A point-by-point response to reviewers

Dear Editor,

We are very pleased to submit a revised manuscript entitled with "The evolution of aerosols mixing state derived from a field campaign in Beijing: implications to the particles aging time scale in urban atmosphere" for possible publication in journal of Atmospheric Chemistry and Physics.

We'd like to thank you for your efforts and time on handling the paper. We also thank the two reviewers for the further comments, which we have addressed in the revision (a point-by-point response to the reviewer as follows).

Yours sincerely,

Fang Zhang

On behalf of all authors

Comments from the reviewer 1:

I appreciate the authors' responses to my comments and the substantial revisions made to the paper, which have significantly improved its quality. I believe it now largely meets the requirements for publication in ACP. The method proposed by the authors, using the proportions of MH and LH to distinguish between small particle growth and primary emissions, has a certain degree of rationality. However, it also involves notable uncertainties that may affect the conclusions of the paper. I suggest that the authors add some discussion on the uncertainties of this classification criterion and its impact on the conclusions.

Re: We appreciate your comments. In the revised version, we have included the statements regarding the uncertainties of the method used to distinguish the impacts of smaller particle aging and primary emissions on the internal mixing fraction of larger particles. See **Lines 149-155**, as follows:

"It is worth noting that these results may involve certain uncertainties, as the influence of other sources was not considered. For example, the more hygroscopic sulfate particles could also be directly emitted from primary sources in urban atmosphere (Dai et al., 2019); in addition, the aerosols are assumed rarely affected by the sea salts. Consequently, the contribution of smaller particle aging and growth to the internally-mixed fraction of larger particles may have been overestimated in this study. More research works are warranted to further evaluate and quantify such

uncertainty in future."

Comments from the reviewer 2:

I feel that the manuscript is greatly improved from its original version, and I appreciate the authors' efforts. However, I note one comment from the other reviewer and one of my own comments from the first round of review that I do not feel have yet been sufficiently addressed. Aside from these, I have only technical corrections to be addressed before publication.

Previously, reviewer # 1 commented that:

"80 and 110 nm aerosols should continue aging and form 150 and 200 nm aerosols. The aging of this group of aerosols should be more advanced—why is the influence of this aged aerosol group on the internal mixing fraction not reflected?"

I don't feel that the authors' addition to the manuscript (lines 210-213) addresses what the reviewer was trying to highlight. Perhaps they understood the reviewer differently than I did. If the same processes that move the particles from the other three mixing-state categories into the MH internally-mixed category also cause the growth of 80 and 110 nm aerosols into the 150 and 200 nm size ranges, one would expect that these particles would contribute to the MH internally-mixed category for the 150 and 200 nm size ranges, and not the 80 and 110 nm size ranges. So if these were the only important processes and all else was equal between the different size ranges, we would expect the MH internally-mixed fraction to be lower for the 80 and 110 nm particles than for the 150 and 200 nm particles. I therefore read the authors current lines 210-213 as being incongruous. Can the authors explain the apparent discrepancy?

Re: In our initial response, we may have misinterpreted the comments raised by Reviewer #1. As the reviewer pointed out, the 80 nm and 110 nm aerosols may continue to age and grow into 150 nm and 200 nm particles. However, the fraction of internally-mixed particles at 150 nm and 200 nm is lower than that of 80 nm and 110 nm particles. In the revised manuscript, we have clarified this point in **Lines 216-226**, as follows:

"In addition, the larger particles (i.e., 150 nm and 200 nm) are closely associated with the growth of smaller particles and undergo a prolonged aging process. However, the fraction of MH internally-mixed particles at 150 nm and 200 nm is lower than that of smaller particles (e.g., 80 nm and 110 nm). This is mainly due to that a considerable amount of accumulated particles observed during the campaign were emitted from primary sources, which could be externally-mixed with most of the aged more hygroscopic 150 and 200 nm aerosol particles. As shown in Fig. 3, the higher proportion of externally-mixed state was obtained for particles with diameters of 150 nm and 200

nm. Furthermore, the more active Brownian coagulation of smaller particles enhances chemical homogenization (Park et al., 2002), resulting in a much higher fraction of MH internally-mixed particles at 80 and 110 nm."

I previously noted the problem of determining Lagrangian properties from fixed-location measurements. I don't yet feel that the authors have adequately either addressed or acknowledged this issue. If the particles required 5-10 hours to age from the externally-mixed category into the MH internally-mixed category, can the authors assure the reader that the source emissions at the location of the air parcel 5-10 hours prior to measurement were similar to source emissions in Beijing? The back trajectories in Fig. S1 would help with this if the time length was indicated, as they would allow the reader an approximation of the location of the air parcels 5-10 hours before measurement. I thank the authors for sharing Fig. S3, but instead of reassuring the reader that MH internally-mixed particles are indeed externally-mixed particles that have aged, the figure could be interpreted as suggesting that for 40 nm and 80 nm particles, the externally-mixed and LH internally-mixed particles are coming from local sources and to the east, while MH internally-mixed particles are coming from a different source to the west.

Re: We appreciate the valuable comments of the reviewer.

(1) We fully acknowledge the challenges in inferring the historical behavior of air parcels from fixed-location measurements. According to the reviewer's comment, we have updated Fig. S1 (Fig. R1) in the revised version to clearly indicate the location of air parcels 5–10 hours before measurement, as follows:

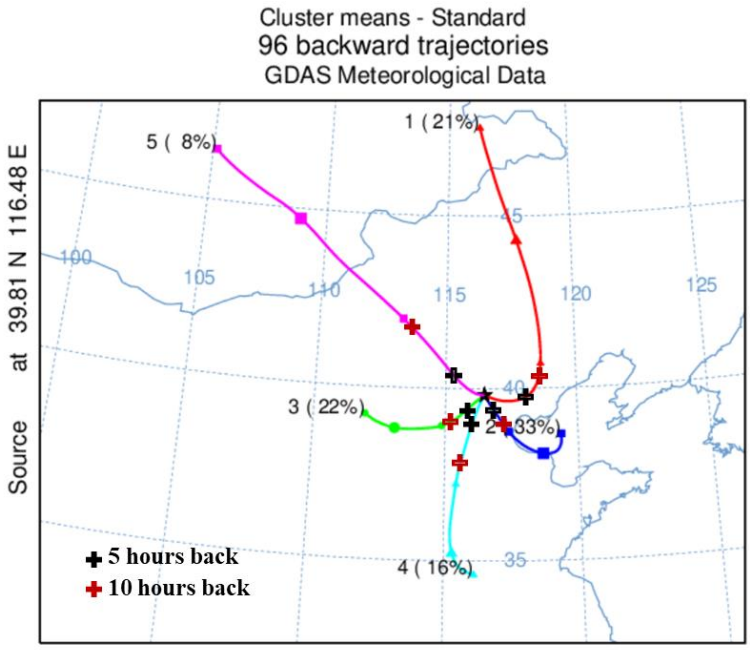

Figure R1. The 48-hour mean air mass backward trajectories for five clusters arriving at the sampling site in Beijing. The black and red crosses indicate the locations of the air parcels 5 and 10 hours prior to the measurement site, respectively.

(2) As the reviewer pointed out, for 40 nm and 80 nm particles, the hydrophobic particles are primarily from local sources, whereas the hygroscopic particles originate from a different source to the west (Fig. S3 or R2). However, the particles exhibit weaker hygroscopicity at lower wind speeds, especially when the wind speed is lower than 4 m s^{-1}. Based on the statistical results during the observation period (Fig. R3), it showed that wind speeds below 4 m s^{-1} accounted for 88% of all cases, indicating that the contribution of regional atmospheric transport sources to MH internally-mixed small particles was minimal. Most of MH internally-mixed particles were from the aging of externally-mixed particles.

To further clarify the origin of particles, we have updated Fig. S1 (Fig. R1) to include time markers, showing that the location of air parcels 5–10 hours prior to measurement was close to the sampling site in Beijing. The air parcels from the northwest (cluster 5) with long-distance transport account for the least fraction (only 8%) of the air trajectories from all originating directions during the campaign. This implies that most MH internally-mixed particles were formed through the aging of locally emitted externally-mixed particles.

We have included more statements to address this issue in the revised text, see **Lines 309-314**, or as follows:

"In addition, the location of air parcels 5–10 hours prior to measurement was close to the sampling site in Beijing, showing that the air parcels from the northwest (cluster 5) with long-distance transport account for the least fraction (only 8%) of the air trajectories from all originating directions during the campaign (Fig. S1). This implies that most MH internally-mixed particles were formed through the aging of locally emitted externally-mixed particles."

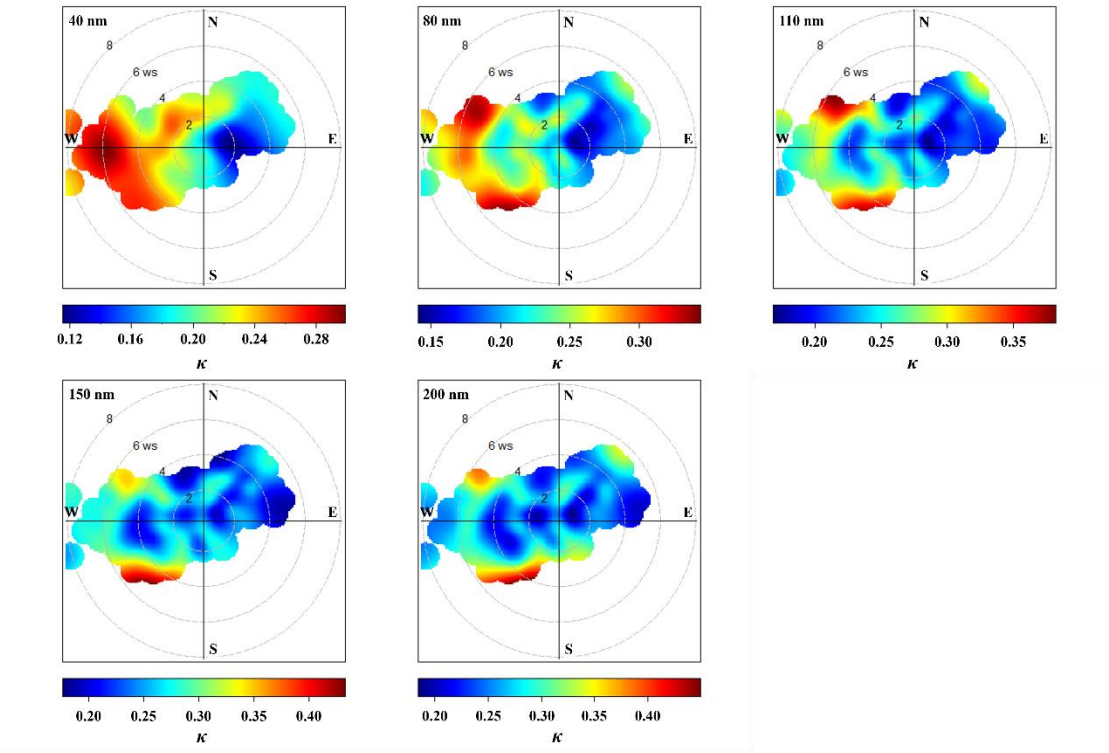

Figure R2. Bivariate polar plot of the κ of particles at the five sizes during the campaign.

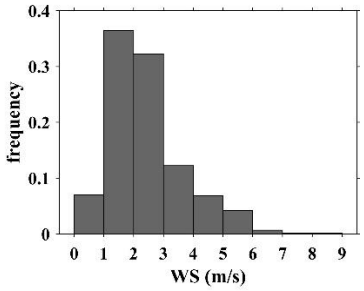

Figure R3. The frequency distribution histogram of wind speed during the campaign in Beijing.

Technical corrections:

p2, line 47: with -> in an

Re: Revised.

p4: line 72: “with the significance of statistics” do you mean statistically significant?

Re: This sentence has been revised as “However, based on TEM technique, a large number of aerosol samples are required so as to make the results statistically significant, which means a high cost both on labors and materials”.

p4, line 81: are with -> have

Re: Revised.

p6, line 130: “refers to that the” please rephrase. Also, you should state the name of Mixing Type 2 here.

Re: The sentence has been revised as “Mixing type 2 (Externally-mixed) is characterized by bimodal distributions in the κ-PDF for both LH and more hygroscopic (MH, $\kappa \geq 0.1$) modes, with less than 30% difference in the fraction of the two modes”.

p6, line 134: of lager -> larger. Also, was it only normally the case of >= 70% in the MH mode, or was it always the case, by definition, that >= 70% of the particles were in the MH mode?

Re: The sentence has been revised as “The κ-PDF of type 4, defined as the MH internally-mixed type, was dominated by the MH mode with a fraction larger than 70%”.

p11, lines 225-226: Based on Fig. 4, this sentence appears to be untrue. κ increases, but for 40 and 80 nm particles, σ is similar (and certainly within the error bars shown) for mixing type 2 (externally-mixed) and mixing type 4 (MH internally-mixed).

Re: This has been revised as “At 40 and 80 nm sizes, the transition from externally-mixed to MH internally-mixed particles results in a marked increase in κ, accompanied by a slight rise in σ”.

p11, line 228: I am sure that the authors must intend to refer only to the MH internal mixing category and not the LH internal mixing category here.

Re: Revised.

p12, lines 244-26: There does appear to be an increase in the externally-mixed state during the evening rush hour compared to the afternoon just before it. Perhaps you meant the LH internally-mixed state?

Re: The reviewer is right, and we have revised the sentence as “Unlike the 40 nm particles, there is no apparent increase of LH internally-mixed state for the particles with sizes of 80, 110, 150, and 200 nm in the rush hours or cooking times”.

p13, line 260: “corresponding period” would seem to refer to the night time which was just discussed, but I assume by “corresponding period” you mean the afternoon, when the LH internally-mixed mode peaks?

Re: The sentence has been revised as “In the early afternoon, the externally-mixed and transitional externally-mixed particles, which represent the intermediate state of the aging process in which particles transition from LH to MH mode, showed a decrease to around 10%, while the proportion

of particles with MH internally-mixed state increased up to 80%".

p13, line 265: changed -> to change

Re: Revised.

p14, line 276: "especially for particles larger than 40 nm" I don't understand why the authors characterize it this way. The difference in the fraction in the MH internally-mixed state is greatest for the 40 nm particles, and I would say that this sentence is not true for the 200 nm particles, where the fraction only achieves a value of ~70%.

Re: The sentence has been revised as "On clear days, the fraction of MH internally-mixed particles increases significantly from ~10-40% before 9:00 to ~70-100% during 12:00–15:00".

p14, line 279: "While" followed by a comma is not an appropriate way to begin a sentence in English. Do the authors mean "However," or "At the same time," or "In addition,"?

Re: The sentence has been revised as "In addition, the fraction of MH internally-mixed particles for 40 nm is noticeably higher on clear days (80%), which is approximately 40% greater than that on cloudy days, indicating that photochemical processes can make particles more internally-mixed and aged (Liu et al., 2021a)". And according to the comment, we have carefully checked and revised the usage of "while" in the manuscript.

p14, lines 284-285: If I interpret "large sizes" to be 150 nm or 200 nm, mean κ decreases from 9:00 through to 17:00 according to Fig. 5.

Re: This sentence has been removed in the revised version.

p20, line 412: the large difference -> there is a large difference

Re: Revised.

Figure S1: Please indicate in the caption the time length of these back-trajectories.

Re: Revised.