestion. We note that Figure 3a and 3b already provides examples of κ-PDFs generated from the PartMC validation library. To make this clearer, we have revised the figure caption to explicitly state that these panels show representative PartMC-derived κ-PDFs used to evaluate the retrieval.

- Figure 3 caption: "(a and b) Representative PartMC-derived κ-PDFs from the validation scenario library for two aerosol populations with high secondary organic aerosol (SOA) content at a dry diameter of 150 nm, corresponding to predominantly externally mixed (a) and internally mixed (b) particle populations."

3. Fig. 1: Please consider adding numerical values of the correlation coefficient, MAE, or RMSE, to the individual panels, so that the size dependence of the retrieval performance can be seen more directly.

Thank you for the suggestion. We have added quantitative performance metrics to Figure 1. Each panel now reports the correlation coefficient and the mean absolute error for that dry diameter.

4. Fig. 4: Based on the current description, I found the color distribution somewhat difficult to interpret. Why are there still green dots in the yellow region? If a higher dot density indicates a larger number of particles sharing the same P_{MH}, would the color not be expected to become more distinctly yellow? A brief clarification of the color mapping would be helpful.

Thank you for pointing this out. Each dot in Figure 4 represents a particle population from the PartMC simulation, and the color denotes its number concentration. The position of the dot suggests it's P_{MH} and χ^{PMC}, with a small random jitter added solely to improve visualization and reduce marker overlap. We have revised the caption to clarify the description.

- Figure 4 caption: "Strip plot of more-hygroscopic (MH) component volume fractions ($P_{\mathrm{MH},j}$) for particles at D_p = 150 nm. The seven aerosol populations shown have identical mean hygroscopicity (κ_{mean} = 0.31) but different mixing state indices (χ^{PMC}). Each dot represents a particle population from the PartMC simulation, and its color indicates number concentration. Dots are grouped by the χ^{PMC} value of each aerosol population, with a small horizontal jitter applied only for visualization."

5. Data Availability: If feasible, I encourage the authors to consider making the model simulation dataset publicly available, including the particle sizes and chemical compositions of the 4900 aerosol populations. Such a dataset could serve as a valuable benchmark for future algorithm development and intercomparison, much like H-TDMA observational datasets.

Thank you for the suggestion. The simulation dataset used in this study had already been deposited in the Illinois DataBank. In response to this comment, we have expanded the archived dataset to include the particle-resolved chemical composition of the 4900 aerosol populations, in addition to the particle size and the LH/MH spcecies volume fractions. The repository link is provided in the Data Availability section and will become publicly accessible upon publication.

We also note that the validation scenario library is designed to be extensible and can be regenerated or customized for different applications. The underlying tools are publicly available on Github, including the PartMC model (`https://github.com/compdyn/partmc`) and the scenario library generation framework (`https://github.com/zhonghua-zheng/code_scenario_generator`).

References

Petters, M. D. and Kreidenweis, S. M.: A Single Parameter Representation of Hygroscopic Growth and Cloud Condensation Nucleus Activity, Atmospheric Chemistry and Physics, 7, 1961–1971, https://doi.org/10.5194/acp-7-1961-2007, 2007.

Responses to Reviewer #2 Comments

General comments:

Liu et al. evaluated the use of HTDMA-measured size-resolved κ to predict the mixing state index (χ, YZ method) with χ predicted by a particle-resolved model. Overall, this paper suggested that the YZ method is valid, especially in urban and continental regions. Liu et al. also provided estimates of the uncertainties associated with the YZ method, which can be applied in the future by others who use it. Overall, Liu et al. provided very detailed evaluations and discussions. However, I feel this paper still has many areas for improvement. I would suggest a major revision.

I feel this paper needs to improve by adding more scientific discussions. Currently, it is a very good technical note with some scientific discussions. One particular section where I want to see more scientific discussion is Section 5. The authors presented long-term measurements but did not provide sufficient discussion. For example, I am interested in the impacts of different sources on κ and χ. What will be the impact of chemical compositions, since most sites have AMS or ACSM? Any seasonal variations? Are there any site dependencies? I am also curious if you have predicted χ using your particle-resolved models at these sites. How will the confidence intervals discussed in previous sessions apply to this session?

> We thank the reviewer for the careful assessment and constructive suggestions. We agree that the long-term ARM HTDMA measurements benefit from additional context and interpretation. In the revised manuscript, we have revised and expanded Section 5 to clarify the role of the observational analysis and to discuss the retrieved κ-derived χ values in the context of site-to-site differences, seasonal variability, aerosol loading, transport, meteorology, trace-gas indicators, and aerosol composition where available.
>
> The primary goal of this study is to evaluate the κ-based YZ retrieval framework using particle-resolved simulations and then demonstrate its application to long-term HTDMA measurements. We did not perform site-specific particle-resolved simulations for the ARM campaigns. Such simulations would require campaign-specific meteorology, emissions, boundary conditions, and chemical evolution and would constitute a separate modeling effort. Instead, the particle-resolved simulations are used here to quantify the assumptions, biases, and uncertainty of the retrieval framework across a broad scenario library, and the evaluated retrieval is then applied to the ARM HTDMA observations.
>
> We have also clarified how the uncertainty estimates derived from the particle-resolved simulations are applied to the field measurements. The uncertainty ranges shown for the ambient χ^{YZ} retrievals are based on the retrieval-error distributions derived from the PartMC-MOSAIC evaluation and are applied by particle size to the corresponding HTDMA-derived χ^{YZ} time series. Thus, the ARM analysis is intended as an application of the evaluated retrieval framework, with model-derived uncertainty bounds, rather than as a site-specific particle-resolved model simulation of each field campaign.
>
> The line numbers referenced below correspond to the revised clean manuscript.

Specific Comments:

1. I am not fully convinced why marine aerosols are not included in both methods, and why including them will cause overestimation of χ. Three of your sites are in the coastal regions (EPC, CRG, and HOU). Excluding marine aerosols will case significantly uncertainties in predicting aerosol composition and κ. I understand that marine aerosols are typically in the coarse mode, but there is growing evidence that fine marine aerosols are also prevalent. It would be beneficial to add more discussion of the exclusion of fine marine aerosols in the paper.

> Thank you for raising this important point. We agree that fine-mode marine aerosol can be present at coastal sites and that marine influence may introduce additional uncertainty when applying a binary κ-based retrieval (we address this issue also in comment 3 below). We have revised the manuscript to clarify this point and to avoid implying that our particle-resolved validation library directly represents marine aerosol populations.

The PartMC-MOSAIC validation library used here does not include primary sea-salt emissions and is therefore most directly applicable to continental and anthropogenic aerosol regimes. For this reason, the model-based uncertainty estimates should not be interpreted as a full validation of the YZ method for aerosol populations dominated by externally mixed marine aerosol. At the same time, the discussion of sea salt is useful because it illustrates a general limitation of the binary hygroscopicity framework: when the aerosol population contains a component with hygroscopicity outside, or substantially different from, the prescribed LH–MH end members, the mapping from κ to composition becomes ambiguous.

To make this clearer, we revised Section 5.3 to state explicitly that the $\kappa_{\mathrm{MH}} = 1.28$ sensitivity test is not a realistic marine aerosol simulation. Rather, it is a diagnostic test showing how the retrieval behaves when a sea-salt-like more-hygroscopic end member is imposed on the same PartMC aerosol populations. In that case, non-sea-salt inorganic species such as sulfate, nitrate, and ammonium become intermediate relative to the prescribed binary end members, which increases ambiguity in the YZ mapping and leads to overestimation of χ^{YZ} relative to the particle-resolved reference χ^{PMC}.

We also added text emphasizing that submicron sea-salt particles have been observed in marine and coastal environments, but that sea salt is discussed here only as an example of a component that can challenge the prescribed binary end-member assumption. We now state more clearly that applications at coastal sites should be interpreted cautiously when marine aerosol influence is substantial, especially if independent chemical information is not available to constrain the presence and mixing state of sea salt.

2. I have some comments related to ARM data. It is not very clear to me where each measurement is located. Moreover, as I mentioned in the previous comment, there are many other measurements in these sites, including aerosol size distribution, aerosol chemical composition, and meteorological measurements. Please consider utilizing the open-source data to provide a comprehensive discussion of χ and κ.

Thank you for the suggestion. We show a map of the ARM sites in Figure 5 of the revised manuscript. We agree that additional ARM measurements provide valuable context for interpreting the HTDMA-derived κ distributions and χ retrievals. To address this comment, we expanded the site description and added supplementary figures showing (1) particle number concentrations from the merged SMPS–APS measurements, (2) meteorological conditions, (3) seasonal wind regimes, (4) trace-gas measurements (O_3, CO, and SO_2), and (5) ACSM-derived bulk submicron aerosol composition (Figures S2–S6). We also revised Section 5 to relate the observed χ variability to differences in aerosol loading, bulk non-refractory composition, transport patterns, source influences, and atmospheric processing inferred from these measurements. This discussion can be found in the revised Section 5.2.

The added measurements support several qualitative interpretations. The size distributions show that the CCN-relevant particle population differs substantially among sites and seasons. Trace gases and wind patterns provide context for source influence and transport, for example at HOU and EPC. The ACSM measurements show site- and time-dependent differences in bulk submicron composition, including organic and inorganic aerosol fractions, which provide additional context for interpreting differences in κ distributions. Together, these measurements indicate that the ARM sites span distinct aerosol environments and that the retrieved χ values should be interpreted in the context of both source variability and atmospheric processing

At the same time, we clarify that these auxiliary measurements are not used as direct inputs to the χ retrieval. ACSM provides bulk non-refractory submicron composition and does not provide particle-resolved composition for the same HTDMA-selected particles. In addition, the ACSM organic aerosol signal does not distinguish POA from SOA without additional source-apportionment analysis, and ACSM does not directly constrain refractory sea-salt mass. Therefore, the colocated measurements are used as qualitative context rather than as direct constraints on the χ retrieval or as a unique attribution of κ modes to specific chemical components.

3. Could you add more types of hygroscopic species to the YZ model? How will that affect your results?

Thank you for this suggestion. We agree that adding additional hygroscopicity classes is a natural exten-

sion of the YZ framework. However, it is not a straightforward modification of the present retrieval. A key advantage of the original YZ method is that, once κ_{LH} and κ_{MH} are prescribed, the measured κ value in each κ bin can be mapped uniquely to the relative LH and MH fractions. If an additional hygroscopicity class is introduced, for example an intermediate-hygroscopicity organic-aerosol class or a highly hygroscopic sea-salt class, the same κ value can be produced by multiple combinations of component fractions. Additional observational constraints would therefore be needed to determine how much of each class contributes to a given κ bin.

Such an extension could reduce some of the biases identified in this study. For example, an intermediate-hygroscopicity class could prevent externally mixed SOA-rich particles from being interpreted as artificial LH–MH mixtures, and a highly hygroscopic class could help represent sea-salt-influenced aerosol. However, this would require independent constraints, such as size-resolved composition, source-apportionment information, or other assumptions about the allowed particle types. Without such constraints, the retrieval would become non-unique and the resulting mixing-state metric would no longer be directly comparable to the binary χ^{YZ} evaluated here.

For this reason, we retain the original binary YZ framework in the present study and focus on quantifying its assumptions, uncertainty, and limitations. We have added this discussion to Section 5.3:

- L338–346: One possible extension would be to represent aerosol populations using more than two hygroscopicity classes, for example by adding an intermediate-hygroscopicity class for organic aerosol or a highly hygroscopic class for sea salt. Such an extension could reduce some of the biases identified here, because intermediate-hygroscopicity particles would no longer be forced into artificial LH–MH mixtures. However, this would also remove a key advantage of the original YZ framework: in the binary case, the measured κ value constrains the relative LH and MH fractions for each κ bin. Adding additional classes introduces additional unknown component fractions, so the same measured κ value can generally be produced by multiple combinations of those fractions. A multi-class retrieval would therefore require additional observational constraints, such as independent size-resolved composition or source-apportionment information. Developing and evaluating such an extension is beyond the scope of the present work.

4. Please make sure to define the acronyms in the first place in the main manuscript.

This comment is closely related to our response to the Minor Comment #3. In addition to the revisions described there, we identified that the Secondary Organic Aerosol Model (SORGAM) scheme had not been defined upon first use and have corrected this oversight:

- L131–L132: "To simulate secondary organic aerosol (SOA) we use the Secondary Organic Aerosol Model (SORGAM) scheme (Schell et al., 2001)."

5. There are some places not well defined at first. Please refer to my minor comments.

This comment is addressed in our response to the Minor Comment #1 and #2.

6. The figure size is too small and hard to read. I suggest make them larger

Thank you for pointing this out. We have increased the figure sizes accordingly.

Minor Comments:

1. L53-56, "Accordingly, . . . is computed." It will be helpful to define MH and LH here since it is the first place these two terms appear.

The acronyms MH and LH are defined at their first occurrence in L55–56 as more-hygroscopic (MH) and less-hygroscopic (LH) components, respectively.

2. L78-80, "For the aerosol … can be calculated as:" It is not clear to me what bin means here. Do you mean size bin or κ bin?

Thank you for noting this ambiguity. Here, "bin" refers to the κ bin. We have revised the sentence to state this explicitly:

- L80–81: "For the aerosol with a given dry diameter and a known κ-PDF with X κ-bins, ..."

3. L151-155, "We then … Na, and Ca." χ^{PMC} was not defined in the main text before. Please define ARO1, ARO2, ALK1, OLE1, API1, API2, LIM1, LIM2, OIN, and OC.

Thank you for pointing this out. "OIN" is defined in L134 as "other inorganic mass". To avoid confusion, we use "POA" instead of "OC" in this grouping, and "POA" is defined in L135 as "primary organic aerosol". We made the following changes:

- L156–159: "The low-hygroscopic group comprised SOA species represented in SORGAM, including aromatic-derived species (ARO1 and ARO2), alkane-derived species (ALK1), alkene-derived species (OLE1), α-pinene-derived species (API1 and API2), and limonene-derived species (LIM1 and LIM2), as well as OIN, POA, and BC, ..."

4. L179-180, "Under the … LH species." Could you explain why this happens?

Thank you. We have added an explanation accordingly.

- L201–203: "Under the binary assumption, the YZ method misinterprets pure SOA particles as artificial mixtures containing 15% MH species and 85% LH species (following Eq. (1): $P_{i,\mathrm{MH}} = (\kappa_{\mathrm{SOA}} - \kappa_{\mathrm{LH}})/(\kappa_{\mathrm{MH}} - \kappa_{\mathrm{LH}}) = (0.1 - 0)/(0.65 - 0) \approx 15\%$)."

5. Would section 4.3 fit better after section 4.1?

Thank you for the suggestion. We agree that presenting the uncertainty intervals immediately after the quantitative comparison improves the logical flow. We have made the change accordingly.

6. Could you label which one is internally mixed and which one is externally mixed in Fig. 2a and b?

Thank you for the suggestion. We have added the labels accordingly and revised the caption.

- Figure 3 caption: "(a and b) Representative PartMC-derived κ-PDFs from the validation scenario library for two aerosol populations with high secondary organic aerosol (SOA) content at a dry diameter of 150 nm, corresponding to predominantly externally mixed (a) and internally mixed (b) particle populations."

7. Figure 6 should come first before Figure 5 to help understand the site locations.

Thank you for the suggestion. We have reordered the figures and adjusted the corresponding text as follows:

- L240–247: "Having quantified the performance and limitations of κ-based mixing state retrievals using particle-resolved simulations, we now apply the method to long-term hygroscopicity measurements to examine aerosol mixing state in real atmospheric environments.

  In this section, we apply the YZ method to multi-year HTDMA datasets (2021–2025) from four U.S. Department of Energy Atmospheric Radiation Measurement (DOE ARM) campaigns (Uin et al., 2012): CoURAGE (CRG), TRACER (HOU), Southern Great Plains (SGP), and EPCAPE (EPC). For each HTDMA dataset, we extracted κ and particle number concentrations at specified dry diameters to construct κ-PDFs, which were then applied in the YZ framework to calculate χ^{YZ}. Figure 5 shows the geographical location of the four ARM sites."

8. L259-260, "The results indicate ... up to 86%." Where are your results, and why do you think χ is an overestimate, and compared to what?

Thank you for pointing this out. We have revised the text to make clear where the result is shown, what the comparison is made against, and why the retrieved value is interpreted as an overestimate. This is now part of the revised Section 5.3. The sensitivity test is now shown in Figure S7. In this test, the YZ retrieval is repeated using a sea-salt-like more-hygroscopic end member, $\kappa_{\mathrm{MH}} = 1.28$, while the reference remains χ^{PMC}, the particle-resolved mixing-state index calculated directly from the PartMC per-particle compositions.

The purpose of this test is not to simulate a realistic marine aerosol population, because the validation library does not include primary sea-salt particles. Instead, it is a diagnostic sensitivity test that illustrates how the binary retrieval behaves when the assumed upper hygroscopicity end member is shifted beyond the hygroscopicity of common non-sea-salt inorganic species. Under this assumption, sulfate-, nitrate-, and ammonium-rich particles become intermediate relative to the prescribed LH–MH end members and can be interpreted as mixtures, leading to systematic overestimation of χ^{YZ} relative to χ^{PMC}.

We made the following changes:

- L315–330: "A more fundamental limitation arises when the aerosol population cannot be represented well by a binary less-/more-hygroscopic system. In such cases, κ no longer maps uniquely onto a two-component composition. This ambiguity is most evident when chemically distinct particle types have intermediate hygroscopicities or when additional highly hygroscopic components are present. For example, externally mixed SOA-rich particles can be misinterpreted as artificial LH–MH mixtures, leading to overestimation of χ. Similarly, in marine-influenced environments, submicron sea-salt particles have been observed and may extend the hygroscopicity range beyond that of typical continental inorganic salts (O'Dowd and Smith, 1993; Murphy et al., 1998; Yao et al., 2003; Bian et al., 2019; Murphy et al., 2019). Because sea salt is not included in the present PartMC validation library, the results presented here should not be interpreted as a full validation of the YZ method for marine aerosol populations.

  To illustrate the sensitivity of the retrieval to this type of end-member mismatch, we repeated the YZ retrieval using a sea-salt-like more-hygroscopic end member, $\kappa_{\mathrm{MH}} = 1.28$, while retaining the same PartMC aerosol populations as the reference (Figure S2). This test is not intended to represent a realistic marine aerosol simulation. Instead, it shows how the binary retrieval behaves when the assumed upper hygroscopicity end member is shifted beyond the hygroscopicity of common non-sea-salt inorganic species. Under this assumption, sulfate-, nitrate-, and ammonium-rich particles become intermediate relative to the prescribed LH–MH end members and can be interpreted as mixtures, leading to systematic overestimation of χ^{YZ} relative to χ^{PMC}."

9. L273-283. "The coexistence ... internally mixed populations." I have a hard time following these two paragraphs.

Thank you for this comment. We agree that the original wording was difficult to follow. We have rewritten this part of Section 5.3 to clarify the main limitation: the retrieval becomes uncertain when the measured κ value does not map uniquely onto the prescribed binary LH–MH composition. The revised text now

distinguishes between modest uncertainty in the prescribed end-member values and the more fundamental ambiguity that arises when important aerosol components are intermediate between, or outside, the assumed end-member range.

- L331–337: "These examples highlight the broader non-uniqueness of κ-based mixing-state retrievals. Retrieval uncertainty increases when multiple chemically distinct particle types can produce similar κ values, or when important aerosol components fall outside the assumed end-member range. Applications in coastal, marine-influenced, or SOA-rich environments should therefore be interpreted cautiously, especially when externally mixed intermediate- or highly hygroscopic components are expected. Colocated bulk composition measurements, such as ACSM, provide useful context for the non-refractory submicron aerosol composition, but they do not directly constrain refractory sea-salt mass, particle-resolved composition, or the mixing state of the HTDMA-selected particles."
- L347–354: Despite these limitations, the YZ method remains useful for aerosol populations in which the dominant hygroscopicity range is reasonably represented by the prescribed LH and MH endmembers and intermediate-hygroscopicity components are not predominantly externally mixed. These conditions are expected to be most common for aged continental and anthropogenic aerosol populations, where condensation, coagulation, and multiphase processing tend to reduce particle-to-particle composi- tional contrasts. In such cases, κ-PDFs provide a physically meaningful constraint on particle-to-particle hygroscopicity variability, and the YZ framework enables statistically consistent mixing-state inference from long-term HTDMA observations. This is an important advantage because comparable time coverage is difficult to obtain from particle-resolved composition measurements.

References

Bian, H., Froyd, K., Murphy, D. M., Dibb, J., Darmenov, A., Chin, M., Colarco, P. R., da Silva, A., Kucsera, T. L., Schill, G., Yu, H., Bui, P., Dollner, M., Weinzierl, B., and Smirnov, A.: Observationally Constrained Analysis of Sea Salt Aerosol in the Marine Atmosphere, Atmospheric Chemistry and Physics, 19, 10 773–10 785, https://doi.org/10.5194/acp-19-10773-2019, 2019.

Murphy, D. M., Anderson, J. R., Quinn, P. K., McInnes, L. M., Brechtel, F. J., Kreidenweis, S. M., Middlebrook, A. M., Pósfai, M., Thomson, D. S., and Buseck, P. R.: Influence of Sea-Salt on Aerosol Radiative Properties in the Southern Ocean Marine Boundary Layer, Nature, 392, 62–65, https://doi.org/10.1038/32138, 1998.

Murphy, D. M., Froyd, K. D., Bian, H., Brock, C. A., Dibb, J. E., DiGangi, J. P., Diskin, G., Dollner, M., Kupc, A., Scheuer, E. M., Schill, G. P., Weinzierl, B., Williamson, C. J., and Yu, P.: The Distribution of Sea-Salt Aerosol in the Global Troposphere, Atmospheric Chemistry and Physics, 19, 4093–4104, https://doi.org/10.5194/acp-19-4093-2019, 2019.

O'Dowd, C. D. and Smith, M. H.: Physicochemical Properties of Aerosols over the Northeast Atlantic: Evidence for Wind-Speed-Related Submicron Sea-Salt Aerosol Production, Journal of Geophysical Research: Atmospheres, 98, 1137–1149, https://doi.org/10.1029/92JD02302, 1993.

Schell, B., Ackermann, I. J., Hass, H., Binkowski, F. S., and Ebel, A.: Modeling the Formation of Secondary Organic Aerosol within a Comprehensive Air Quality Model System, Journal of Geophysical Research: Atmospheres, 106, 28 275–28 293, https://doi.org/10.1029/2001JD000384, 2001.

Uin, J., Cromwell, E., Hayes, C., and Salwen, C.: Atmospheric Radiation Measurement (ARM) User Facility. Humidified Tandem Differential Mobility Analyzer (AOSHTDMA), updated daily. 2025-03-13 to 2025-11-30, ARM Mobile Facility (CRG), Baltimore, MD: Supplemental Facility 2 in rural setting (S2); 2023-02-15 to 2024-02-13, ARM Mobile Facility (EPC), La Jolla, CA: AMF1 (main site for EPCAPE on Scripps Pier) (M1); 2021-10-01 to 2022-09-30, ARM Mobile Facility (HOU), Houston, TX: AMF1 (main site for TRACER) (M1); 2021-04-27 to 2023-10-24, Southern Great Plains (SGP), Lamont, OK (Extended and Co-located with C1) (E13). Compiled by Uin, J., Cromwell, E., Hayes, C., and Salwen, C. Data set accessed 2025-08-06 at https://doi.org/10.5439/1776643, 2012.

Yao, X., Fang, M., and Chan, C. K.: The Size Dependence of Chloride Depletion in Fine and Coarse Sea-Salt Particles, Atmospheric Environment, 37, 743–751, https://doi.org/10.1016/S1352-2310(02)00955-X, 2003.