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.
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> 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.
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> 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.
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> 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.

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