

Below we addressed the reviewer's comments carefully, with the reviewers' comments in black and our response in blue.

This manuscript investigates the temporal variability and controlling factors of organic aerosol hygroscopicity (κ_{OA}) at a rural site in eastern China using humidified scattering measurements, aerosol size distributions, chemical composition for a closure study approach. The study addresses an important topic for understanding aerosol–cloud interactions and the representation of organic aerosol hygroscopicity. The manuscript presents an interesting result: bulk oxidation state alone does not adequately explain the observed variability in κ_{OA} , while biomass-burning influence is positively associated with κ_{OA} and appears to modify the relationship between oxidation state and hygroscopicity. The combination of statistical analysis and the January pollution episode provides useful observational evidence for this interpretation. Overall, I find the study scientifically interesting and suitable for publication after minor revision.

Response: We sincerely thank the reviewer for his/her positive and constructive assessment of our manuscript. We are very pleased that they found the study scientifically interesting and the results on the role of biomass burning in modifying the relationship between the oxidation state and hygroscopicity of organic aerosols to be a valuable contribution. In accordance with their recommendation for minor revision, we have carefully addressed all points listed below to improve the clarity and precision of the manuscript. We believe these revisions have further strengthened the paper.

Specific comments:

1. better quantify κ_{OA} uncertainty. κ_{OA} is derived indirectly from bulk aerosol hygroscopicity using the ZSR framework and assumed hygroscopicities of inorganic components and refractory material. Since κ_{OA} is subsequently used as the central variable throughout the paper, it would be useful to provide at least a quantitative estimate of its uncertainty. For example, the observation size ranges of PNSD, ACSM, scattering growth, and AE are different, how this influence your analysis. During the drying process, volatile OA may loss, how much of this could influence the analysis of bulk κ_{OA} .

Response: We thank the reviewer for this important comment. We agree that the uncertainty in κ_{OA} warrants explicit quantification, given that it is indirectly derived from bulk aerosol hygroscopicity using the ZSR framework and serves as a central variable in this study.

To address this concern, we performed a Monte Carlo uncertainty propagation analysis

to quantify the effects of uncertainties in the input parameters on the derived κ_{OA} . Specifically, 10,000 Monte Carlo realizations were performed for each measurement point by perturbing the bulk hygroscopicity parameter (κ_{inv}), the mass concentrations of non-refractory aerosol species measured by the ToF-ACSM, the total particle volume concentration derived from the PNSD, and the hygroscopicity parameter of refractory particulate matter other than BC (κ_{rPM}). The assumed uncertainties were based on those reported by Kuang et al. (2021), whose methodology for retrieving aerosol hygroscopicity is consistent with that used in this study. For example, a relative uncertainty of 20% was assigned to the mass concentrations of all non-refractory species (including sulfate, nitrate, ammonium, chloride, and OA) measured by the ToF-ACSM. For κ_{rPM} , a baseline value of 0.05 and an absolute standard deviation of 0.03 were used to represent its uncertainty. The uncertainty assigned to κ_{inv} followed the estimate reported by Kuang et al. (2021).

As shown in Figure R1-1, the Monte Carlo mean values of κ_{OA} closely agreed with the baseline estimates reported in the manuscript. Both approaches yielded a campaign-average κ_{OA} of 0.11, with a correlation coefficient of 0.99 between the Monte Carlo mean values and the baseline estimates. These results indicate that the campaign-average estimate and temporal pattern remained similar under the prescribed input uncertainties. The standard deviation of the Monte Carlo distribution at each measurement point was used to quantify the propagated uncertainty associated with these input parameters. These standard deviations varied substantially over time, ranging from 0.01 to 0.18 (Figure R1-1). Larger uncertainties were generally associated with higher κ_{OA} values and lower OA volume fractions (Figure R1-2), consistent with the greater sensitivity of the ZSR inversion when the OA contribution to total particle volume is relatively small.

We further conducted sensitivity analyses by perturbing the input parameters individually. The results indicated that the retrieved κ_{OA} was most sensitive to uncertainties in the total particle volume concentration and κ_{rPM} (Figure R1-1c). These findings identify the input parameters that exert the greatest influence on the retrieval under the prescribed uncertainty assumptions. We emphasize that the resulting uncertainty estimates represent the propagation of the specified input uncertainties and do not encompass all potential sources of systematic error.

We also examined the implications of differences in particle-size coverage among the measurements used in the analysis. All relevant measurements were conducted downstream of PM_{2.5} size-selective inlets, providing a common nominal aerodynamic size cutoff at the sampling-inlet level. Nevertheless, the effective particle-size ranges and transmission efficiencies may differ among instruments. As described in Section

2.3.1, the PNSD was obtained by merging SMPS and Grimm-OPC measurements, and data spanning approximately 15 nm to 2 μm were used in the subsequent hygroscopicity inversion and subsequent κ_{OA} calculation. The upper size limit was selected to account for the differences between aerodynamic and volume-equivalent diameters, as discussed in Section 2.3.3. The ToF-ACSM, equipped with a $\text{PM}_{2.5}$ aerodynamic lens, measured the mass concentrations of non-refractory species, including sulfate, nitrate, ammonium, chloride, and OA, in $\text{PM}_{2.5}$. The BC and scattering-growth measurements were also conducted on $\text{PM}_{2.5}$ aerosol samples.

To evaluate the consistency of the PNSD-derived particle volume and optical measurements, we compared the dry scattering coefficients calculated from the measured PNSD with those directly measured using the Aurora 3000 nephelometer. The good agreement between the two estimates (Figure S4 in the supplemental file) supports the consistency of the PNSD-based representation of dry aerosol scattering over the size range considered. However, this comparison does not completely eliminate potential biases associated with differences in the effective particle-size ranges and transmission efficiencies among instruments.

Finally, the potential influence of OA loss during the drying process could not be quantitatively assessed because neither the extent of the loss nor the chemical composition and hygroscopicity of the lost OA components could be characterized in this study. Such losses may alter both the amount and composition of the residual OA, potentially affecting the derived κ_{OA} . Consequently, this potential systematic uncertainty is not included in the Monte Carlo analysis, and its magnitude and direction remain unconstrained.

We have clarified the measurement-size-range considerations and the corresponding methodological details in Sections 2.3.1 and 2.3.3, and added the Monte Carlo uncertainty analysis and its results to Sections 2.3.3 and 3.3. The additional results are presented in Figures R1-1 and R1-2 in this response and in Figure S15 and S16 of the Supplementary Information.

Section 2.3.3, lines 278-289: *“The derived κ_{OA} may be subject to uncertainties in the input parameters used in the inversion, thus, we performed a Monte Carlo uncertainty propagation analysis, with 10,000 realizations for each data point in the κ_{OA} time series. In each realization, the input variables in Eqs. 10 and 11 were randomly perturbed according to their prescribed uncertainties. Given the similarities in the measurement and inversion methods, the uncertainties assigned to the input variables, including the mass concentrations of non-refractory aerosol species measured by the ToF-ACSM, V_{PM} , κ_{inv} and κ_{rPM} , were based on the estimates*

reported in Table 2 of Kuang et al. (2021). It should be noted that the derived κ_{OA} does not account for the potential contribution of OA components lost during the drying process before the aerosol enters the measurement instruments. In addition, the potential contribution of co-condensation to aerosol hygroscopic growth (Gunthe et al., 2021) is not explicitly considered because gas-phase precursor measurements (e.g., HCl and NH₃) and a dedicated thermodynamic analysis are not available in this study. These factors may introduce additional uncertainties that are not captured by the Monte Carlo analysis.”

Section 3.3, lines 353-359: “Monte Carlo uncertainty analysis showed that the standard deviations of the simulated κ_{OA} distributions at individual measurement points ranged from 0.01 to 0.18 (Fig. S15). Larger uncertainties generally occurred at higher κ_{OA} values and lower OA volume fractions, indicating greater sensitivity of the ZSR-based retrieval under these conditions (Fig. S16). Despite the substantial point-by-point uncertainties, the Monte Carlo mean values agreed well with the baseline estimates (Fig. S15a), yielding the same campaign-average κ_{OA} of 0.11 and a correlation coefficient of 0.99 between the two sets of estimates. Additional Monte Carlo sensitivity tests, in which each input parameter was perturbed individually while the others were held constant, showed that uncertainties in V_{PM} and κ_{rPM} contributed most strongly to the uncertainty in the retrieved κ_{OA} (Fig. S15c).”

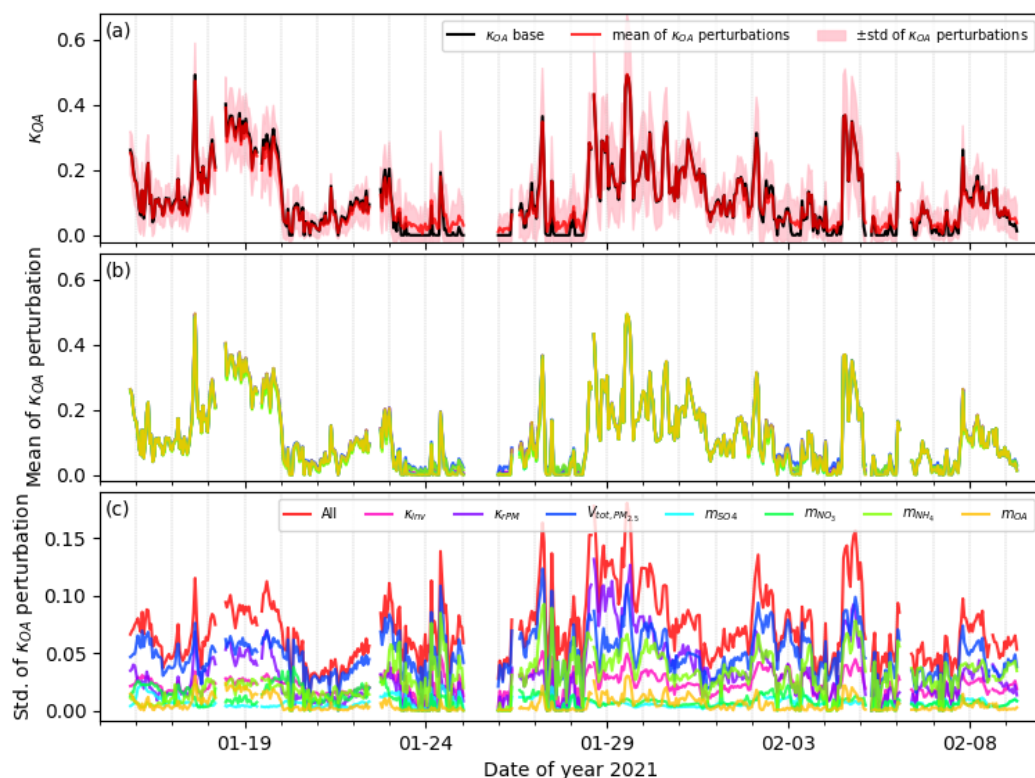


Figure R1-1. Time series of (a) Monte Carlo mean values of κ_{OA} (red line) and the ± 1 standard deviation range around the Monte Carlo mean (light red shading), compared with the baseline estimates (black line); (b) Monte Carlo mean values of κ_{OA} obtained by perturbing individual input parameters including κ_{inv} , the mass concentrations of non-refractory species, the total particle volume concentration, and κ_{rPM} ; and (c) the corresponding standard deviations of κ_{OA} for each individual perturbation..

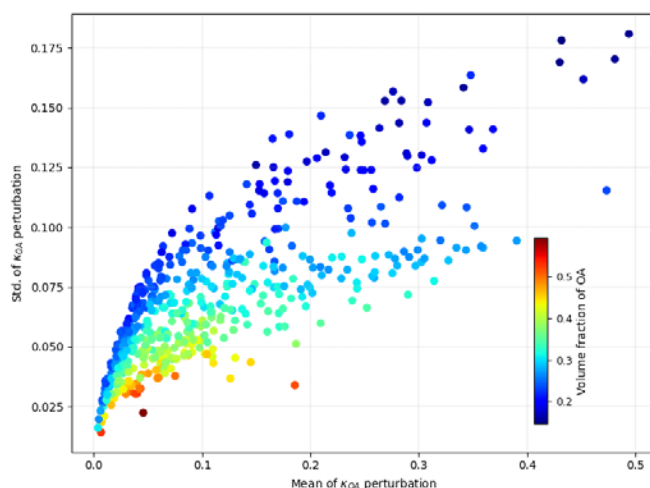


Figure R1-2. Monte Carlo standard deviations of κ_{OA} as a function of the corresponding Monte Carlo mean values, colored by the volume fraction of OA in $PM_{2.5}$.

2. κ_{OA} is estimated by the κ_{inv} subtracting other known $\kappa_{components}$, as in eq.11. While, the direct impact of other components has been considered with this equation, the indirect impacts could also influence the κ_{OA} estimation, such as co-condensation. Previous studies have reported high impact of co-condensation on hygroscopic growth associated with chloride and nitrate particles. Please discuss how this may impact the uncertainty of κ_{OA} estimate.

Response: We thank the reviewer for pointing out this important issue. Previous studies have shown that the uptake of gaseous precursors can enhance aerosol particle growth under humid conditions. For example, the uptake of gaseous HCl into aerosol water has been reported to substantially enhance particle growth in Delhi (Gunthe et al., 2021; Mandariya et al., 2024). Such processes may contribute to observed aerosol growth beyond that attributable to equilibrium water uptake by the pre-existing aerosol composition. Consequently, the κ_{inv} retrieved from scattering enhancement may not exclusively reflect equilibrium water uptake, potentially introducing additional uncertainty into the subsequent ZSR-based estimation of κ_{OA} .

However, the pronounced effects reported in previous studies were associated with environments characterized by high gaseous HCl and NH₃ concentrations and a substantial chloride contribution to non-refractory PM₁ (approximately 10% by mass). In contrast, the mean chloride concentration in non-refractory PM_{2.5} in our study was only 0.9 µg m⁻³, accounting for approximately 2% of the total non-refractory aerosol mass. This relatively low chloride contribution suggests that HCl-related effects on aerosol growth may be less pronounced under our study conditions than those reported in the aforementioned studies. Nevertheless, because gas-phase precursor concentrations and the relevant gas-particle partitioning processes were not directly characterized, we cannot exclude a potential contribution from co-condensation or quantitatively constrain its effect on the derived κ_{OA} . We have therefore acknowledged co-condensation and gas-phase precursor uptake as additional potential sources of uncertainty in the revised manuscript.

3. The manuscript retrieves κ over several RH intervals but uses 80–90% RH as the representative value. Please briefly demonstrate that the main κ_{OA} – f_{bb} relationship is not sensitive to the selected RH interval.

Response: We thank the reviewer for this helpful comment. As discussed in the second paragraph of Section 3.2 of the manuscript, the retrieved hygroscopicity parameter (κ) exhibited a systematic decrease with increasing RH. This RH dependence may arise from non-ideal solution thermodynamics, RH-dependent solute mass fractions, liquid–liquid phase separation, and other factors. Because measurements of aerosol hygroscopicity under subsaturated conditions are commonly reported for RH values of 80–90%, both from humidified tandem differential mobility analyzer (H-TDMA) measurements (Wu et al., 2016; Hong et al., 2018) and humidified nephelometer systems (Kuang et al., 2020; Titos et al., 2021), we use κ retrieved over this RH interval as the representative value throughout the main analysis.

As shown in Figure R1-3, the κ values retrieved at lower RH are systematically higher than those retrieved at 80–90% RH, while exhibiting similar temporal variations. A similar RH dependence has been reported by Zhao et al. (2022) for both individual inorganic aerosols (e.g., ammonium sulfate, AS) and ambient aerosols, and was attributed, at least in part, to changes in solute mass fraction in the aerosol–water system. Notably, the difference between κ retrieved at 60–70% RH and that retrieved at 80–90% RH ($\Delta\kappa$) also exhibits temporal variations that closely track those of the retrieved κ (Figure R1-3). This pattern suggests that the magnitude of the RH dependence may increase with aerosol hygroscopicity, although the underlying physical mechanisms

require further investigation.

The component-specific hygroscopicity parameters used in the Zdanovskii–Stokes–Robinson (ZSR) mixing rule for ammonium nitrate (AN), ammonium sulfate (AS), ammonium bisulfate (ABS), and particulate chloride (PC) correspond to values representative of approximately 85% RH. Accordingly, the κ_{OA} values derived in the main analysis should also be interpreted as representative of this RH range.

To examine the sensitivity of the inferred κ_{OA} – f_{bb} relationship to the selected RH interval, we additionally estimated κ_{OA} at approximately 65% and 75% RH. Zhao et al. (2022) reported a decrease in the hygroscopicity parameter of AS from approximately 0.73 at 60% RH to 0.42 at 95% RH. In the absence of comparable RH-dependent parameterizations for the other inorganic components considered here, we used the corresponding average decrease rate for AS (approximately 0.009 per percentage point of RH) as a first-order approximation to adjust their component-specific κ values to lower RH. We then applied the ZSR mixing rule to the bulk κ values retrieved at 60–70% RH and the adjusted inorganic-component parameters to estimate κ_{OA} at approximately 65% RH. The same procedure was applied to estimate κ_{OA} at approximately 75% RH using the bulk κ values retrieved at 70–80% RH.

As shown in Figure R1-3, the κ_{OA} estimates at approximately 65% and 75% RH are consistent with those at approximately 85% RH reported in the manuscript, with correlation coefficients of 0.71 and 0.90, respectively. These results suggest that the overall κ_{OA} – f_{bb} relationship is qualitatively robust to the choice of RH interval, although the estimated κ_{OA} values vary somewhat with RH. In particular, the κ_{OA} – f_{bb} relationships at 75% and 85% RH exhibit similar increasing trends, with κ_{OA} values at 75% RH being systematically higher than those at 85% RH (Figure R1-4). Given the additional uncertainty associated with the incompletely characterized RH dependence of κ for the relevant inorganic components, we focus on κ_{OA} at approximately 85% RH in this study.

In the revised manuscript, we have added a further explanation of why κ retrieved over the 80–90% RH interval is used as the representative value throughout the main analysis.

Section 2.3.2, lines 244-245: “Unless otherwise specified, κ_{inv} values retrieved over the 80–90% RH range are used to represent bulk aerosol hygroscopicity, as the results are directly comparable *with* previous studies that report κ_{inv} within this RH range (Kuang et al., 2020; 2021) *and are consistent with the RH conditions corresponding to the κ values adopted for well-characterized inorganic species when estimating OA hygroscopicity, as discussed below.*”

Section 2.3.3, lines 273-275: “*Since κ is RH dependent under sub-saturation*

conditions (Zhao et al., 2022), the selected values are assumed to represent aerosol hygroscopicity at an RH of $\sim 85\%$, consistent with the κ_{inv} values retrieved over the 80–90% RH range.”

Section 3.2, lines 333-337: “A similar decrease in κ with increasing RH was reported by Zhao et al. (2022) for both individual inorganic aerosols (e.g., AS) and ambient aerosols, which was attributed, at least in part, to variations in solute mass fraction within the aerosol-water system. A higher inorganic fraction generally leads to larger κ values and greater RH-induced variability in κ . Therefore, aerosol populations with higher κ_{inv} values, which are likely associated with larger inorganic fractions, may exhibit stronger RH dependence.”

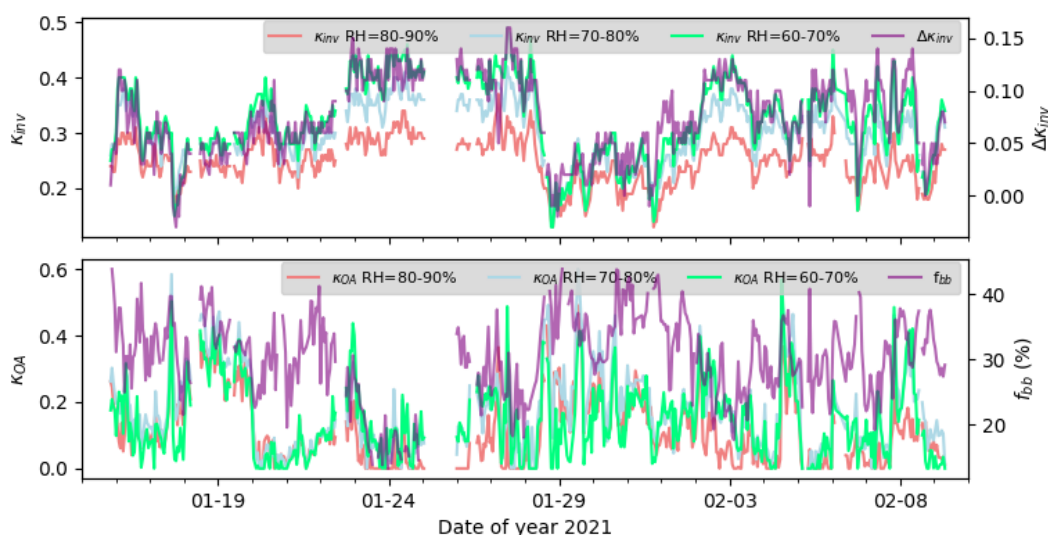


Figure R1-3. Bulk κ retrieved for RH intervals of 80–90% (red), 70–80% (blue), and 60–70% (green), along with the difference between κ at 80–90% and 60–70% RH (purple) in the upper panel. The lower panel shows the corresponding κ values of OA for the three RH intervals and the biomass-burning contribution.

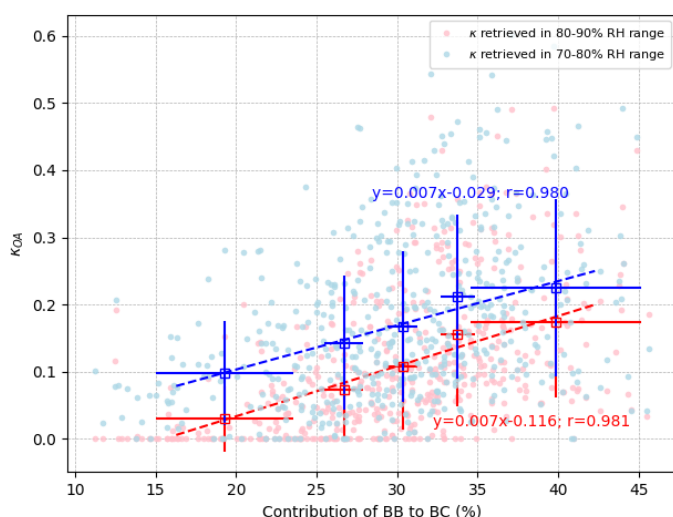


Figure R1-4. Variation of κ_{OA} retrieved for RH intervals of 80-90% (red) and 70-80% (blue) as a function of relative contribution of biomass burning to BC (f_{bb}). Open squares represent binned mean κ_{OA} values based on f_{bb} bins defined by 20th-percentile intervals, with error bars indicating one standard deviation. The dashed line shows a linear regression fitted to the binned means.

4. Fig.3. Around Jan. 22nd, there seems to be a gap of data in vol. frac. and just in vol. frac., and still with successful retrieval of κ_{OA} . Could you explain a bit more about this.

Response: We sincerely thank the reviewer for their careful observation. The gap in the volume fraction data in Fig. 3b, occurring approximately from 11:00 to 18:00 on January 22nd, was due to a temporary loss of particle number size distribution (PNSD) measurements. Since the total aerosol volume concentration - used to compute the volume fractions - is derived from the PNSD data, this interruption also led to the absence of refractory particulate matter (rPM) concentration. The latter is calculated as the difference between the total aerosol volume and the sum of known chemical species (AN, AS, ABS, KCl, Org, and BC), as reflected by the missing brown data in Fig. 3a. Furthermore, the unavailability of PNSD data prevented the retrieval of κ_{OA} during the same period, as shown in Fig. 3d, since the κ_{OA} calculation relies on both humidified scattering measurements and aerosol volume concentration obtained from the PNSD. Other gaps observed in the time series are attributed to intermittent losses of either PNSD or ToF-ACSM data. We have revised Fig. 3 to more clearly indicate all periods affected by data loss from either instrument.

References:

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