

Responses to reviewers' comments

We thank the reviewers for their detailed, helpful, and overall supportive comments. We have revised the manuscript to account for each comment. Responses to the individual comments are provided below. Reviewer comments are in **bold**. Author responses are in plain text. Modifications to the manuscript are in *italics*. Line numbers in the response correspond to those in the revised manuscript text file.

Reviewer #1:

Comment 1: The particle-phase sulfur-to-nitrogen ratio (pSNR) is derived from the relative peak areas of sulfate and nitrate ions measured by SPA-MS. Because the ionization and detection efficiencies of these species may differ and may also be affected by particle composition and matrix effects, further clarification is needed regarding the interpretation of pSNR. In particular, can pSNR be regarded as an absolute chemical ratio, and how robust are comparisons among different particle types and environmental conditions?

Response: We thank the reviewer for raising this important methodological issue. We agree that the relative peak areas measured by SPA-MS cannot be directly converted into absolute sulfate-to-nitrate molar or mass ratios without compound- and matrix-specific calibration. Accordingly, pSNR is used in this study as a relative spectral indicator of the balance between particulate sulfate and nitrate, rather than as an absolute chemical ratio. The pSNR was consistently calculated as the ratio of the relative peak areas of sulfate-related ions (m/z –97 and –96) to nitrate-related ions (m/z –62 and –46). All particles were analyzed using the same instrument, ionization settings, peak-selection criteria, and data-processing procedure. Consequently, although differences in ionization efficiency and matrix effects cannot be fully eliminated, the internally consistent measurements allow meaningful comparisons of relative changes across observation periods, RH regimes, and operationally defined particle classes.

We have clarified the interpretation and limitations of pSNR in the Methods. The text has been revised as follows:

Line 215~217: *“Because ion responses and matrix effects may vary, pSNR is interpreted as a relative spectral indicator rather than an absolute sulfate-to-nitrate molar or mass ratio, consistent with prior SPA-MS studies.”*

Comment 2: The distinction between fresh-like and aged-like particles is important for the interpretation of particle aging. However, CN-containing particles may persist after atmospheric processing, whereas sulfate- and nitrate-rich particles may originate from source mixing or rapid secondary formation. Please clarify whether the “-CN” and “-sec” categories represent actual particle ages or operational compositional states.

Response: We appreciate this careful observation. We agree that the “-CN” and “-sec” categories do not provide a direct measurement of particle aging states. They are compositional classifications representing particles with relatively stronger primary combustion-related signatures and particles with stronger secondary inorganic signatures, respectively.

The interpretation of these classes as fresh-like and aged-like states is supported by several consistent observations. First, the “-CN” particles contain stronger cyanide-related and carbonaceous ion signals commonly associated with relatively fresh combustion emissions. Second, the corresponding “-sec” particles exhibit enhanced sulfate and nitrate signals. Third, within the same major particle group, “-sec” particles generally show larger vacuum aerodynamic diameters and more pronounced secondary components, which are consistent with atmospheric processing.

Nevertheless, these observations do not demonstrate that every “-sec” particle evolved directly from a corresponding “-CN” particle. Source mixing, transport, and rapid secondary formation may also contribute. We have therefore clarified that these categories represent composition-based fresh-like and aged-like states, rather than directly determined particle ages. The text has been updated accordingly:

Line 195~199: “Together with the systematic increase in D_{va} from “-CN” to “-sec”, these diagnostics support interpreting “-CN” and “-sec” as fresh-like and aged-like compositional states within each principal group. We therefore define four dominant fresh-like/aged-like pairs: BC-CN/BC-sec, BCOC-CN/BCOC-sec, BF-CN/BF-sec, and BFOC-CN/BFOC-sec.”

Line 425~426: “These comparisons represent population-level contrasts rather than trajectories of individual particles.”

Line 479~481: “Dotted and solid arrows indicate aging relationships during Stage I in normal periods (NPs) and additional Stage II processing in emission control periods (ECPs), respectively.”

Comment 3: The RH-dependent analysis is potentially important, but the selected RH thresholds appear to be related mainly to literature-reported deliquescence points of ammonium nitrate, ammonium sulfate, and their mixtures. Ambient particles contain complex mixtures of organics, black carbon, salts, and other components that may modify their phase behavior. Were particle phase states directly measured, and how should the RH regimes be physically interpreted?

Response: We thank the reviewer for this important comment. Particle phase state and aerosol liquid water content were not directly measured in this study. The RH regimes should therefore be interpreted as approximate physicochemical reference ranges rather than exact phase-transition boundaries applicable to every individual particle.

The selected ranges were informed jointly by the observed nonlinear changes in SNRs, particle size and particle number, as well as published deliquescence characteristics of major secondary inorganic components. In particular, ammonium nitrate typically deliquesces at approximately 61% RH, mixed ammonium sulfate ammonium nitrate systems may undergo mutual deliquescence around 69-75% RH, and ammonium sulfate deliquesces near 80% RH under representative atmospheric temperatures.

We agree that organic coatings, internally mixed salts, aerosol acidity, temperature, and deliquescence-efflorescence hysteresis may shift or broaden these transitions. Therefore, terms such as “solid”, “semi-solid” and “liquid” describe the likely dominant phase behavior of the aerosol population rather than directly observed states of individual particles. We have revised the manuscript accordingly and explicitly identified the lack of direct phase-state and aerosol-liquid-water measurements as a limitation. The RH classification is used primarily to organize the observed nonlinear responses and support process interpretation, rather than to define universal phase boundaries.

Comment 4: The manuscript uses a directed acyclic graph to interpret the relationship among gSNR, pSNR, and nSNR. However, causal discovery based on observational data relies on assumptions such as causal sufficiency, faithfulness, and the absence of important unmeasured confounders. Please clarify the interpretation and limitations of the inferred $\text{gSNR} \rightarrow \text{pSNR} \rightarrow \text{nSNR}$ pathway.

Response: We thank the reviewer for this important methodological clarification. We agree that a DAG derived from observational data cannot establish definitive causality. The analysis identifies directed conditional-dependence structures that are compatible with potential process relationships under assumptions including causal sufficiency and faithfulness.

The inferred $\text{gSNR} \rightarrow \text{pSNR} \rightarrow \text{nSNR}$ structure is physically consistent with a sequence linking gas-phase precursor composition, particle-level sulfate-nitrate signals,

and population-level mixing characteristics. However, ammonia availability, aerosol acidity, oxidant composition, reaction processes, and regional transport were not fully characterized and may influence the inferred relationships.

We have therefore revised the manuscript to describe the inferred structure as a process-consistent directed dependency and a hypothesized pathway rather than definitive evidence of causality. The revised text reads as follows:

Line 258~260: *“Causal networks, expressed as directed acyclic graphs (DAGs), characterize conditional dependence structures and identify directed relationships compatible with potential causal pathways among variables (Koller, 2009).”*

Line 273~276: *“The resulting DAGs identified direct and indirect dependency pathways linking SNR evolution to meteorological and chemical drivers. The statistical support and physical plausibility of these pathways provide a process-consistent structural basis for subsequent predictive modeling.”*

Comment 5: The manuscript suggests that air-quality models should consider RH- and particle-type-dependent sulfur-nitrogen partitioning. This implication is potentially valuable, but the observations were obtained at a single urban site during four relatively short episodes. Please clarify which modeling processes may be informed by the results and avoid implying that the identified RH ranges can be directly used as universal parameterizations.

Response: We appreciate this constructive suggestion. We agree that observations from a single urban site during four short episodes cannot support universal RH thresholds or directly transferable model parameterizations. The modeling relevance of this study is therefore process-oriented.

The observed RH- and particle-type-dependent relationships among gSNR, pSNR, and nSNR may inform the evaluation of gas–particle mass transfer, thermodynamic partitioning, aerosol phase behavior, and mixing-state representation. Under low-RH conditions, weaker cross-phase coupling and greater particle-type heterogeneity highlight potential limitations of assuming rapid equilibration and compositionally uniform particles. Under humid conditions, stronger coupling is consistent with enhanced mass transfer and a closer approach to population-mean equilibrium, although this interpretation requires model-based evaluation. The particle-type-resolved observations further provide qualitative constraints for assessing how BC-containing, OC-rich, and BC-free populations are represented in models.

We have revised the text to clarify that the RH intervals are operational ranges specific to the observed episodes rather than universal parameterizations. The revised text reads as follows:

Line 498~502: *“Guided by these physicochemical thresholds and the observed SNR evolution, we divide the observations into four characteristic RH regimes (Figure 5). Because particle phase state and ALW were not directly measured, these regimes are operational ranges rather than fixed phase-transition boundaries.”*

Reviewer #2:

Comment 1: The authors state in the Methods that both pSNR and κ_{eff} are relative indicators derived from semi-quantitative SPA-MS measurements and several simplifying assumptions. However, these parameters are subsequently used as quantitative evidence of particle aging, hygroscopicity, and broader atmospheric implications throughout the Results and Discussion. The manuscript would therefore benefit from a discussion of how the assumptions underlying the derivation of pSNR and κ_{eff} (e.g., relative ionization efficiency, matrix effects, and the adopted mixing rule) may influence their interpretation. In particular, it would be helpful to discuss the robustness of the reported trends to these assumptions. A simple sensitivity analysis of the κ_{eff} calculation would further strengthen confidence in the reported trends. This is especially important for the relatively small changes in κ_{eff} , where it remains unclear whether the observed differences exceed the uncertainty associated with the underlying assumptions.

Response: We thank the reviewer for this important methodological comment. We agree that pSNR and inferred κ_{eff} should not be interpreted as directly measured absolute chemical composition or hygroscopicity.

Because SPA-MS provides semi-quantitative ion signals, pSNR is treated as a relative spectral indicator rather than an absolute sulfate-to-nitrate molar or mass ratio. Consistent acquisition and processing procedures provide a common basis for evaluating relative variations, particularly within the same operational particle class. However, comparisons among compositionally distinct classes are interpreted cautiously because differences in ionization efficiency and matrix effects may influence their relative ion responses.

We also conducted a sensitivity analysis of inferred κ_{eff} by independently varying the hygroscopicity parameters assigned to ammonium sulfate and ammonium nitrate over literature-reported ranges. Their lower and upper values were combined into four alternative parameter sets, while the parameters of other components and the adopted mixing rule were held constant. We then recalculated κ_{eff} changes for each particle class, season, and aging stage (**Table S3; Figure S4**). Of the 16 comparisons, 12 retained positive κ_{eff} changes across all tested parameter combinations. The strongest and most robust increases occurred for BC particles during Stage I. The remaining four comparisons crossed zero, indicating that these relatively small changes were sensitive to the parameter assumptions and should be interpreted cautiously. These ranges represent sensitivity to the prescribed hygroscopicity values of ammonium sulfate and ammonium nitrate within the adopted mixing rule, rather than the full uncertainty in inferred κ_{eff} .

We have clarified these assumptions and limitations in the Methods, added the sensitivity-analysis parameters and results in Table S3 and Figure S4, and incorporated their interpretation into Section 3.3. The corresponding changes are provided below.

Lines 241-247: “**Table S3** lists the lower, mean, and upper κ_i values for ammonium sulfate and ammonium nitrate and the prescribed values for the other components. The mean values were used in the baseline calculation. Sensitivity was evaluated using four combinations of the lower and upper values for ammonium sulfate and ammonium nitrate (lower-lower, lower-upper, upper-lower, and upper-upper), while the component volume fractions, densities, κ_i values of the other components, and ZSR mixing rule were held constant.

The resulting κ_{eff} represents an hourly, particle-type-resolved estimate derived from aggregated SPA-MS spectra. SPA-MS ion signals are semi-quantitative and may be affected by species-dependent ionization efficiencies and matrix effects. The estimates also assume ammonium salts for sulfate and nitrate and volume-additive mixing under the ZSR rule. Accordingly, κ_{eff} is interpreted as a relative indicator for comparisons among particle classes, periods, and aging states, rather than as a direct hygroscopicity measurement.”

Lines 426-460: “To evaluate the robustness of inferred κ_{eff} , calculations were repeated using alternative hygroscopicity values for ammonium sulfate and ammonium nitrate (**Table S3**; **Figure S4**). The resulting ranges represent parameter sensitivity within the adopted mixing rule rather than the full uncertainty in κ_{eff} . Because relative ionization efficiencies and matrix effects can affect SPA-MS signals, pSNR changes are interpreted as relative ion-signal shifts rather than absolute composition changes.

For OC-rich fresh particles (BCOC-CN and BFOC-CN), Stage I aged-like populations had an approximately 5% lower mean D_{va} and an 83% higher pSNR than their fresh-like counterparts, whereas κ_{eff} changes were generally small or parameter dependent. No consistent κ_{eff} increase or decrease was obtained for BCOF in either season or BFOF in winter; while the summer BFOF response remained positive (2.5% to 17.0%). This pattern may reflect compaction and the formation of an organic-rich shell that retains sulfate while limiting additional water uptake (Mikhailov et al., 2009; Riemer et al., 2019). During Stage II, stronger oxidation is associated with an increase in D_{va} of about 25% and a further rise in pSNR of about 80%, again with minimal change in κ_{eff} , consistent with continued sulfate accumulation and coating growth on a compact and relatively hydrophobic matrix.

For BC particles with weaker organic signatures, the transition from BC-CN to BC-sec exhibits the largest κ_{eff} increase (~31%). This response remained positive across all tested parameter combinations, ranging from 16.8% to 27.5% in winter and from 28.5% to 47.1% in summer (**Figure S4**). Together with substantial size growth (~24%), and a modestly rises pSNR, this pattern indicating dominant inorganic uptake under ordinary conditions. In Stage II, κ_{eff} changes little, but pSNR increases markedly (~105%) and D_{va} expands to ~700 nm (~36%), whereas the κ_{eff} response remained small across the sensitivity tests (1.0%-4.6%). This shift indicates enhanced sulfate-rich coating growth

as gSNR and oxidant levels rise.

For BC-free particles (BF-CN to BF-sec), pSNR remained relatively low and changed only slightly. Stage I κ_{eff} changes remained positive but small in both winter (1.3%-5.6%) and summer (1.3%-7.3%). The Stage II κ_{eff} response was also modest in winter (0.9%-7.3%) but stronger in summer (11.6%-18.2%). Together with the approximately 22% increase in D_{va} , these changes are consistent with increased secondary inorganic contributions, particularly during summer ECPs.”

Table S1. Values of hygroscopic parameter κ and dry bulk density ρ .

Species	κ_{low}	κ_{mean}	κ_{up}	ρ (g cm ⁻³)	Reference
(NH ₄) ₂ SO ₄	0.33	0.53	0.72	1.76	(Petters and Kreidenweis, 2007)
NH ₄ NO ₃	0.577	0.67	0.753	1.72	(Petters and Kreidenweis, 2007)
KCl	-	0.99	-	1.99	(Carrico et al., 2010)
OC	-	0.03	-	1.00	(Saxena and Hildemann, 1996)
BC	-	0	-	1.80	(Bond and Bergstrom, 2006)

Densities are taken from Lide (1995).

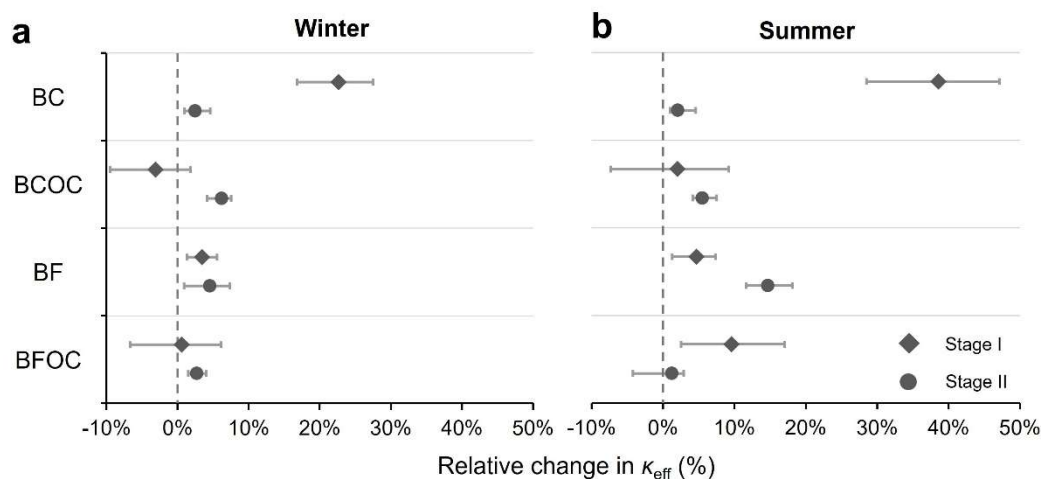


Figure S1. Sensitivity analysis of stage-specific relative changes in inferred effective hygroscopicity parameter (κ_{eff}) for four particle classes in winter (a) and summer (b). Diamonds and circles represent the baseline estimates for Stages I and II, respectively. Horizontal bars show the ranges obtained from four combinations of the lower and upper hygroscopicity values for ammonium sulfate and ammonium nitrate listed in Table S3. The dashed line denotes zero change; ranges crossing zero indicate that the

direction of change was not consistent across the tested parameter combinations.

Comment 2: Section 2.1: Please specify the measurement size range of the SPA-MS

Response: Thank you for this suggestion. We have now specified the measurement size range of the SPA-MS in Section 2.1. The instrument primarily detected individual particles with vacuum aerodynamic diameters (D_{va}) ranging from 0.2 to 2.0 μm .

Lines 117-121: *“Single-particle chemical composition, vacuum aerodynamic diameter (D_{va}), and mixing state were measured in real time using a single-particle aerosol mass spectrometer (SPA-MS; Hexin Analytical Instrument Co., Ltd., China). The instrument primarily detected particles with D_{va} ranging from 0.2 to 2.0 μm , as detailed previously (Dai et al., 2024). ”*

Comment 3: Line 56: should be “mixing-state diversity”?

Response: Thank you for pointing this out. We have revised “mixing state diversity” to “mixing-state diversity”.

Lines 54-57: *“However, SNR is still often interpreted using bulk or time-averaged measurements (Snider et al., 2016; Sun et al., 2016; Xu et al., 2019), which may inherently obscure particle-type heterogeneity and mixing-state diversity that matter for multiphase processing.”*

Comment 4: Line 352-353: there appears to be a grammatical issue in the phrase “... photo-induced the formation of reactive oxygen species (ROS)”

Response: Thank you for this suggestion. We have corrected the grammatical issue and the text is updated as follows:

Lines 366-370: *“This behavior is consistent with the hypothesis of enhanced sulfate formation on BC-containing particles during photochemically active periods, potentially linked to BC-mediated HONO/NO₂ release (Liang et al., 2021; Ye et al., 2017) and photo-induced formation of reactive oxygen species (ROS) that accelerate the conversion of SO₂ to sulfate (Zhang et al., 2022; Zhu et al., 2020)”*

Comment 5: Section 3.3: The opening summary (Lines 412–416) presents a generalized aging framework, whereas the subsequent discussion highlights distinct aging behaviors among OC-rich, BC-containing, and BC-free particles. Although the authors acknowledge that the proposed aging pathways are strongly composition-dependent (Lines 416–417), this distinction could be reflected more consistently throughout the discussion.

Response: Thank you for this helpful comment. We agree that the previous opening summary could be interpreted as implying a uniform aging pattern across particle classes. Because the subsequent discussion already distinguishes the responses of OC-rich, BC-containing, and BC-free particles, we have made targeted revisions to the opening summary and concluding synthesis of Section 3.3 to reflect these composition-dependent differences more consistently. Stage I and Stage II are now described as a common conceptual framework for population-level comparisons, while the direction and magnitude of the inferred changes are explicitly distinguished among particle classes. The text is updated as follows:

Lines 420-431: *“To characterize particle-type-dependent aging, we jointly examined changes in inferred κ_{eff} , pSNR, and D_{va} and developed a conceptual framework in the κ_{eff} -pSNR space (**Figure 4**). As defined in **Section 2.3**, each fresh-like subtype was paired with its dominant aged-like counterpart. Stage I compares fresh-like and aged-like populations during NPs, whereas Stage II compares aged-like populations between NPs and ECPs. These comparisons represent population-level contrasts rather than trajectories of individual particles. To evaluate the robustness of inferred κ_{eff} , calculations were repeated using alternative hygroscopicity values for ammonium sulfate and ammonium nitrate (**Table S3**; **Figure S4**). The resulting ranges represent parameter sensitivity within the adopted mixing rule rather than the full uncertainty in κ_{eff} . Because relative ionization efficiencies and matrix effects can affect SPA-MS signals, pSNR changes are interpreted as relative ion-signal shifts rather than absolute composition changes.”*

Lines 462-470: *“Overall, the coupling between inferred κ_{eff} and pSNR strengthened under higher gSNR and stronger oxidative conditions, although the response remained particle-type dependent. BC-containing particles showed pronounced sulfate enrichment, consistent with the accumulation of secondary sulfate coatings on soot particles. OC-rich particles also exhibited strong pSNR enhancement but comparatively limited changes in inferred hygroscopicity, whereas BC-free particles showed weaker compositional adjustment and more gradual particle growth. Thus, the two-stage framework captures distinct composition-dependent responses rather than a uniform aging pathway, reflecting differences in core type, coating chemistry, and mixing state.”*

Comment 6: The interpretation of Figure 4 would benefit from further clarification. As the proposed Stage I and Stage II pathways are inferred from population-level comparisons under different atmospheric conditions rather than direct observations of continuous particle evolution, I suggest explicitly describing Figure 4 as a conceptual aging framework in both the main text and the figure caption. It would also be helpful to clarify that the arrows represent inferred relationships between particle populations, rather than the temporal evolution of the same particles or air masses.

Response: We thank the reviewer for this helpful suggestion. We have revised the main text and figure caption to describe Figure 4 explicitly as a conceptual aging framework. We also clarify that the arrows indicate inferred relationships between particle populations based on population-level comparisons, rather than directly observed particle evolution.

Lines 420-426: “To characterize particle-type-dependent aging, we jointly examined changes in inferred k_{eff} , pSNR, and D_{va} and developed a conceptual framework in the k_{eff} -pSNR space (**Figure 4**). As defined in **Section 2.3**, each fresh-like subtype was paired with its dominant aged-like counterpart. Stage I compares fresh-like and aged-like populations during NPs, whereas Stage II compares aged-like populations between NPs and ECPs. These comparisons represent population-level contrasts rather than trajectories of individual particles.”

Lines 471-481: “

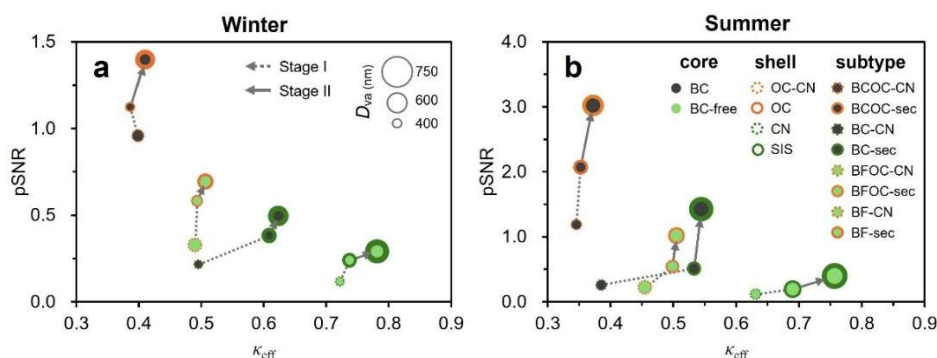


Figure 4. Conceptual framework for the co-evolution of particle-phase sulfur-to-nitrogen ratio (pSNR) and inferred hygroscopicity (k_{eff}) among particle classes during winter (a) and summer (b). Particles are represented by core-shell schematics. The inner circle indicates BC-containing (dark gray) or BC-free (light green) particles, and the outer ring indicates coatings dominated by organic carbon (OC, orange) or secondary inorganic species (SIS, green). Dashed and solid rings denote fresh-like and aged-like populations, respectively. Marker size scales with vacuum aerodynamic diameter (D_{va}). Shell thickness estimates from the D_{va} of aged-like and fresh-like particles. Dotted and solid arrows indicate aging relationships during Stage I in normal periods (NPs) and additional Stage II processing in emission control periods (ECPs), respectively.”

Comment 7: *The manuscript occasionally extrapolates the results to cloud activation, visibility, and climate impacts (e.g., Lines 444–446) in the Results and Discussions. Since these impacts are not directly measured or evaluated in this study, I suggest moving this discussion to the implications section rather than the Results and Discussion. In addition, please include references to support the discussion in Lines 444–446.*

Response: We thank the reviewer for this helpful suggestion. We have moved the discussion of potential cloud, visibility, and climate-related effects from Section 3.3 to “Conclusions and atmospheric implications” and added supporting references. We have also clarified that these effects were not directly evaluated in this study and require independent validation. The text is updated as follows:

Lines 674-679: *“Associated changes in particle size, hygroscopicity, and mixing state could influence cloud condensation nuclei (CCN) activation, humidity-dependent light scattering, and aerosol radiative effects (Matsui et al., 2018; Rosenfeld et al., 2014; Titos et al., 2021; Xu et al., 2021). The observed relationships provide a physical basis for investigating these atmospheric consequences across particle types and humidity conditions under evolving emission controls.”*

- Matsui, H., Hamilton, D.S., Mahowald, N.M., 2018. Black carbon radiative effects highly sensitive to emitted particle size when resolving mixing-state diversity. *Nat Commun* 9, 3446. <https://doi.org/10.1038/s41467-018-05635-1>
- Rosenfeld, D., Andreae, M.O., Asmi, A., Chin, M., de Leeuw, G., Donovan, D.P., Kahn, R., Kinne, S., Kivekäs, N., Kulmala, M., Lau, W., Schmidt, K.S., Suni, T., Wagner, T., Wild, M., Quaas, J., 2014. Global observations of aerosol-cloud-precipitation-climate interactions. *Reviews of Geophysics* 52, 750–808. <https://doi.org/10.1002/2013RG000441>
- Titos, G., Burgos, M.A., Zieger, P., Alados-Arboledas, L., Baltensperger, U., Jefferson, A., Sherman, J., Weingartner, E., Henzing, B., Luoma, K., O’Dowd, C., Wiedensohler, A., Andrews, E., 2021. A global study of hygroscopicity-driven light-scattering enhancement in the context of other in situ aerosol optical properties. *Atmospheric Chemistry and Physics* 21, 13031–13050. <https://doi.org/10.5194/acp-21-13031-2021>
- Xu, W., Fossum, K.N., Ovadnevaite, J., Lin, C., Huang, R.-J., O’Dowd, C., Ceburnis, D., 2021. The impact of aerosol size-dependent hygroscopicity and mixing state on the cloud condensation nuclei potential over the North-East Atlantic. *Atmospheric Chemistry and Physics* 21, 8655–8675. <https://doi.org/10.5194/acp-21-8655-2021>