The evolution of aerosols mixing state derived from a field campaign in Beijing: implications to the particles aging time scale in urban atmosphere

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Abstract

The mixing states and aging time scale of aerosol particles play a vital role in evaluating their climate effects. Here, by using the field measurement at a site of the urban Beijing, we have identified four different real-time mixing patterns of size-resolved particles, which are defined as ~~using the field measurement by a humidity tandem differential mobility analyzer (H-TDMA) in the urban Beijing. The show that the~~ less hygroscopic (LH) internally-mixed, externally-mixed, transitional externally-mixed and more hygroscopic (MH) internally-mixed particles, with atmospheric fraction of ~~with external, transitional and internal mixing state during the campaign account for~~ ~~20-48%, 17-24% and 27-56%~~ 0-10%, 20-46%, 17-24% and 27-56% respectively. ~~and~~ ~~And t~~The fraction ~~highly~~ depends on particles size, with the maximum fraction of MH internally-mixed particles ~~peaking~~ at 80 and 110 nm~~(> 50%)~~, ~~among the five sizes~~ and the minimum fraction of LH internally-mixed particles across all

sizes, implying rapid mixing and aging of ambient particles during the observational period.due to enhanced aging in intermediate particles The distinct relationshipthe probability density function of κ () between particles indicates The diurnal variations of the mixing states of particles in all sizes investigated (40, 80, 110, 150 and 200 nm) present an apparent aging process from externally-mixed to MH internally- -mixing stateed, which typically spanning spans a duration of approximately 5–8 10 hours from 8:00–10:00 to 15:00–17:00, revealing the mixing (aging) timescale of aerosols in polluted urban atmosphere. Additionally, our results suggest that those fine aerosol particles experience aging through both the photochemical process and non-photochemical growth during the campaign. photochemical processes promote significant aging of fine aerosol particles in the polluted atmosphere of urban Beijing. Additionally, the results illustrate that high ambient temperature during daytime or more humid atmosphere accelerates the aging process of aerosol particles, leading to the particles from external to internal mixing on both clear and cloudy days. Also, with the evolution of particulate pollution, the aerosol particles become more internally mixed. Our result implies that those fine aerosol particles experience aging through both the photochemical process and aqueous growth in the polluted atmosphere of urban Beijing. Furthermore, through a comprehensive review of the mixing/aging timescale of particles adopted in current models and derived from observations, we show the great discrepancy between observations and models, highlighting the importance to parameterize their aging time scale based on more field campaigns.

1 Introduction

The mixing state of atmospheric aerosol particles can affect the hygroscopicity and the ability to serve as cloud condensation nuclei (CCN), and thus the air quality and climate (Müller et al., 2017; Xu et al., 2021; Yao et al., 2022; Ge et al., 2024). It has been shown that

the aerosol mixing state is closely related to the hygroscopicity (Chen et al., 2022; Fan et al., 2020). Ren et al. (2018) predicted the concentration of CCN using five different mixing state schemes and found that the influence of aerosol mixing state on its activation characteristics ranged from –34% to +16%. Neglecting particle mixing structure can also lead to significant overestimation of the aerosol absorption efficiency (Yao et al., 2022). Therefore, it is important to account for the information of mixing state of ambient particles in climate models so as to reduce the uncertainty in evaluating their environmental and climate effects.

The mixing states of ambient particles are complex. Particles in areas affected by primary emissions are mainly with external mixing state (i.e., the chemical components of particles exist independently), while aerosols in relatively clean areas are mainly transported from elsewhere and have a higher degree of internal mixing (Swietlicki et al., 2008; Enroth et al., 2018; Chen et al., 2022). Internal mixing typically includes uniform composition or core–shell structures (Jacobson et al., 2001). The former refers to the same proportion of species in any part of the aerosol component, while the latter is defined as the mixing state formed by certain chemical components coating or condensing on the surface of other components during the aging process. Also, the mixing state of aerosol particles is variable. Freshly emitted particles undergo various processes, including photochemical and aqueous-phase processes, as well as physical processes such as coagulation and condensation, leading to an increase in their degree of internal mixing. This gradual transition from external to internal mixing characterizes the aging process of particles. The aging timescale varies greatly between clean and polluted areas (Peng et al., 2016; Chen et al., 2017; Ghosh et al., 2021). However, the timescale of aging process of particles was commonly fixed in many models and did not depend on environmental conditions (Chen et al., 2017; Ghosh et al., 2021),

which may introduce great uncertainty in the prediction of regional aerosol concentration and the evaluation of aerosol climate effects (Ghosh et al., 2021). Therefore, capturing the temporal scales of the evolution of the aerosol mixing state based on field campaigns is crucial for accurately parameterizing the aging timescale of aerosol particles in models, thereby enhancing the precision of simulations pertaining to the environmental and climatic impacts of aerosols.

At present, some studies have characterized the mixing state and aging process of black carbon (BC) aerosols using different instruments. Transmission electron microscopy (TEM) has been used to determine the mixing state of individual particles in China (Li et al., 2016; Zhang et al., 2023). However, based on TEM technique, a large number of aerosol samples are required so as to make the results with the significance of statistics, which means a high cost both on labors and materials. The most important issue is that the mixing state of particles may change during collection and transportation. Recently, aerosol time-of-flight mass spectrometry (ATOFMAS) and soot-particle aerosol mass spectrometry (SP-AMS) have been used to measure the mixing state of BC and coated aerosol species in real time (Liu et al., 2019; Xie et al., 2020). Overall, previous studies focused more on the mixing state of BC of single-particles (Saha et al., 2018; Xie et al., 2020; Chen et al., 2020). While, the mixing state of particles across a population in ambient atmosphere is more complex (Riemer et al., 2019). According to Winkler's definition, the "internal mixing" means when all particles within the bulk aerosol populations are with the same compositions. While, the "external mixing" means when all particles consist of pure species and have distinct compositions (Winkler et al., 1973; Riemer et al., 2019). Note that in Riemer et al. (2019), the definition

refers to the bulk not the sized-resolved mixing state of aerosol particles. In this study, the size resolved mixing state of aerosol particles has been identified according to the patterns of the probability density function of hygroscopic growth factor/hygroscopic parameter (κ) (Gf-PDF; κ-PDF) measured using a humidity tandem differential mobility analyzer (H-TDMA) (Hong et al., 2018; Shi et al., 2022; Spitieri et al., 2023). For example, the internally-mixed aerosol populations with diameter of 40 nm are characterized by the single hygroscopic mode of Gf-PDF/κ-PDF, while the externally-mixed particles have bi- or trimodal distributions of Gf-PDF/κ-PDF. ~~thateach individual particleof the aerosol population sFor example, aerosols containing two or more components may also exhibit external mixing, as evidenced by the bi- or trimodal distributions of the probability density function of hygroscopic growth factor/hygroscopic parameter (κ) (Gf-PDF; κ-PDF) measured using a humidity tandem differential mobility analyzer (H-TDMA) (Fan et al., 2020; Chen et al., 2022; Zhang S. et al., 2023). The mixing state of particles has been retrieved according to the patterns of Gf-PDF/κ-PDF (Hong et al., 2018; Shi et al., 2022; Spitieri et al., 2023).~~ TaHowever, most studies based on the H-TDMA measurements only made qualitative descriptions of the particle mixing state when explaining the variations in the aerosol hygroscopicity (Wang et al., 2019; Chen et al., 2022; Shi et al., 2022).

In this study, with the aim of obtaining insights into the mixing state and mixing (aging) time scale of ambient particles in urban area, we have identified four different types of size-resolved particles mixing states, and characterized their real-time variations using the field measured hygroscopic growth factor by the H-TDMA in urban Beijing. ~~The dependence of mixing state of particles on temperature (T), relative humidity (RH) and the pollution levels~~

~~was investigated.~~ The evolution of mixing state of particles with specific sizes was ~~also~~ explored to imply the mixing (aging) timescale of their aging from the diurnal variations during clear and cloudy days. Finally, we compared the mixing/aging timescale of aerosol particles with that adopted in current models and other field observations reported in previous literatures.

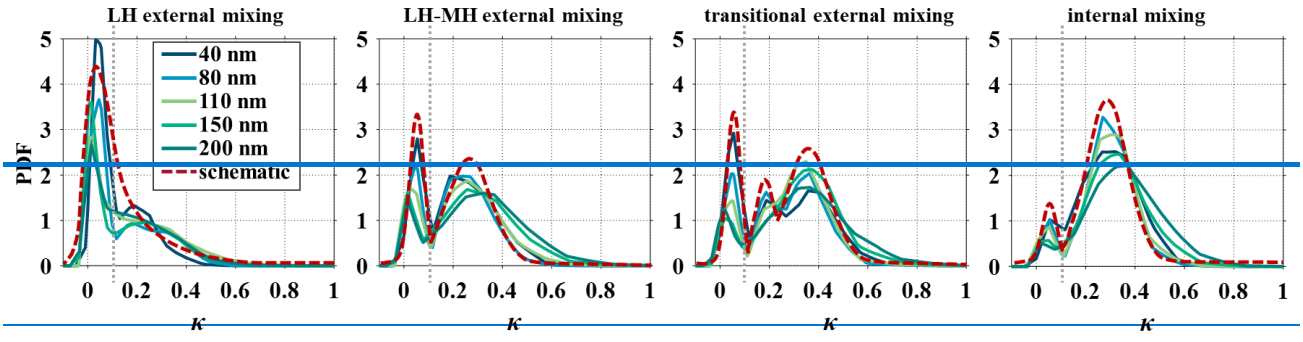
2 Methods

The campaign was conducted at the meteorological tower branch of the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences to measure the physical and chemical properties of particles and the meteorological conditions from 19 May to 18 June 2017 in Beijing. The instruments used in this study were deployed in a container at ground (the sampling inlet is located at ~8 m on the meteorological tower). The hygroscopicity of aerosols with different dry sizes (40, 80, 110, 150 and 200 nm) and particle number distribution in the size range of 10–550 nm was measured using a H-TDMA and a Scanning Mobility Particle Sizer (SMPS), respectively. The mass concentration of the non-refractory chemical compositions in particulate matter with diameter < 1 μm (PM_1) was measured by an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) (Xu et al., 2019), and the BC was measured by a 7-wavelength aethalometer (AE33, Magee Scientific Corp). More details about the sites, instruments and calibrations can be found in previous literatures (Zhang et al., 2017; Wang et al., 2019; Fan et al., 2020; Chen et al., 2022). Since the campaign site was located at the urban area of Beijing, where the atmospheric fine aerosols are more frequently affected by local traffic and cooking sources (Sun et al., 2015). In addition, during the observation period of summertime, the site was predominately affected by the warm and humid southeastern air parcels (Figure S1); while the dust events normally originate from northwestern regions occurring in springtime (Li et al., 2020) and

typically with particle sizes in coarse mode (Wang et al., 2023). Therefore, the contribution from dust aerosols could be negligible in this study. ~~The campaign was conducted to measure the Gf of particles with different dry sizes (40, 80, 110, 150 and 200 nm) using a H-TDMA from 19 May to 18 June 2017 in Beijing. The instrument used in this study has been described previously (Zhang et al., 2017; Wang et al., 2019; Fan et al., 2020; Chen et al., 2022).~~

Here, we mainly describe the interpretation criteria for the mixing state of particles. The Gf-PDF was obtained by $TDMA_{inv}$ algorithm in this study (Gysel et al., 2009). Then, the κ-PDF of size-resolved particles was retrieved according to the κ-Köhler theory (Petters and Kreidenweis, 2007). Subsequently, we accurately defined four mixing states based on the κ-PDF patterns and the number of peaks in κ-PDF (Figure 1, Figure ~~S1~~S2). The κ-PDF of type 1 exhibits bimodal distributions with a much higher proportion (> 70%) of hydrophobic mode or less hygroscopic mode (LH; the peak of κ-PDF occurs at $\kappa < 0.1$), was thus defined as LH internally-mixed state (type 1). Mixing type 2 refers to that the κ-PDF exhibits bimodal distributions in both LH and more hygroscopic (MH, $\kappa \geq 0.1$) modes, with the difference of less than 30% between the fraction of the two modes. The κ-PDF pattern with trimodal distributions was named as transitional externally-mixed state (type 3). The κ-PDF of type 4 was dominated by MH mode, normally with a fraction of lager than 70%, was defined as MH internally-mixed type. ~~Given that the freshly emitted hydrophobic particles showed an external mixing state (Li et al., 2016), the κ-PDF, that exhibited only one nearly hydrophobic mode or less hygroscopic (LH; the peak of κ-PDF occurs at $\kappa < 0.1$) mode, was defined as LH external mixing state (type 1). Mixing type 2 indicates that the maximum peak of κ-PDF occurs at LH mode or more hygroscopic (MH, the peak of κ-PDF occurs at $\kappa \geq 0.1$) mode, and the bimodal distributions of the LH and MH modes are present in κ-PDF. Moreover, the κ-PDF pattern with trimodal distributions calledwas named transitional external mixing state~~

~~in this study (type 3). The κ-PDF of type 4 was dominated by MH mode, displaying nearly unimodal patterns, was defined as internal mixing type.~~ It should be noted that the four categories defined in our study have covered all cases of the observational results. In this study, we also calculated the standard deviation of κ-PDF (σ) according to Spitieri et al. (2023), which indicates the degree of dispersion in the data, and is thought to reflect the mixing degree of particles to a certain extent. Given that the aerosol particles sampled at the campaign site in this study are rarely affected by other hygroscopic aerosols (e.g., aerosols from marine sources), the MH internally-mixed particles (110, 150 and 200 nm) are thus mainly from the aging and growth of smaller particles. In contrast, the larger LH internally-mixed particles are predominantly from primary emissions. Therefore, the proportion of MH and LH internally-mixed particles at 100-200 nm can be used to distinguish the contribution to the internally-mixed fraction of larger particles from smaller aerosol aging and primary emissions respectively. Specifically, the result shows that a significant proportion of the internally-mixed particles at larger size originate from the aging and growth of smaller particles, accounting for 99%, 96% and 92% respectively for 110, 150 and 200 nm particles, whereas the contribution from primary emissions to these larger internally-mixed particles is less than 10%.



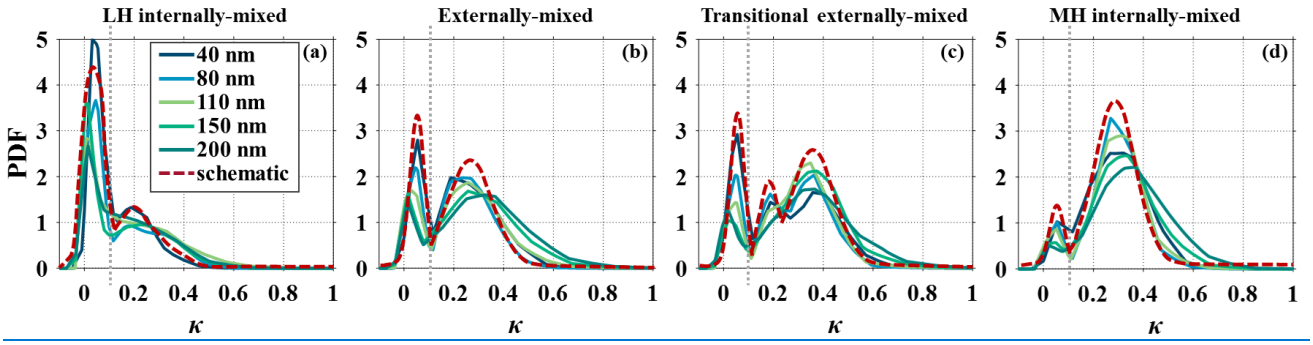


Figure 1. The mean κ-PDF of five particle sizes and the schematic diagram of κ-PDF for four mixing types.

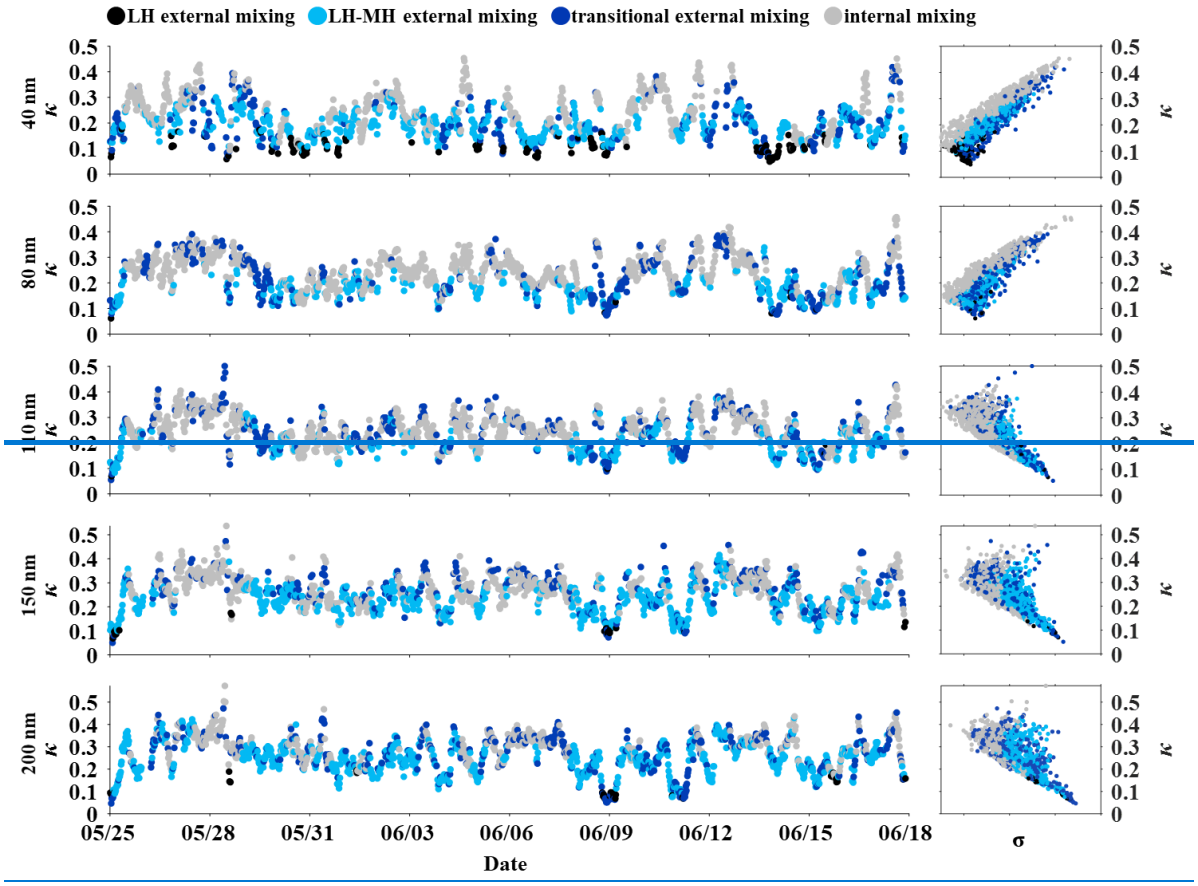
3 Results and discussion

3.1 Overview of the mixing state of size-resolved particles

Figure 2 shows the time series of size-resolved κ, and κ versus σ. The real-time changes in the mixing states of particles are represented by different filled colors. The κ values vary from 0 to 0.5 shows large variations in each of the five particle sizesfive particle sizes, ranging from 0 to 0.5, accompanied by significant changes in mixing states. In general, the mixing state of particles gradually transitions from externally-mixinged to MH internally-mixeding along with increases in κ. For example, particles with size of 40 nm are dominated by LH externalinternally-mixinged and LH MH externally-mixed ing states at κ < 0.2; and the transitional externally-mixinged state take up an increasingly proportion often corresponding to κ values of > 0.2 and the MH internally-mixed particlesing state occurs when κ greater than 0.3 (shown by the light gray dots in Figure 2).

However, there exists different correlations between κ and σ for the five sizes. For particles with diameter of smaller than 100 nm (i.e., 40 and 80 nm), the σ increases as the κ increases from 0.1 to 0.4 along with slight increase in the fraction of MH internally-mixed particles, showing a positive correlation. While, unlike the small particles, the σ for particles larger than 100 nm (i.e., 110, 150 and 200 nm) exhibits a negative trendcorrelation to κ variations, showing that the particles were with themore MH internal internally-mixing mixed

and with stronger ~~particles~~ hygroscopicity when ~~but~~ the smaller σ values were derived ~~the value of σ~~. The different sources and chemical compositions of aerosol particles could explain the distinct relationship between σ, mixing states and hygroscopicity among particles of different sizes. Here, the standard deviation of *κ*-PDF, σ, reflects the degree of dispersion in the pattern of *κ*-PDF. Taking 40 nm particles as an example, the obtained larger σ value indicates more diversity in particles hygroscopicity and chemical compositions, and thus a higher degree of external mixing state. This is because that, besides the local emissions (Ren et al., 2023), the 40 nm particles during the campaign were also from the growth of newly formed particles which are much more hygroscopic (Liu et al., 2021a). Therefore, the composition of those small particles is more heterogeneous, resulting in both greater σ and *κ*. The cases where both the σ and *κ* of small particles are lower suggest that the particles may consist of a mixture of different species originating from primary emissions (e.g., BC, hydrocarbon-like and/or cooking organic aerosols). While, for most of larger particles, their chemical composition tends to become homogeneous after aging and growth processes, exhibiting stronger hygroscopicity, a higher degree of internal mixing, and thus the smaller σ. However, a small number of larger particles with weak hygroscopic properties from primary emissions coexist with the aged ones in the atmosphere, which would result in larger σ and higher degree of external mixing.~~Our result contrasts with that previously observed in a vegetated site by Spitieri et al. (2023), which used only σ of Gf-PDF as a single indicator to characterize the particles mixing state. Our result indicates that the parameter σ alone cannot characterize the mixing state of particles in megacity of Beijing, where the aerosol particles are usually severely affected by local anthropogenic emissions.~~


LH external mixing
LH-MH external mixing
transitional external mixing
internal mixing
40 nm
80 nm
110 nm
150 nm
200 nm
κ
0.5
0.4
0.3
0.2
0.1
0
05/25
05/28
05/31
06/03
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06/12
06/15
06/18
Date
σ

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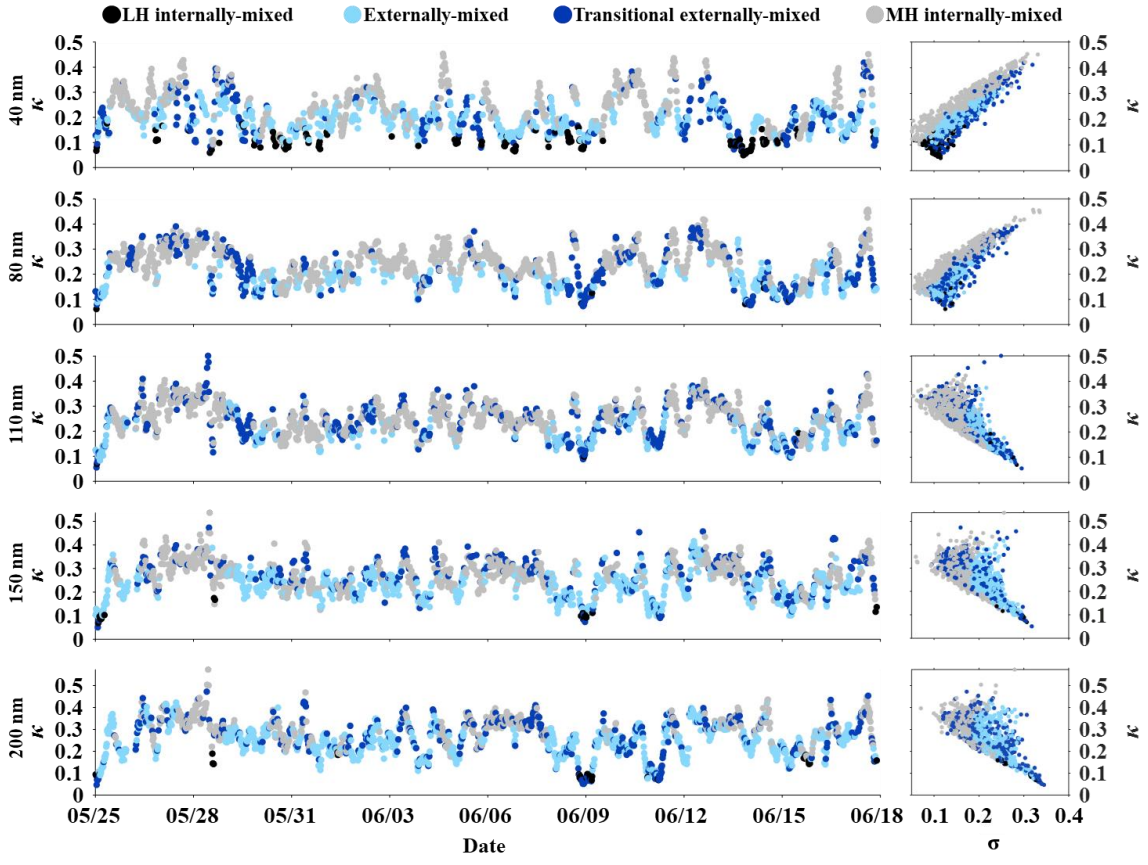
LH internally-mixed
Externally-mixed
Transitional externally-mixed
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40 nm
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0.1
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σ

229

Figure 2. Time series of hygroscopic parameter (κ), and plots of κ versus standard deviation of κ-PDF (σ) for 40, 80, 110, 150 and 200 nm particles (from top to bottom). The colors denote the different mixing types.

The size dependence of mixing type fractions and σ are shown in Figure 3. The external mixing types, including ~~LH~~ externally-mixed ~~mixing state~~ and transitional ~~LH-MH~~ externally-mixed ~~mixing~~ states, dominate in 40, 150 and 200 nm particles, accounting for ~~47~~53%, ~~41~~57% and ~~48~~70% respectively of all mixing types. The elevated fraction ~~in particles with~~of externally ~~mixing~~ mixed ~~state~~ particles is intimately associated with the local sources. For instance, a previous study revealed the particle size distribution of aerosols from different sources in urban Beijing, suggesting that the particles with diameter of 40 nm during rush hours and cooking times predominantly originated from primary emissions, and particles at 150 and 200 nm displayed a strong correlation with regional atmospheric transport sources (Ren et al., 2023).~~For instance, previous study revealed the particle size distribution of aerosols from different sources in urban Beijing, suggesting that the particles with 40 nm predominantly originated from primary emissions, and particles with 150 and 200 nm displayed a strong correlation with transportation sources and biomass burning sources (Ren et al., 2023).~~ In this study, the particles exhibit weaker hygroscopicity at lower wind speeds, indicating that hydrophobic particles are primarily from local sources (Figure S3). Furthermore, for 40 nm particles, the relatively higher fraction of MH internally-mixed particles (37%) is likely due to the growth and aging of newly formed particles (Liu et al., 2021a).~~Furthermore, for 40 nm particles, besides the impact from primary sources, the relative higher fraction of particles with internal mixing state (37%) is likely due to that the~~

~~growth and aging process of newly generated particles that are with high hygroscopicity (Wu et al., 2016; Liu et al., 2021a).~~ This is similar to the result observed in Athens, Greece, in which the particles with 30 nm were more internally-mixed (Spitieri et al., 2023). While, for particles with sizes of 80 and 110 nm, the transitional externally-mixed and MH ~~internal~~ internally-~~mixing~~ mixed states totally account for 50-80% of all mixing types, corresponding to a significant decrease from about 10% to less than 1% of the fraction of the LH ~~external~~ internally-~~mixing~~ mixed type. Note that the proportion of transitional externally-~~ mixing~~ mixed ~~state~~ particles remain~~s~~ relative constant, with a mean value of 21% across all sizes in this study, implying a continuous influence of atmospheric aging process on the particles mixing state. In addition, the 80 and 110 nm aerosols may continue aging and form 150 and 200 nm aerosol particles. Therefore, the aging of this group of aerosols should be more advanced, showing that the fraction of internally-mixed particles at 80 and 110 nm was the highest among the five particle sizes. On average, the result reveals that the externally and internally mixed particles accounted for ~~56~~53%±~~12~~11% and ~~44~~47%±~~12~~11% respectively. The mixing state of particles derived in this study differs from that reported by Zhang et al.~~,~~ (2017), in which they conducted the measurements at a suburban site of Xinzhou, where the aerosols ~~is~~ are much less affected by sources nearby, and the aerosols are mainly transported from elsewhere and are thus more aged and well mixed. The result implies that the influence of mixing state on hygroscopicity should be explored at specific particle sizes due to the heterogeneity of chemical compositions with particle size (Fan et al., 2020, Figure ~~S2~~S4).

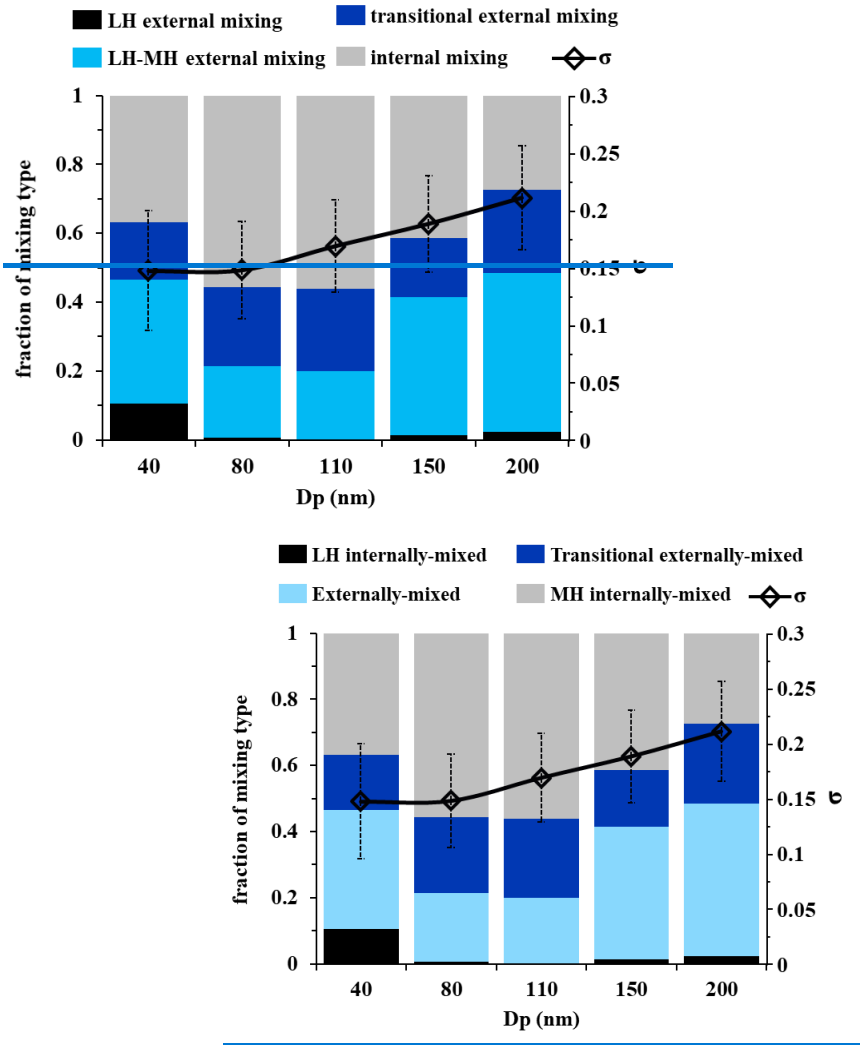
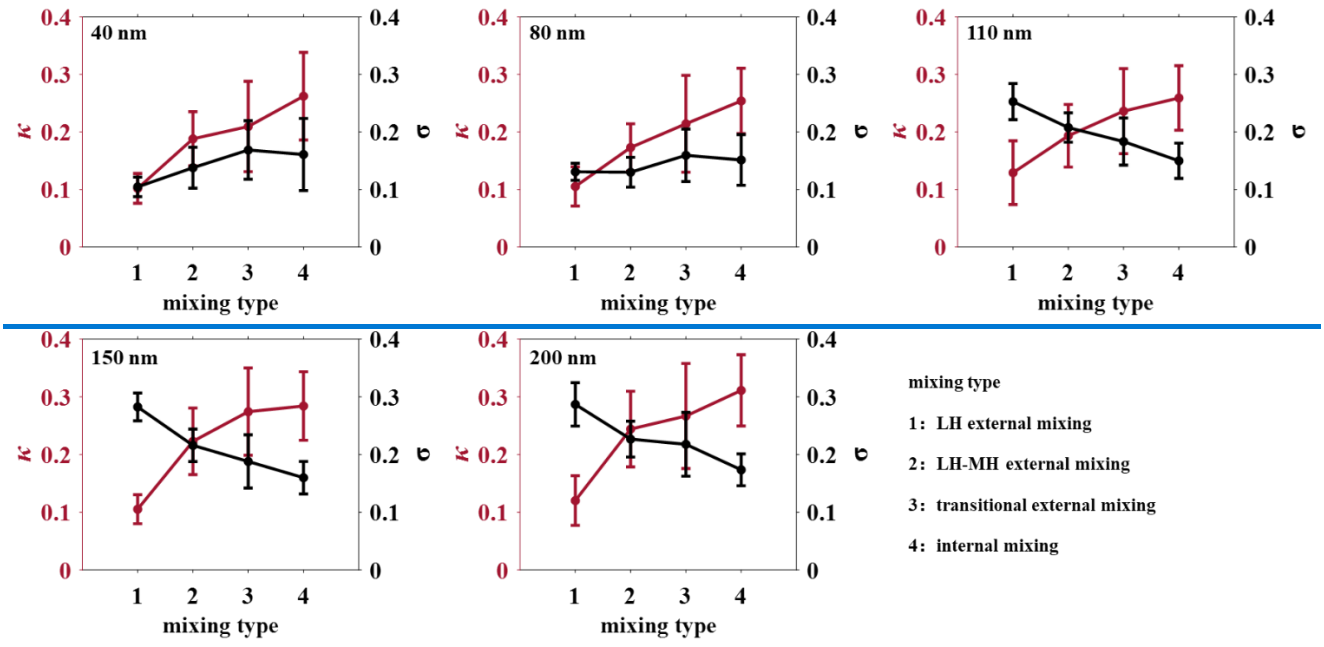


Figure 3. The size dependence of fraction of particles mixing types and σ.

Further, we compared the dependence of κ and σ on the variations of mixing states for five particle sizes (Figure 4). At 40 and 80 nm sizes, it shows that both κ and σ increases markedly when the particles change from externally-mixed to MH internally-mixing stateed. While, for particles with sizes of 110, 150 and 200 nm, the σ reduced but the κ increased when the particles change from externally to internally-mixing mixed state. In other words, the σ of the particles larger than 80 nm shifts to lower values as the particles become more internally mixed. While, the highly similar mixing state dependence of hygroscopicity and σ for five particle sizes was captured in Xinzhou, presenting that when particles transition from external mixing to internal mixing state, the σ of all particle sizes decreases, but the κ increases (Figure S4). Although the mean σ of κ-PDF in Xinzhou (0.10-0.18) is smaller than

~~that in Beijing (0.15-0.25), the absolutely different relationships between mixing state and σ of particles in suburban and urban sites~~~~Our results indicate that the standard deviation of κ-PDF alone is insufficient to characterize mixing degree in polluted area.~~ This contrasts with that previously observed in a vegetated site by Spitieri et al. (2023), which used only σ of Gf-PDF as a single indicator to characterize the particles mixing state. The distinct relationship between mixing type and σ for small particles (i.e., 40 and 80 nm) in urban sites indicates that the standard deviation of κ-PDF can effectively characterize mixing degree and chemical composition heterogeneity of larger particles in polluted area, where smaller aerosol particles are usually severely affected by local anthropogenic emissions.~~Our result indicates that the parameter σ alone cannot characterize the mixing state of particles in megacity of Beijing, where the aerosol particles are usually severely affected by local anthropogenic emissions.~~



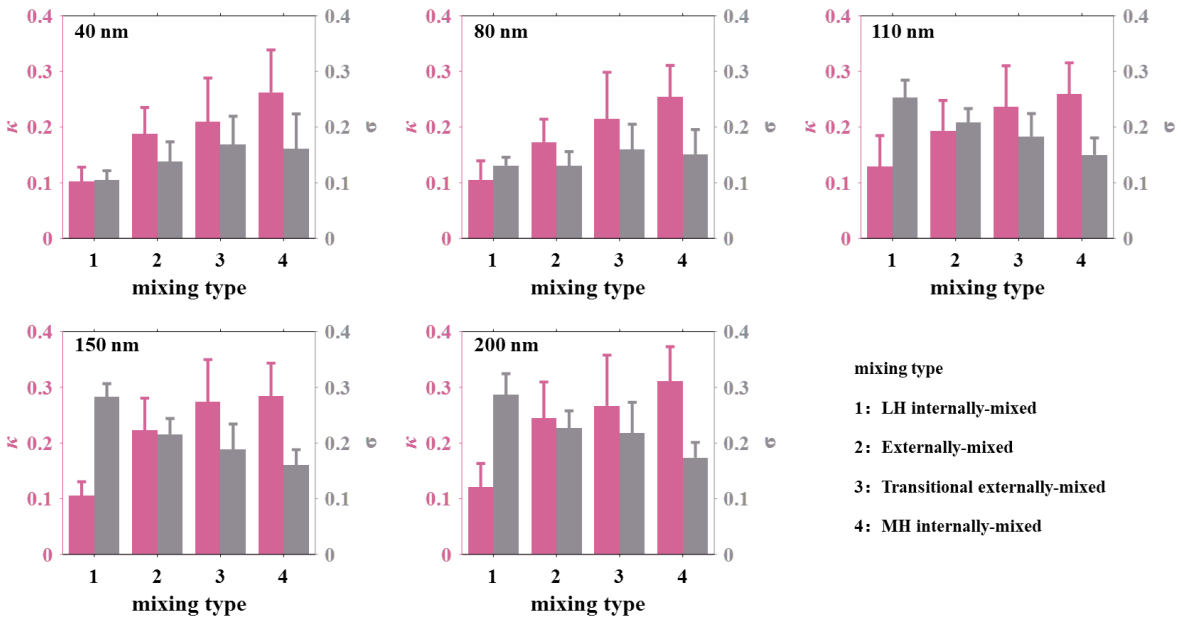


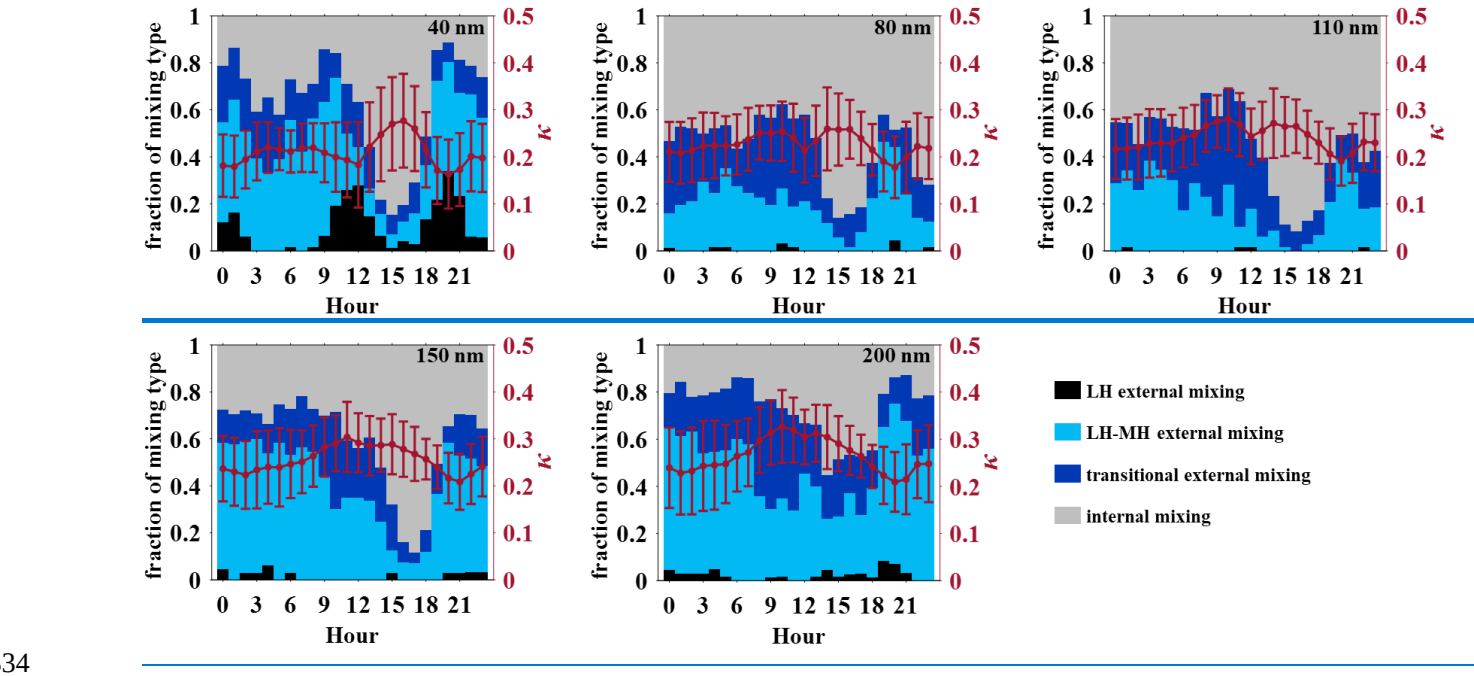
Figure 4. The mixing type dependence of hygroscopicity and σ for five particle sizes.

3.2 Evolution of mixing state of the particles

~~3.2.1 Diurnal variations~~

The average diurnal variations of the mixing state and κ of different particle sizes are shown in Figure 5. For 40 nm particles, the fraction of LH ~~external~~ internally-~~mixing~~ mixed ~~state~~ particles present~~s~~ three peaks at morning (9:00–12:00 local time; LT), evening rush hours (18:00–20:00 LT) and nighttime (0:00–03:00 LT). This is accompanied with the impacts from those primary cooking and traffic emissions (Xu et al., 2021; Liu et al., 2021b). Unlike the 40 nm particles, there is no apparent increase of externally-~~mixing~~ mixed state for the particles with sizes of 80, 110, 150, and 200 nm in the rush hours or cooking times. The results indicate that the particles emitted from local primary sources are small mainly with sizes around 40 nm during the campaign. Correspondingly, the proportion of the particles with MH internally-mix~~ing~~ed state was smallest in the morning and nighttime, but exhibiting a rapid increase from about 9:00 until the evening rush hours (about 16:00–18:00). This is accompanied by the increase of hydrophobic modes in κ-PDFs of small particle sizes during rush and cooking hours measured in Beijing (Figure S5). Moreover, the increase of

externally-mixed particles of 40 nm at nighttime may be highly associated with the emissions of primary species from heavy trucks in urban Beijing at nighttime (Hua et al., 2018), which can also be evidenced by the increased hydrophobic mode of the 150 nm and 200 nm particles observed from 00:00 to around 3:00 in Figure S5. In addition, the absence of photochemical aging and the lower boundary layer height during nighttime could also result in a higher proportion of externally-mixed particles. In addition, ~~T~~the ~~particles with LH-MH~~ externally-mixed ~~mixing~~ and transitional externally- ~~mixing~~ mixed ~~state~~ particles represent the intermediate state of the aging process in which particles transition from ~~external mixing~~LH ~~-~~to MH mode~~internal mixing~~, and both showed a decrease to around 10% during the corresponding period of the day as the proportion of particles with MH internally-mixed~~ing~~ state increased up to 80%. As a result, an obvious enhancement in particles hygroscopicity was observed during the daytime, indicating the impact of particles mixing and aging on their hygroscopicity (Hersey et al., 2013; Müller et al., 2017). Overall, ~~T~~the diurnal variation~~s~~ ~~imply~~implies an apparent aging process that leads the particles changed from ~~external~~ externally-~~mixing~~ mixed in the early morning to MH ~~internal~~ internally-~~mixing~~ mixed in the afternoon. ~~The aging process also changes particles physiochemical properties. As a result, an obvious enhancement in particles hygroscopicity was observed during the daytime, indicating the impact of particles mixing and aging on their hygroscopicity (Hersey et al., 2013; Müller et al., 2017).~~



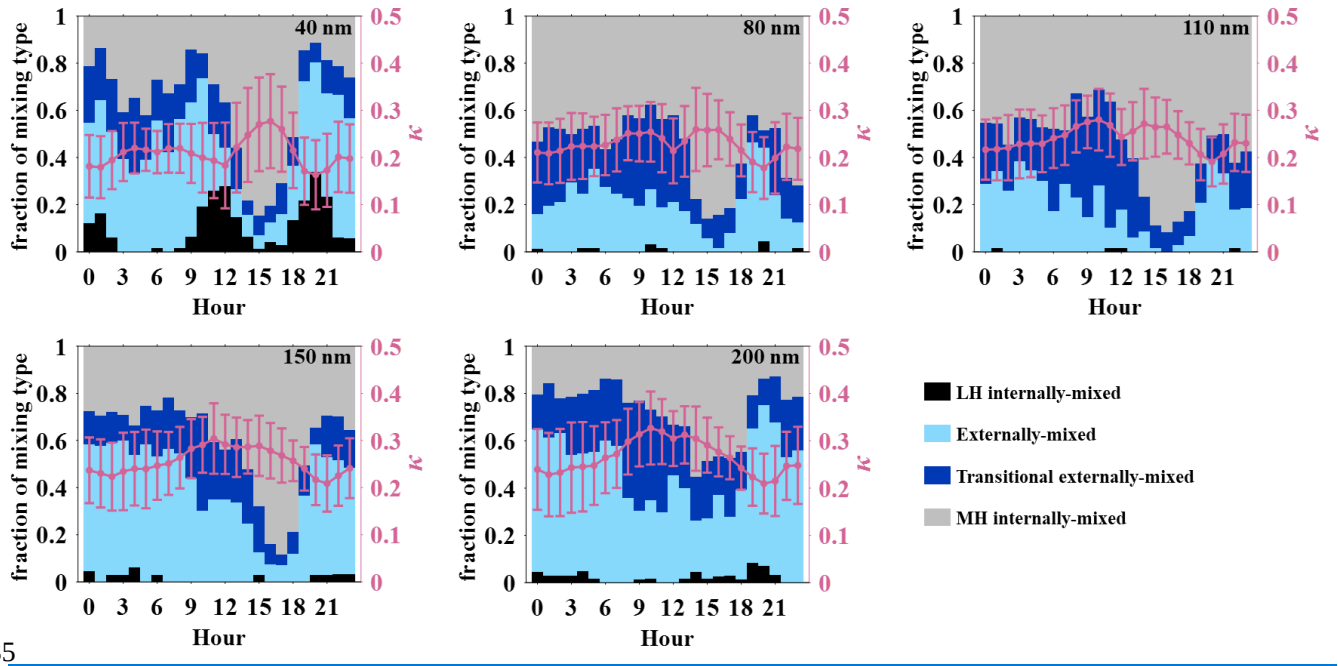


Figure 5. Diurnal variations of the mixing state fraction and κ for five particle sizes.

~~3.2.2 Dependence of the mixing state on T, RH and PM_1~~

~~To elucidate the effect of meteorological condition and particulate pollution level on mixing state of particles, the dependences of particles mixing types on ambient T, RH and PM_1 mass concentrations are further examined (Figure 6). It shows that there is a clear~~

~~dependence of mixing state of the particles across all observed sizes on T, for example, for the 40 nm particles, the fraction with external mixing state reduces from 60% to 20%, while that of the internal mixing state increases from 30% to 70% with the increase of T from <20°C to >35°C. This can be easily explained that the higher ambient T (usually corresponding to the periods in daytime) will generally promote the photochemicalaging and mixing of the particles (Riemer et al., 2004; Zhang et al., 2015). But note that, the fraction of particles with internal mixing state decreases evidently when the T increases from 15 °C to about 25°C. With the increase of RH from 20% to 80%, the fraction of particles with internal mixing state at 40 nm reduces from 60% to 20%. However, the fraction of the internal mixing state for particles larger than 80 nm is reduced with the increase of RH when its value <60%, while it increases with the RH increase as it larger than 60%, indicating that the very humid atmosphere with high RH is more favorable for particle aging that was reported promoted by the aerosols aqueous process (Zhang et al., 2021).~~

~~With the evolution of PM_1 pollution, the fraction of internal mixing state for 40 nm particles significantly decreases to less than 10% due to accumulation of small particles from local primary emissions under heavy pollution conditions, which thus leads to enhanced heterogeneity of particles chemical composition and externally mixed degree (Fan et al., 2020). While for particles with sizes of 80, 110, 150 and 200 nm, the proportion of internally-mixed state increase to nearly 90% under heavy PM_1 pollution, which is consistent with previous observations in winter of urban Beijing (Chen et al., 2020) and in Xi'an (Wang et al., 2014). Our result implies that those fine aerosol particles experience aging through both the photochemical processes and aqueous growth in the polluted atmosphere of urban Beijing, thereby affecting their mixing state.~~

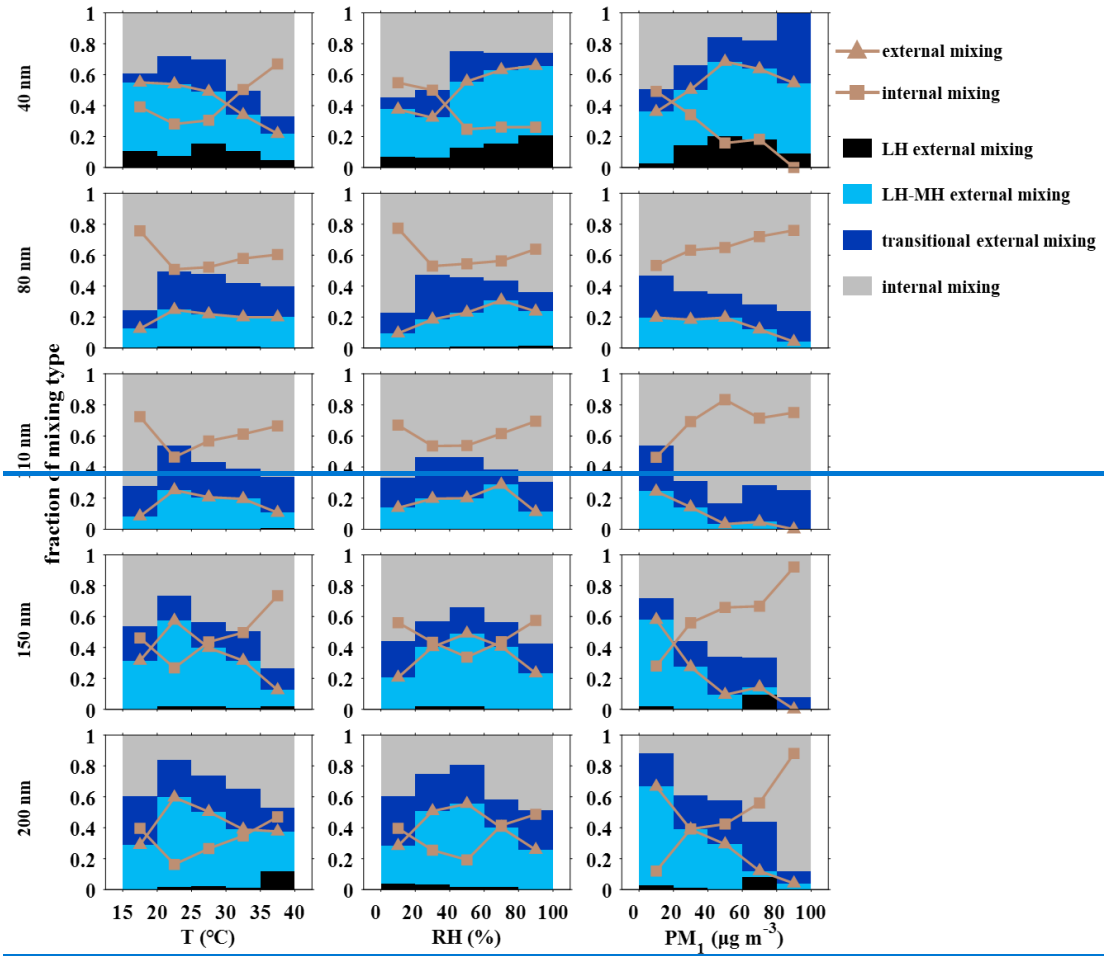


Figure 6. Mixing type fraction as a function of T, RH and PM_1 for five particle sizes. Solid triangles and solid squares represent the fraction of internal and external (LH external mixing + LH-MH external mixing state) mixing states, respectively.

3.3 Particles mixing (aging) timescale: on clear and cloudy days

The aerosol particles mixing and aging process is usually accompanied by the growth of particle sizes. In order to derive the mixing and aging timescale of particles, we further analyzed the averaged diurnal variations of particles fraction with MH internally-mixed state, particle number size distributions (PNSD) and the variations of mean κ-PDF during the growth periods on both clear and cloudy days (Figure 6). On clear days, the fraction of MH internally-mixed particles increases significantly from ~10-40% before 9:00 to nearly 100% during 12:00–15:00, especially for particles larger than 40 nm. Such enhancement is nearly as large as that on cloudy days. In detail, the proportion of MH internally-mixed particles

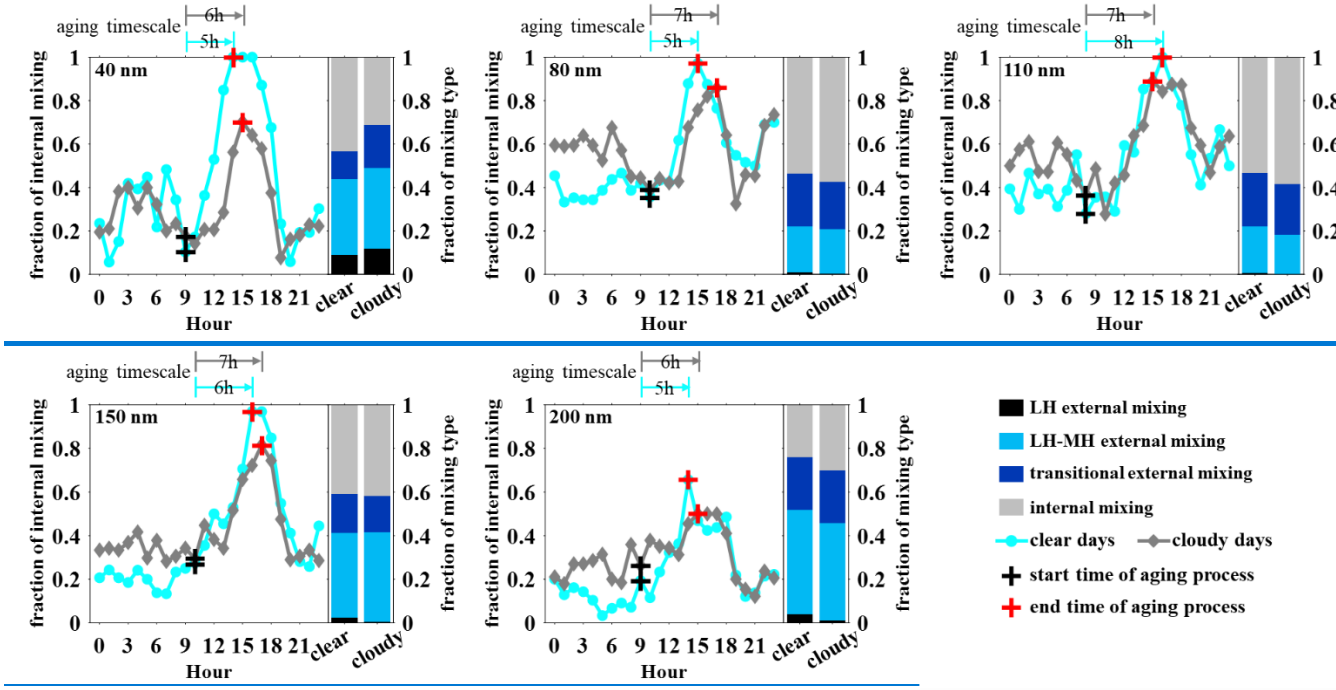
usually increased by less than 50% between the period before 9:00 and during 12:00–17:00, and its maximum fraction was around 50%-90%. While, the fraction of MH internally-mixed particles for 40 nm is noticeably higher on clear days (80%), which is approximately 40% greater than that on cloudy days, indicating that photochemical processes can make particles more internally-mixed and aged (Liu et al., 2021a). Furthermore, the diurnal variations of PNSD show that the growth of particle size is highly consistent with the increase of the fraction of MH internally-mixed particles. Additionally, the particles κ with large sizes at the corresponding times in the PNSD also shows an increase on both clear and cloudy days. Specifically, as the particle size grows from less than 40 nm before 9:00 to ~100 nm around 17:00, the fraction of MH internally-mixed particles increases from less than 40% to >90%. And, the peak value for κ shifts from $\kappa < 0.1$ to $\kappa > 0.2$, and the count for the peak value of κ-PDF increases accordingly (Figure 6). Overall, on clear days, the particles undergo a gradual shift from externally-mixed to MH internally-mixed states during 8:00–16:00 accompanied by a growth in particle size from 20 nm to about 100 nm, which is generally 1–2 hours shorter than that observed on cloudy days.

The obvious banana-shape growth of newly formed particles was captured in the diurnal variations of PNSD, which characterizes that the aging and growth of non-hygroscopic particles (e.g., BC) of primary emission and newly generated particles. Overall, the mixing and aging process is confirmed by the transition of particle from externally-mixed to MH internally-mixed, as well as the growth of particle size, which typically spans a duration of approximately 5 to 10 hours, as is similar to the aging timescale of aerosol particles in the polluted Indo-Gangetic Plain (< 10 hours) (Ghosh et al., 2021)~~Figure 7 shows the average diurnal variations of the fraction of particles with internal mixing state and the mean fractions of all the four mixing types on clear and cloudy days. On clear days, the fraction of internal mixing state increases significantly from ~10-40% before 9:00 to nearly 100% during 12:00–~~

~~15:00, especially when particle size smaller than 150 nm. While, there is no such notable enhancement on cloudy days. The difference in the proportion of particles with internal mixing state between the period before 9:00 and during 12:00–17:00 usually does not exceed 50% on cloudy days, and the maximum fractions of particles with internal mixing state on cloudy days were about 50%–90%. Compared with the cloudy days, the fraction of particles with internal mixing for 40 nm is noticeably higher on clear days, which accounts for about 40% of all mixing states, indicating that the 40 nm particles are likely from nucleation processes. On clear days, the particles undergo a gradual shift from external to internal mixing states during 8:00–16:00 accompanied by a growth in particle size from 20 nm to about 100 nm (Figure S3), which is generally 1–2 hours shorter than that observed on cloudy days.~~

~~Overall, the aging process is confirmed by the transition of particle from external to internal mixing states, the growth of particle size, and the increase of secondary organic aerosol (Figure S3), which typically spans a duration of approximately 5 to 8 hours, as is similar to the aging timescale of aerosol particles in the polluted Indo-Gangetic Plain (< 10 hours) (Ghosh et al., 2021)~~. Actually, the aerosol particles aging would be largely affected by local atmospheric conditions, and thus would vary both spatially and temporally (Pöschl et al., 2001; Huang et al., 2013). For example, using an environmental chamber approach, Peng et al. (2016) revealed that the timescale of BC aerosols aging is 2.3 and 4.6 hours, 9 and 18 hours over two cities—Beijing and Houston respectively. Note that the faster aging time in Beijing derived in the chamber experiment is probably due to the different levels in the concentration of gaseous precursors. In addition, there is only photochemical aging occurred in the chamber experiment, however, in the atmosphere, the particles aging is also through coagulation process which usually occurs slower than the photochemical reaction and condensation processes (Chen et al., 2017). This can also explain our observed faster mixing

(aging) time on clear days when the photochemical process is more significant considering that the difference of the pollutant concentrations in daytime between clear and cloudy days is not obvious (i.e., ~~SO_2, NO_2,~~ O_{3X} ,and PM_1; Figure ~~S4~~S6).



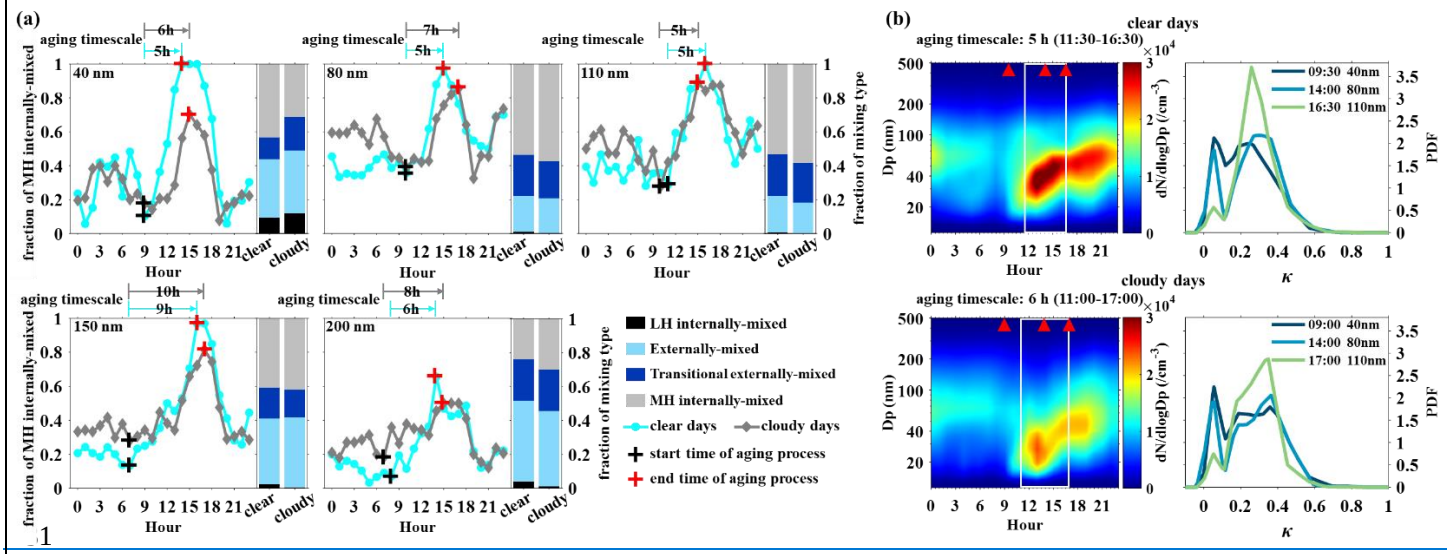


Figure 6. (a) Diurnal variations of the proportion of MH internally-mixed particles and statistical results of the fraction of mixing state for five particle sizes on clear and cloudy days. The start time of particle mixing/aging was selected when the proportion of MH internally-mixed particles is minimum between sunrise and noon, and the end time was

defined as when the fraction of MH internally-mixed particles reaches its maximum. (b) The averaged diurnal variations in PNSD and the variations of mean κ-PDF during the growth periods on clear and cloudy days (right panels). The red triangles indicate 2 hours before the start of the aging, during the growth and end of the aging process respectively.~~Figure 7. Diurnal variations of internal mixing proportion and statistical results of the fraction of mixing state for five particle sizes on clear and cloudy days. The line segments and time above the graph represent the aging timescale of particles. The start time and end time of particle aging process was selected when the proportion of particles with internal mixing state is closest after sunrise, and when the fraction of internally-mixed particles reaches its maximum, represented by black and red cross respectively.s~~

3.4 Implications to parameterization of the current models

The mixing/aging timescale of aerosol particles significantly impacts their physiochemical properties, which in turn affects their atmospheric lifetime, transport characteristics (Zhang et al., 2023), hygroscopicity and the direct radiative forcing of aerosol particles (Moffet and Prather, 2009; Wang et al., 2018; Stevens and Dastoor, 2019). We further compared our results with the results derived from five field sites and the values adopted in current models (Table S1). In most models, the aging processes of carbonaceous aerosols were treated with a simple parameterization, which generally obtained aging time based on the transformation of aerosols from hydrophobic to hydrophilic (Chen et al., 2017; Ghosh et al., 2021). Unlike the models, the aging timescale of BC aerosols in field measurements and laboratory studies was commonly derived by tracking changes in hygroscopicity, morphology, coating thickness or optical properties (Moffet and Prather, 2009; Akagi et al., 2012; Krasowsky et al., 2016; Peng et al., 2016). These methods were used to quantify the aging timescale of particles indirectly. While, in our study, the mixing (aging) time was inferred based on the changes in hygroscopic modes and mixing states of non-BC

particles in the ambient atmosphere. Note that although there may be some differences in the results based on different methods, the aging timescales obtained all represent the mixing and aging rate of aerosol particles in the atmosphere, which affects aerosols atmospheric lifetime, thus the environment and climate effects. As shown in Figure 7, the derived aging timescale of aerosols in this study is comparable to the observational results reported in other urban areas, such as Mexico City (3 hours; Moffet and Prather, 2009) and Los Angeles (3 hours; Krasowsky et al., 2016). ~~As shown in Figure 8, the mixing/aging timescale of particles in Beijing achieved in this study is 5–8 hours, which is comparable with the observations of that reported in other urban areas like Mexico City (3 hours; Moffet and Prather, 2009) and Los Angeles (3 hours; Krasowsky et al., 2016).~~ The result is also close to the aging timescale of particles in source area of biomass burning in California (4 hours; Akagi et al., 2012). However, the aging time of particles displays large spatial variations at different sites. For example, the aging timescale of particles observed in Beijing (4.6 hours) was four times faster than that in Houston (18 hours) where the precursors concentrations are extremely low (Peng et al., 2016). Overall, the mixing/aging timescale of particles in Beijing achieved in this study is 5–10 hours, which falls within the range of 2–10 hours in polluted areas obtained by other studies. Therefore, our results are likely representative of the aging time scale of aerosols in polluted urban areas. Furthermore, the aging time of particles obtained in ambient atmosphere is much shorter than the default values adopted in most models, which is commonly with a duration of 1.15–2.5 days. In addition, the values among different models range greatly from 1 to 20 days (Figure ~~8~~7). For example, a timescale of 20 days was used to represent a slow aging process (i.e., coagulation) by Liu et al. (2011), as may be not properly applied in regions with high particle number concentration where the particles coagulation is also efficient (Chen et al., 2017).

Although using a dynamic parameterization scheme ~~of~~ for particles aging in models

could achieve the application of different ~~particles~~ aging times to different regions, the simulated values show large variations ~~and uncertainties~~ among different models. For example, in RegCM4 model, the conversion time from fresh to aged BC ranges from about 5 hours to 7 days (Ghosh et al., 2021). The range in the KAMM/DRAIS, however, is only 2 hours to about 1.6 days (Riemer et al., 2004). Moreover, even in central-eastern China, the aging timescale has been reported to range from 12 hours to 7 days based on a regional chemical transport model (Chen et al., 2017), which is much longer than that derived in urban Beijing by this study. Additionally, the aging times of carbonaceous aerosols simulated by the GEOS-Chem model exhibit large spatial and temporal variations, with the global average calculated to be 3.1 days (Huang et al., 2013). This value is much longer than the default values used in other global models (1-2 days) (Pierce et al., 2007). ~~The aging timescales has been reported ranging from 12 hours to 7 days over central-eastern China based on a regional chemical transport model by Chen et al. (2017), which is much longer than that derived in urban Beijing by this study.~~ Note that although the mixing (aging) timescale of particles was determined by examining diurnal variations in the mixing state of aerosol particles in this study, compared with laboratory studies, various factors in the real ambient atmosphere change over time, including meteorological conditions, emission sources, and atmospheric processes etc. Therefore, the result derived in this study warrants further verifications. The long-term field measurements at more sites should be conducted in the future.

The large uncertainties in the aging timescale can significantly affect the accuracy of simulation and assessment for atmospheric lifetime, loading and radiation forcing of aerosols. For example, to better simulate the intercontinental transport of aerosols, Huang et al. (2013)

implemented a variable aging scheme in the GEOS-Chem model, which showed that the total atmospheric burdens and global average lifetimes of BC (OC, organic carbon) were increase by 8% (2%) compared to the default value (1.15 days). Similarly, due to the implementation of the dynamic aging scheme in models, the column burden and surface mass concentration of carbonaceous aerosols increased during the dry season in the polluted Indo-Gangetic Plain, and the atmospheric heating increased by at least 1.2 W m^{-2} (Ghosh et al., 2021). Therefore, given the large spatiotemporal variations in aging timescale of particles, the study emphasizes the urgency of conducting investigations at more field sites. In addition, the other factors such as the meteorology~~, aerosol mass loading~~ and particle sizes that affect the aerosols aging should be accounted for so as to improve the dynamic aging schemes in climate models.

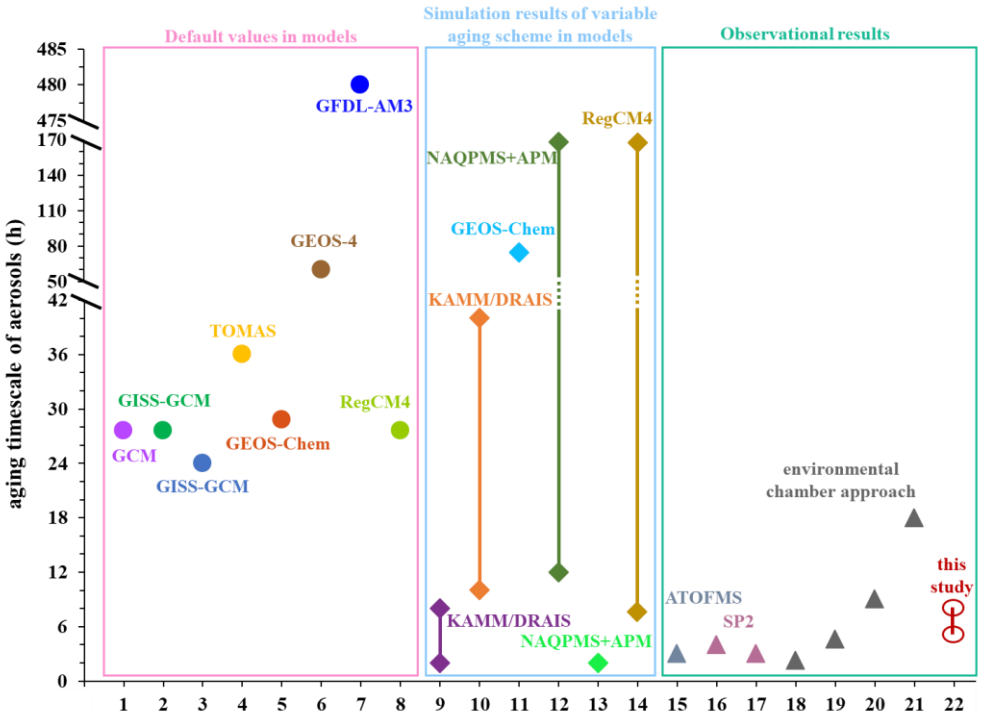


Figure ~~8~~7. The mixing/aging timescale of particles reported in literatures (1. Cooke et al., 2002; 2. Chung and Seinfeld, 2002; 3. Koch and Hansen, 2005; 4. Pierce et al., 2007; 5. Yu and Luo, 2009; 6. Colarco et al., 2010; 7. Liu et al., 2011; 8, 14. Ghosh et al., 2021; 9, 10.

Riemer et al., 2004; 11. Huang et al., 2013; 12, 13. Chen et al., 2017; 15. Moffet and Prather, 2009; 16. Akagi et al., 2012; 17. Krasowsky et al., 2016; 18-21. Peng et al., 2016). The solid circle, diamond and the triangle denote the default aging time of particles used in models and stimulation results of variable aging scheme in models, as well as the observational results, respectively.

4 Conclusions

The real-time mixing state of ambient aerosol particles with dry particle sizes of 40, 80, 110, 150 and 200 nm was investigated in urban Beijing, according to PDF of hygroscopic growth factor measured using the H-TDMA system. Four mixing states of ambient size-resolved particles were captured in this study. In general, particles with LH ~~external~~internally-mixed, ~~LH-MH~~ externally-mixed, transitional externally-mixed and MH internally-mixed ~~-mixing~~ state account for 0-10%, 20-46%, 17-24% and 27-56% respectively, which depends on particles size greatly. The fraction of internally-mixed particles peaks at 80 and 110 nm due to enhanced aging in intermediate particles. The diurnal variation of mixing state of particles in all sizes considered presents a visible aging process, showing that the fraction of particles with MH internally-mixed ~~-mixing~~ state increases significantly from ~10-40% before 9:00 to about 100% during 12:00–15:00 on clear days, accompanied by a growth in particle size from 20 nm to 100 nm~~, which is more notable for particles at 40 nm than that on cloudy days~~. Typically, the mixing/aging process of particles takes approximately 5–10 hours, which reveals the mixing (aging) timescale of aerosols during the campaign.~~Specifically, the aging process of particles within approximately 5-8 hours.~~ Additionally, our results suggest that fine aerosol particles undergo significant aging through

photochemical processes in the polluted atmosphere of urban Beijing. ~~In addition~~Furthermore, the ~~mixing state of particles was observed to be dependent both on T and RH, showing that the particles with internal mixing state elevates obviously when T or RH exceeds 25°C or 60% respectively. Moreover, with the intensification of particulate pollution, the particles become more internally mixed. The results indicate that both high ambient temperature and very humid atmosphere are more favorable for particle aging in polluted atmosphere. The~~ large difference of mixing/aging timescale of particles between values in models and the timescale achieved by observations, emphasizing the vital role of exploring the aging timescale through more field measurements to improve the accuracy of aging schemes in climate models. The results revealed in our study highlight the considerable impact of atmospheric aging on mixing state of fine aerosol particles in polluted megacities.

Data availability

All data used in the study are available from the corresponding author upon request (zhangfang2021@hit.edu.cn).

Author contributions

FZ and JL conceived the conceptual development of the paper. FZ directed and performed of the experiments with JR, LC and JL. JL conducted the data analysis and wrote the draft. All authors edited and commented on the various sections of the paper.

Competing interests

The authors declare that they have no conflict of interest.

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