Response to Reviewers

We sincerely thank the anonymous reviewers for their valuable comments and constructive suggestions. Their feedback has helped us improve the scientific rigor, clarity, and overall quality of the manuscript. We have carefully revised the manuscript in response to all comments. Below, we provide a point-by-point response to each comment and describe the corresponding changes made in the revised manuscript.

Anonymous Referee #1

This manuscript presents an integrated analysis of refractory black carbon (rBC) measurements from an SP2, single-particle chemical information from SPAMS, and bulk aerosol optical measurements from a PAX during an urban field campaign in Shenzhen. The main contribution of the study is the attempt to connect diurnal changes in rBC coating state and chemical composition with corresponding changes in light absorption, and to distinguish between nighttime heterogeneous aging and daytime photochemical aging pathways. The dataset is valuable, and the combined SP2–SPAMS–PAX perspective has the potential to provide useful observational constraints on the evolution of BC mixing state and optical properties in an urban environment.

Response: We sincerely thank the reviewer for the thoughtful assessment of our work. We have carefully considered all comments and revised the manuscript accordingly. Detailed point-by-point responses are provided below.

1. **The explanation for the daytime secondary coating-thickness mode needs stronger support.**The manuscript reports the emergence of a daytime secondary mode in coating thickness, around 60 nm, and attributes this to accelerated photochemical aging of a subset of BC particles and the effect of PBL expansion, which dilutes freshly emitted BC and thereby increases the relative contribution of aged particles. This explanation as written it is not fully convincing.
   The explanation invoking PBL dilution is not physically sufficient as written. Uniform dilution would reduce the concentrations of all coating-thickness classes proportionally and would not change the normalized coating-thickness distribution or generate a secondary mode. The observed daytime secondary maximum would require a change in the relative contributions of distinct BC populations, for example entrainment/mixing of more aged particles from aloft, preferential dispersion of fresh near-surface emissions, or rapid aging of a subset of particles. The authors should clarify which mechanism they intend and provide supporting evidence. Alternatively, the interpretation should be softened and framed as one possible explanation rather than a demonstrated mechanism.

   Response: We thank the reviewer for this insightful comment. We agree that uniform PBL dilution alone cannot generate a secondary mode in the normalized coating-thickness distribution, as it would proportionally reduce the concentrations of all coating-thickness classes without altering the distribution shape.

   We have revised the discussion to clarify that the daytime secondary mode at ~60 nm is not attributed to PBL dilution itself, but may instead reflect changes in the relative contributions of

distinct BC populations. Specifically, enhanced daytime photochemical activity may promote rapid aging of a subset of BC particles, while PBL development may facilitate vertical exchange and the entrainment or downward mixing of more aged BC particles from aloft or the residual layer. Together with the continuous input of freshly emitted BC near the surface, these processes could contribute to the observed bimodal coating-thickness distribution.

Because direct vertical measurements are unavailable, we cannot distinguish the relative contributions of rapid photochemical aging and vertical mixing/entrainment. We have therefore revised the manuscript to present these mechanisms as plausible interpretations rather than demonstrated processes. The revised text reads as follows:

Distinct aging pathways during day and night are further corroborated by the diurnal distribution of rBC coating thickness (Fig. 3). During nighttime, BC particles exhibited gradual growth, with the coating thickness of the dominant population increasing by ~10 nm. In contrast, daytime BC particles generally exhibited thinner coatings, primarily reflecting the continuous input of freshly emitted BC from intense daytime traffic emissions. Under active photochemical conditions, however, a secondary mode emerged at a coating thickness of ~60 nm. The thinly coated mode was likely maintained by continuous local emissions near the surface, whereas the thickly coated secondary mode may have resulted from several concurrent processes, including rapid photochemical aging of a subset of BC particles and the entrainment or downward mixing of more aged particles from aloft or the residual layer during PBL development. Although the available observations do not allow us to distinguish the relative contributions of these processes, their combined effects provide a plausible explanation for the observed daytime bimodal distribution. The emergence of this bimodal distribution highlights the pronounced heterogeneity of the BC mixing state during daytime, in contrast to the more uniform coating characteristics observed at night.

2. **The nighttime nitrate aging mechanism is over-attributed to N_2O_5 hydrolysis.** The manuscript argues that nighttime aging is driven by heterogeneous nitrate uptake, likely through NO_3/N_2O_5 chemistry and subsequent N_2O_5 hydrolysis on BC surfaces. While this pathway is certainly possible under nighttime urban conditions, the presented observations do not seem sufficient to uniquely identify it as the dominant mechanism.
An alternative explanation is thermodynamic partitioning of nitrate during cooler nighttime conditions, especially involving HNO_3/NH_4NO_3. If temperature decreases and aerosol liquid water or ammonium availability favors particulate nitrate, then increased nitrate on BC-containing particles could occur without requiring N_2O_5 hydrolysis as the dominant pathway. The authors should discuss this possibility explicitly. If they wish to maintain the N_2O_5 interpretation, they should provide additional evidence, such as constraints from O_3, NO_2, RH, temperature, aerosol liquid water, nitrate partitioning calculations, or other indicators that distinguish heterogeneous N_2O_5 chemistry from nighttime partitioning.
A more cautious framing would be that nighttime nitrate accumulation is consistent with heterogeneous nitrogen chemistry, potentially including N_2O_5 hydrolysis, but that thermodynamic partitioning of nitrate may also contribute.

Response: We thank the reviewer for this important comment. We agree that our original interpretation placed excessive emphasis on heterogeneous N_2O_5 hydrolysis and that the available observations do not allow this pathway to be uniquely identified as the dominant mechanism of nighttime nitrate accumulation on BC-containing particles.

In the revised manuscript, we have therefore explicitly incorporated thermodynamic gas-particle partitioning as an alternative pathway and substantially softened the interpretation of the N_2O_5 mechanism. We now interpret the nighttime nitrate enhancement as potentially resulting from multiple processes, including heterogeneous nitrogen chemistry and thermodynamic partitioning of semi-volatile nitrate. Although the observed nighttime NO_2 and O_3 conditions may permit NO_3/N_2O_5 chemistry, the absence of direct measurements of NO_3, N_2O_5, HNO_3, and aerosol liquid water, as well as nitrate partitioning calculations, prevents us from quantitatively distinguishing the contributions of these pathways. We therefore no longer identify N_2O_5 hydrolysis as the dominant mechanism and have revised the text accordingly:

A substantial increase in the Nitrate factor was observed during nighttime, indicating enhanced nitrate accumulation on BC-containing particles. Several processes may have contributed to this nighttime enhancement. The elevated nighttime NO_2 levels, together with the presence of O_3, may provide conditions favorable for NO_3/N_2O_5 chemistry, and heterogeneous hydrolysis of N_2O_5 on particle surfaces could therefore contribute to nitrate formation. However, this pathway cannot be directly constrained in the absence of NO_3 and N_2O_5 measurements. Thermodynamic gas–particle partitioning may also contribute to the observed nitrate enhancement. In particular, lower nighttime temperatures and higher RH may favor the partitioning of semi-volatile nitrate into the particle phase, while the presence of sufficient NH_3 and aerosol liquid water could further promote particulate NH_4NO_3 formation. Therefore, the observed nighttime nitrate accumulation likely reflects the combined influence of heterogeneous nitrogen chemistry and thermodynamic partitioning, although their relative contributions cannot be quantified with the available measurements.

3. **The claim that BC surfaces specifically promote sulfate formation should be softened or better supported.**The manuscript states that enhanced sulfate signals in BC-containing particles indicate that the BC surface specifically promotes sulfate formation. This is an interesting possibility, but the current evidence appears indirect. SPAMS relative peak areas provide valuable particle-level chemical information, but they are not direct formation-rate measurements. Differences between BC-containing and non-BC particles could also reflect particle size, source covariance, condensation/coagulation history, detection efficiency, classification biases, or differences in mixing state rather than surface-catalyzed sulfate production specifically.
   The authors should either provide stronger support for this claim or rephrase it more cautiously. For example, they could state that the observations are "consistent with preferential sulfate accumulation on BC-containing particles" rather than concluding that BC surfaces specifically promote sulfate formation.

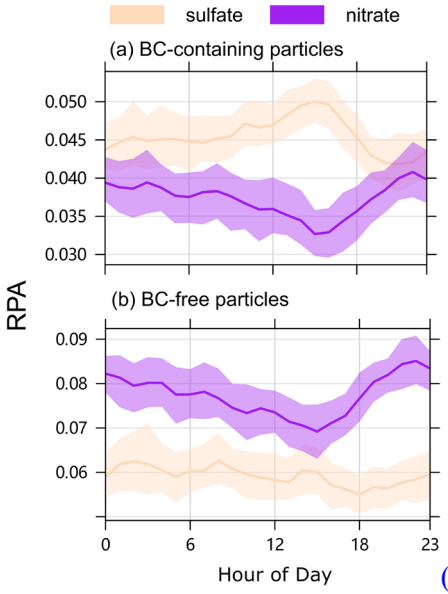
   Response: We thank the reviewer for pointing out this important issue. We agree that SPAMS relative peak areas provide particle-level chemical information but do not directly measure sulfate formation rates. Therefore, the stronger sulfate signals observed in BC-containing particles cannot demonstrate that BC surfaces specifically promote sulfate formation by themselves.

   Our original interpretation was partly motivated by Zhang et al. (2021; DOI: 10.1029/2021JD035226), who reported enhanced sulfate-to-nitrate ratios in BC-containing particles and suggested a potential role of BC-involved photochemistry based on additional

statistical analyses, including multilinear regression and random forest analysis. In our study, we observed a qualitatively similar pattern, with stronger sulfate signals in BC-containing particles than in non-BC particles (Fig. 4). However, we recognize that such differences may also arise from other factors, including particle size, source characteristics, atmospheric processing history, and differences in mixing state. Our SPAMS observations alone cannot distinguish among these possibilities.

We have therefore softened the relevant statement and no longer interpret the enhanced sulfate signal as direct evidence that BC surfaces promote sulfate formation. Instead, we describe the observation as preferential sulfate accumulation on BC-containing particles, while treating BC-involved photochemistry only as one possible interpretation. The revised text reads as follows:

The stronger sulfate signals observed in BC-containing particles are consistent with preferential sulfate accumulation on these particles, although the underlying mechanisms cannot be uniquely determined from the SPAMS measurements alone. BC-involved photochemistry has been proposed as one possible mechanism for enhanced sulfate accumulation in previous studies (Zhang et al., 2021), but its contribution to the present observations requires further investigation.



(Zhang et al. 2021, Fig. 5)

4. **Role of coagulation in BC mixing-state evolution.**The discussion focuses primarily on condensation and heterogeneous uptake as mechanisms that increase rBC coating thickness and MR. However, coagulation between BC-containing and non-BC particles can also transfer secondary material to the BC-containing population and contribute to internal mixing. This distinction is important because an increase in nitrate, sulfate, ammonium, or organic material associated with BC-containing particles does not necessarily imply that these species formed or condensed directly on BC surfaces. It may also reflect coagulation with pre-existing non-BC particles that already contain these species. The authors should discuss whether coagulation is expected to be important under the observed number concentrations and timescales, and how it could affect their interpretation of daytime and nighttime aging mechanisms. At minimum, the manuscript should acknowledge that SP2/SPAMS observations of increased coating or enhanced

secondary ion signals on BC-containing particles cannot unambiguously distinguish condensation/heterogeneous uptake from coagulation-driven mixing.

Response: We thank the reviewer for this important comment. We agree that coagulation represents an additional pathway for the evolution of the BC mixing state. In particular, coagulation between BC-containing and non-BC particles can transfer pre-existing secondary material to the BC-containing population. Therefore, increases in rBC coating thickness or enhanced nitrate, sulfate, ammonium, and organic signals associated with BC-containing particles cannot be unambiguously attributed to direct condensation or heterogeneous uptake on BC-containing particles.

Coagulation is generally favored by higher particle number concentrations and longer residence times. In our observations, particle concentrations were higher during nighttime (Fig. 2c), when the shallower boundary layer and weaker atmospheric dispersion may have provided conditions more favorable for coagulation than during daytime. The observed nighttime increase in MMD (Fig. 2f) is consistent with particle growth but cannot be uniquely attributed to coagulation, as condensation, heterogeneous uptake, and changes in particle sources may also contribute. During daytime, boundary-layer development and stronger atmospheric dispersion may reduce particle concentrations and thus decrease the likelihood of coagulation. However, because quantitative coagulation timescales cannot be constrained with the available measurements, we cannot determine the relative contribution of coagulation compared with condensation and heterogeneous uptake.

We have therefore revised the manuscript to explicitly acknowledge coagulation as a potential pathway for BC mixing-state evolution and to clarify that the present SP2/SPAMS observations cannot unambiguously distinguish coagulation-driven mixing from condensation and heterogeneous uptake. The revised text reads as follows:

Coagulation may also contribute to the diurnal evolution of the BC mixing state by transferring pre-existing secondary material from non-BC particles to the BC-containing population. This process may be more favorable under higher particle number concentrations and weaker atmospheric dispersion, conditions that occurred more frequently during nighttime in this study (Fig. 2c). The observed nighttime increase in MMD (Fig. 2f) is consistent with particle growth but cannot be uniquely attributed to coagulation, because condensation, heterogeneous uptake, and changes in particle sources may also contribute. During daytime, PBL development and stronger atmospheric dispersion may reduce particle concentrations and thereby decrease the likelihood of coagulation. Nevertheless, quantitative coagulation timescales cannot be constrained with the available measurements. Therefore, the observed increases in rBC coating thickness and secondary species associated with BC-containing particles cannot be unambiguously attributed to direct condensation or heterogeneous uptake, as coagulation-driven mixing may also contribute.

5. **The derived MR and coating thickness are central to the manuscript, but the associated uncertainties need more discussion.**The authors appropriately note that MR is not directly measured but is estimated from SP2-derived quantities using a core–shell Mie model, assumed refractive indices, and assumed densities. However, MR and coating thickness are then used heavily throughout the interpretation, including the discussion of diurnal aging, the MR > 3

threshold, and the calculation of MAC for thickly coated BC.

The authors should provide a clearer uncertainty discussion for the inferred coating thickness and MR. In particular, the assumed rBC core refractive index m = 2.26 + 1.26i should be accompanied by the wavelength. Since this value is high compared with commonly used visible-wavelength BC refractive indices, the authors should clarify that it is used for the SP2 scattering/LEO retrieval, presumably at 1064 nm, and not for interpreting the 532 nm optical measurements. A sensitivity test or discussion of the effect of alternative core refractive indices, coating refractive index, coating density, core density, and core–shell morphology would make the paper more robust.

Response: We thank the reviewer for this important comment. We agree that the uncertainties associated with the inferred coating thickness and MR require a clearer discussion, particularly because these quantities are central to our interpretation of BC aging and optical properties.

We first clarify that the rBC core refractive index of m = 2.26 + 1.26i is specified at 1064 nm, corresponding to the wavelength of the SP2 intracavity laser, and is used specifically for the SP2 scattering/LEO retrieval. It is not used for the interpretation of the optical measurements at 532 nm. We have clarified this point in the revised manuscript:

The total particle diameter (D_p) was then derived by applying the measured D_c and reconstructed scattering signal to a core-shell Mie model, assuming a complex refractive index of m = 2.26 + 1.26i for the rBC core (Moteki et al., 2010) and m = 1.50 + 0i for the coating material (Laborde et al., 2012) at 1064 nm.

We also acknowledge that the inferred coating thickness and MR are model-dependent estimates rather than directly measured quantities. The refractive indices and densities adopted in the retrieval and mass conversion follow values commonly used in previous SP2-based studies, thereby facilitating comparison with the existing literature (Laborde et al., 2012, Moteki et al., 2010). Nevertheless, we agree that the use of these conventional parameter values does not eliminate the associated uncertainties. Alternative assumptions regarding the rBC core and coating refractive indices can affect the modeled optical response and thus the retrieved coating thickness, while uncertainties in the assumed core and coating densities propagate into the calculated MR. In addition, deviations of ambient BC-containing particles from the idealized concentric core-shell morphology introduce further uncertainty into the retrieval.

A comprehensive sensitivity analysis involving alternative refractive indices and particle morphologies would require reprocessing the LEO retrieval under multiple optical assumptions and is beyond the scope of the present study. We have therefore not attempted to assign quantitative uncertainty ranges that cannot be robustly constrained by our measurements. Instead, we have expanded the uncertainty discussion in the revised manuscript and now explicitly state that the absolute values of coating thickness and MR, as well as the classification of particles near the operational MR = 3 threshold, should be interpreted with these model-dependent uncertainties in mind. Accordingly, we have also revised the relevant discussion to avoid treating the MR = 3 threshold as an exact physical boundary.

The coating thickness and MR derived from the SP2 LEO-fit analysis should be regarded as model-dependent estimates rather than directly measured quantities. The assumed rBC refractive index (m = 2.26 + 1.26i at 1064 nm) is used specifically for the SP2 scattering retrieval and is distinct from the optical parameters used for the 532 nm measurements. The retrieved coating

thickness is sensitive to assumptions regarding the refractive indices of the rBC core and coating, while the calculated MR additionally depends on the assumed core and coating densities. Deviations from the idealized concentric core–shell morphology may introduce further uncertainty. Consequently, these assumptions may affect the absolute values of the retrieved coating thickness, MR, and the classification of particles close to the operational MR = 3 threshold. These uncertainties should therefore be considered when interpreting the quantitatively derived coating properties. The parameter sensitivity was further evaluated by varying the MR threshold, coating density, and MAC_{fresh}. For each parameter combination, $MAC_{C\text{-}S\text{-}like}$ and $F_{C\text{-}S\text{-}like}$ were recalculated, and the daytime and nighttime rates were derived. As shown in Fig. 9, the derived rates varied with the MR threshold, coating density, and MAC_{fresh}. The nearly vertical contours in the daytime panels indicate a stronger sensitivity to MAC_{fresh}, reflecting the larger daytime variation in $F_{C\text{-}S\text{-}like}$. In contrast, the nighttime rates were more sensitive to coating density, likely because density-induced changes in MR resulted in stronger reclassification of particles near the prescribed threshold. The sensitivity results are summarized in the boxplots (Fig. 9d and h), with daytime and nighttime $R_{MAC,C\text{–}S\text{-}like}$ values of 0.51 ± 0.11 and 0.36 ± 0.05 $m^2\ g^{-1}\ h^{-1}$, respectively.

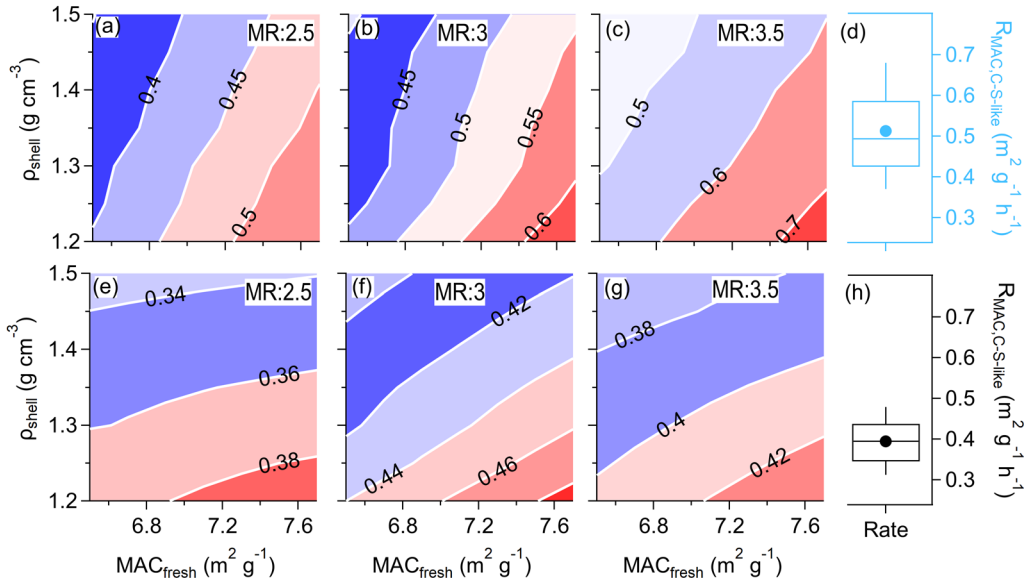


Fig .9

6. **The fresh-BC MAC baseline of 7.13 $m^2\ g^{-1}$ is important and should be treated more cautiously.** The manuscript estimates a fresh-BC MAC by extrapolating the relationship between MAC and the fraction of thickly coated particles to zero thickly coated fraction. This value is then used as the baseline in Eq. 4 to estimate excess absorption due to aging. Because this baseline directly affects the inferred absorption enhancement and the subsequent MAC calculations for thickly coated BC, the uncertainty in this value should be discussed more explicitly.

   The intercept-based fresh-BC MAC is an empirical estimate, not a direct measurement of freshly emitted BC. The authors should provide the uncertainty in the intercept and discuss how sensitive the derived b_{Eabs}, $MAC_{thickly}$, and enhancement rates are to the choice of baseline MAC. This is

especially important because the reported diurnal MAC changes are relatively modest, on the order of 0.8–1.0 $m^2\ g^{-1}$.

Response: We thank the reviewer for this important comment. The value of 7.13 $m^2\ g^{-1}$ was obtained from the intercept of the empirical relationship between MAC and the fraction of thickly coated BC particles, and therefore represents an extrapolated fresh-BC-equivalent MAC rather than a direct measurement of freshly emitted BC.

We have therefore revised the manuscript in two respects. First, we now report the 95% confidence interval of the regression intercept. The intercept-derived MAC_{fresh} is 7.13 $m^2\ g^{-1}$, with a 95% confidence interval of 6.57–7.78 $m^2\ g^{-1}$. We have also clarified that this value should be interpreted as an empirical fresh-BC-equivalent MAC baseline rather than a direct measurement of the MAC of nascent BC.

We have accordingly expanded the uncertainty discussion and revised the manuscript to emphasize the empirical nature of MAC_{fresh}. The revised text reads as follows:

The fresh-emission trajectory (black arrow), in which absorption and rBC mass increase proportionally, was defined using an empirical fresh-BC-equivalent MAC baseline (MAC_{fresh}). This baseline was obtained by extrapolating the empirical relationship between MAC and the fraction of thickly coated BC particles to a zero thickly coated fraction. The resulting MAC_{fresh} was 7.13 $m^2\ g^{-1}$, with a 95% confidence interval of 6.57–7.78 $m^2\ g^{-1}$. This value is comparable in magnitude to previously reported MAC values for fresh or uncoated BC, including 6.5 ± 0.5 $m^2\ g^{-1}$ at 532 nm in urban Shenzhen (Lan et al., 2013), 7.5 ± 1.2 $m^2\ g^{-1}$ at 550 nm for uncoated carbonaceous particles (Bond and Bergstrom, 2006), and 8.0 ± 0.7 $m^2\ g^{-1}$ at 550 nm for freshly emitted BC (Asmi et al., 2025). Although these values were obtained under different measurement conditions and definitions of fresh BC, their comparable magnitudes provide useful context for the empirical baseline derived here.

Second, we evaluated the sensitivity of the subsequent calculations to this baseline by recalculating b_{Eabs}, $MAC_{C\text{-}S\text{-}like}$, and the apparent rates of change in the MAC of core--shell-like BC using the lower and upper bounds of the 95% confidence interval (6.57-7.78 $m^2\ g^{-1}$). The resulting sensitivity of the derived rates is discussed in our response to Comment 5.

7. **The optical enhancement "rates" should be framed as apparent rates rather than intrinsic process-specific rates.**The manuscript reports nighttime and daytime MAC enhancement rates and attributes them to nighttime heterogeneous aging and daytime photochemical aging, respectively. However, the observed bulk optical evolution is also influenced by emissions, dilution, PBL evolution, and removal processes. The authors acknowledge that removal cannot be fully isolated, but the language in the conclusions still implies a stronger process-level attribution than the measurements can support.

   I suggest referring to these as "apparent" or "campaign-specific" enhancement rates associated with the observed nighttime and daytime periods. The authors should avoid implying that these

are intrinsic kinetic rates of nitrate-driven or photochemical aging unless additional process-level constraints are provided.

Response: We thank the reviewer for this important comment. We agree that the reported MAC enhancement rates should not be interpreted as intrinsic kinetic rates of specific aging processes.

We have therefore revised the terminology throughout the manuscript, including the Results and Conclusions, to refer to these values as "apparent MAC enhancement rates" or "campaign-specific apparent enhancement rates." We have also revised the corresponding discussion to avoid directly attributing the nighttime and daytime rates to individual aging mechanisms. Instead, the reported rates are now interpreted as the net apparent changes in MAC observed during the respective nighttime and daytime periods under the specific atmospheric conditions of this campaign. Nighttime heterogeneous chemistry and daytime photochemical processing are discussed only as potential contributors to these observed changes rather than as uniquely identified processes controlling the enhancement rates:

*It should be emphasized that these rates are **campaign-specific estimates** derived from the temporal changes in MAC observed during this campaign and evaluated over the empirical parameter ranges considered in the sensitivity analysis.*
*These values represent **campaign-specific apparent rates** for core--shell-like BC during the selected urban episode.*

8. **The BrC correction at 532 nm should be summarized more clearly in the main text.**The MAC is calculated from PAX absorption at 532 nm divided by SP2-derived rBC mass. The authors correctly note that brown carbon may also absorb at 532 nm and that a correction was applied, with details in the Supporting Information. Because the paper's conclusions depend on relatively subtle MAC changes, the main text should include enough information for the reader to evaluate whether residual BrC absorption could influence the reported diurnal trends.
At minimum, the authors should briefly summarize the correction method, its magnitude, and whether the correction varies systematically between daytime and nighttime. This is particularly relevant because daytime photochemical aging and organic aerosol formation could plausibly affect BrC absorption.

Response: We thank the reviewer for this helpful suggestion. We have therefore expanded Section 2.4 to summarize the BrC correction method, the magnitude of the correction, and its diurnal characteristics.

Briefly, following Cappa et al. (2019), we estimated the absorption attributable to coated BC using the rBC mass concentration, the fresh-BC-equivalent MAC baseline, and the MR-dependent absorption enhancement. The difference between the measured total absorption and the estimated BC absorption was then used to estimate the potential BrC contribution at 532 nm. During daytime, the estimated BrC contribution accounted for 2-9% of the measured absorption, corresponding to a MAC correction of 0.25-1.15 $m^2 g^{-1}$.

Given that some BrC is known to absorb at 532 nm (Zhai et al., 2025) and measurements at longer wavelengths were unavailable, we adopted the method proposed by Cappa et al. (2019) to isolate the BrC contribution from the total absorption. First, the relative coating thickness of individual

rBC particles was inferred based on the time lag between the peaks of the incandescence and scattering signals recorded by the SP2. Particles exhibiting a lag time greater than 2 μs were classified as thickly coated (Fig. S5a). Assuming that freshly emitted BC corresponds to a thinly coated population under ambient conditions, the intercept of the MAC obtained by extrapolating to a zero fraction of thickly coated particles was interpreted as the MAC of fresh BC (Lan et al., 2013), yielding a value of 7.13 $m^2\ g^{-1}$, with a 95% confidence interval of 6.57–7.78 $m^2\ g^{-1}$ (Fig. S5b). The apparent absorption enhancement for each hourly interval was calculated as:

$$b_{abs,BrC} = b_{abs,obs} - b_{abs,BC} = b_{abs,obs} - MAC_{BC,fresh} \cdot E_{abs}(MR) \cdot [rBC]$$

where $b_{abs,BrC}$, $b_{abs,obs}$, and $b_{abs,BC}$ are the absorption by BrC, the observed absorption, and the estimated absorption for coated BC particles, respectively. The resulting $b_{abs,BrC}$ estimates were subsequently averaged by hour of day to obtain a mean diurnal profile (Fig. 1b). When calculating the MAC of rBC, the mean $b_{abs,BrC}$ over the predefined daytime period was subtracted from the observed absorption during the corresponding daytime hours, after which the MAC was recalculated using the adjusted absorption coefficient. During daytime, the estimated BrC contribution accounted for 2–9% of the measured absorption, corresponding to a MAC correction of 0.25–1.15 $m^2\ g^{-1}$. In contrast, because high rBC concentrations dominate the optical absorption at night and yield physically meaningless negative $b_{abs,BrC}$ values (Fig. 1b), the BrC contribution was not further corrected during nighttime. These negative values indicate that the nighttime BrC contribution could not be robustly resolved and was likely minor relative to BC absorption. This treatment does not imply the absence of nighttime BrC absorption, and the daytime correction should be regarded as a model-dependent adjustment. All optical and single-particle measurements were averaged to the same hourly time resolution before regression analysis and diurnal averaging.

9. **The "natural chamber" framing should be used with caution.**The selected period appears to be relatively dominated by local emissions and minimally affected by long-range transport, which makes it useful for studying diurnal aging. However, the term "natural chamber" may give the impression of a more closed system than is warranted. The period still includes strong diurnal variations in emissions, boundary-layer dynamics, non-zero wind speed, dilution, and removal. I suggest either softening this language or explicitly acknowledging the limitations of the analogy.

   Response: We appreciate the reviewer's careful comment. We agree that the term "natural chamber'" may overstate the degree to which the selected period represents a closed system. To avoid this ambiguity, we have softened the wording and no longer describe the period as a closed system. Instead, we now refer to it as a period with relatively weak regional transport influence, which provides a useful observational window for examining local diurnal aging processes:

Characterized by consistent diurnal variations in both meteorology and pollutants, relatively weak long-range transport, and traffic-dominated BC emissions, this episode provided a useful observational window for examining local diurnal BC aging processes.

Minor comments and technical corrections

1. In Section 2.2, where the rBC core refractive index m = 2.26 + 1.26i is introduced, please specify the wavelength. It should also be clear that this refractive index is used in the SP2 coating retrieval and not in the 532 nm PAX-based MAC analysis.

   Response: Thank you for pointing this out. We have clarified in Sect. 2.2 that the rBC core refractive index of m = 2.26 + 1.26i corresponds to the SP2 laser wavelength of 1064 nm and is used specifically for the SP2 coating-thickness retrieval. This refractive index is not used in the 532 nm PAX-based MAC analysis. The revised text reads as follows:

   The total particle diameter (D_p) was then derived by applying the measured D_c and reconstructed scattering signal to a core-shell Mie model, assuming a complex refractive index of m = 2.26 + 1.26i for the rBC core (Moteki et al., 2010) and m = 1.50 + 0i for the coating material (Laborde et al., 2012) at 1064 nm.

2. In Eq. 4, the asterisk should be replaced by a proper multiplication sign or centered dot.

   Response: Thank you for this comment. The asterisk in Eq. 4 has been replaced by a centered dot.

3. Figure 1: Please explain C1, C2, and C3 in the figure caption. The reader should not have to infer from the text that these refer to trajectory clusters.

   Response: Thank you for this suggestion. We have clarified the figure caption by explicitly defining C1, C2, and C3 as trajectory clusters.

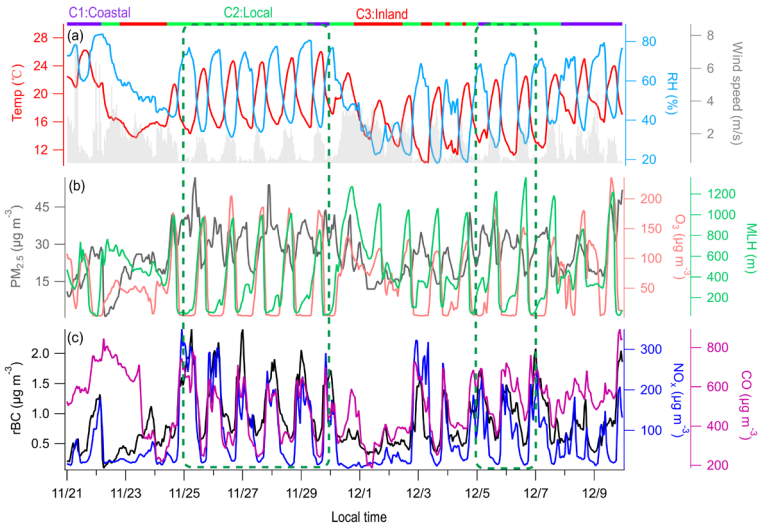


Fig. 2

4. Figure 2: It would be useful to know whether the diurnal variations shown are robust when the data are split by the trajectory clusters C1, C2, and C3, or at least whether the selected local-emissions period behaves similarly to the full-period diurnal average. If the main conclusions are based on the C2/local period, this should be made visually and methodologically clear.

Response: We thank the reviewer for this helpful suggestion. Following the reviewer's suggestion, we added a supplementary figure comparing the diurnal variations during the selected local-emissions period with those averaged over the full campaign. This comparison provides a direct assessment of whether the key diurnal patterns identified during the selected period are also evident in the full dataset. We have also clarified in the revised manuscript that the mechanistic discussion focuses primarily on the selected local-emissions period. The revised text reads as follows:

To evaluate the representativeness of the selected period, we further compared its diurnal variations with the full-campaign average (Figs. 3 and S6). The selected period showed generally consistent timing and direction of the key diurnal variations observed over the full campaign, whereas the full-period data exhibited greater variability, likely reflecting the influence of air masses associated with different trajectory clusters. These similarities suggest that the key diurnal patterns were not unique to the selected period, while the local-emissions subset provided a less heterogeneous observational context for examining daytime and nighttime BC evolution.

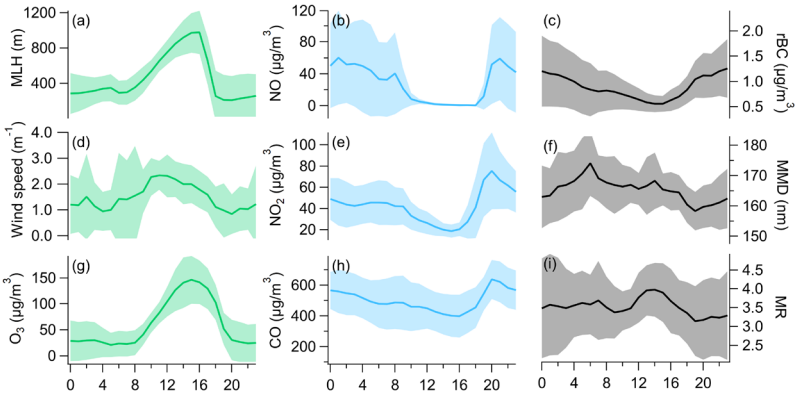


Fig. S6

5. Figure 6: Please define the blue symbols in the caption and/or legend.

Response: Thanks for pointing this out. We have revised the caption of Fig. 6 and added a legend to clearly define the symbols. The black, blue, and gray symbols represent the nighttime aging period, daytime photochemical aging period, and other periods, respectively:

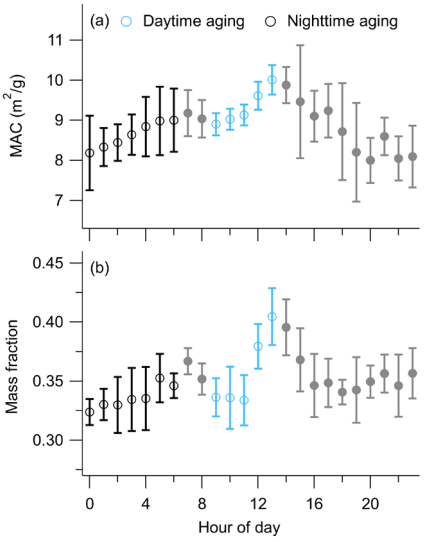


Fig. 7

6. The reported MAC values and MAC enhancement rates should be put into context with previous studies. For example, how do the inferred fresh-BC MAC, observed MAC range, and enhancement rates compare with prior urban SP2/PAX or SP2/photoacoustic studies?

Response: We thank the reviewer for this helpful suggestion. In the revised manuscript, we have added comparisons with previous studies using SP2 combined with PAX or other photoacoustic absorption measurements:

The diurnal aging of BC observed during the sampling period was accompanied by corresponding changes in its optical properties. As shown in Fig. 6a, the MAC reached a minimum of approximately 8.1 m^2 g^{-1} at 22:00 LT. Thereafter, it increased by approximately 0.8 m^2 g^{-1} overnight, reaching 8.9 m^2 g^{-1} by 06:00 LT. A comparable enhancement occurred during the daytime photochemically active period, when MAC increased by approximately 1.0 m^2 g^{-1}, from 8.9 to 9.9 m^2 g^{-1}. The observed MAC range of 8.1–9.9 m^2 g^{-1} falls within the range previously reported for urban BC. At a wavelength of 532 nm, Lan et al. (2013) reported MAC values of 5.0–8.5 m^2 g^{-1} in summertime Shenzhen. A higher campaign-average MAC of 14.6 ± 5.6 m^2 g^{-1} was reported for urban Xi'an using an SP2–PAX system (Wang et al., 2017). In urban Beijing, Liu et al. (2019) further showed that the modeled MAC at 550 nm varied substantially with BC mixing state, ranging from approximately 5.3–7.3 m^2 g^{-1} for largely uncoated or thinly coated BC to 11.2–12.4 m^2 g^{-1} for moderately or thickly coated BC. Overall, the observed MAC values fall within the range reported for urban BC across previous studies.

The daytime apparent MAC enhancement rate of 0.59 m^2 g^{-1} h^{-1} obtained in this study is very close to the daytime rate of 0.60 m^2 g^{-1} h^{-1} reported by Wang et al. (2017) in Xi'an:

This daytime rate is nearly identical to the increase of 0.60 m^2 g^{-1} h^{-1} reported for urban Xi'an during a daytime photochemical period by Wang et al. (2017). More broadly, Peng et al. (2016) showed that the BC absorption enhancement factor could reach approximately 2.4 within about 5 h in Beijing and 18 h in Houston, indicating that substantial optical evolution can occur over timescales of several hours under polluted urban conditions. Similar diurnal optical evolution was also observed in urban Guangzhou, where Sun et al. (2020) reported afternoon enhancement of E_{abs} during the dry season associated with photochemical aging, as well as elevated nighttime

E_{abs} during the wet season. Although these metrics are not directly equivalent, they collectively provide useful context for the campaign-specific apparent enhancement rates derived here.

7. The manuscript should be careful with wording such as "direct observational evidence" when the conclusion depends on multiple inferred quantities, including coating thickness from LEO fitting, MR from assumed densities and core–shell geometry, and BrC-corrected MAC from bulk absorption.

   Response: Thanks for this important comment. To avoid overstatement, we have revised the manuscript by replacing ``direct observational evidence" with more cautious wording:

   This study provides observationally constrained insights into the contrasting diurnal evolution of BC mixing state and optical properties and quantifies the campaign-specific apparent MAC enhancement rates under urban atmospheric conditions.

8. Some statements would benefit from being changed from causal to observational language. For example, "BC enhances sulfate formation" could be revised to "BC-containing particles showed enhanced sulfate signals" unless the causal mechanism is directly demonstrated.

   Response: We thank the reviewer for this suggestion. We agree that the original wording implied a causal mechanism that was not directly demonstrated. We have therefore revised the relevant statements throughout the manuscript:

   This distinct enhancement indicates that BC-containing particles exhibited stronger sulfate signals, suggesting preferential sulfate accumulation on these particles and possibly reflecting the influence of BC-involved photochemistry.

9. Please clarify whether the MR > 3 threshold from Liu et al. (2017) is expected to apply quantitatively to this dataset, source region, and SP2 retrieval approach, or whether it is used only as a qualitative indicator of thick coating.

   Response: We thank the reviewer for this suggestion. In the present study, the MR (>3) threshold is not regarded as a universal quantitative boundary. Instead, it is used as a qualitative indicator to identify BC-containing particles that have entered a highly coated regime with the potential for significant lensing-induced absorption enhancement. Liu et al. (2017) showed that particles with MR (>3) exhibited scattering behavior well represented by the core-shell model. Although this criterion was originally established using CPMA-SP2 measurements, subsequent studies have applied it within SP2 LEO-based MR retrieval frameworks incorporating the Liu et al. (2017) parameterization (Taylor et al. 2020, Wu et al. 2021), supporting its use in the present analysis. We have revised the manuscript to explicitly clarify that MR (>3) is used here only as a qualitative classification criterion, rather than as a universal quantitative threshold:

   Although the daytime increase occurred over a shorter period than the nighttime increase, the comparable net enhancements in MAC during both periods indicate that multiple atmospheric processes jointly influenced the evolution of BC optical properties. BC particles in the early stages of aging exhibit negligible light absorption enhancement, however, as aging proceeds and a core-shell morphology develops, coating-induced lensing can substantially enhance their light absorption. Following Liu et al. (2017), MR > 3 was used as a qualitative indicator to identify

highly coated BC-containing particles whose optical behavior is consistent with a core–shell morphology. The mass fraction of rBC associated with these particles was calculated as:

$$F_{C-S-like} = \frac{\sum_{i,MR>3} m_{rBC,i}}{\sum_i m_{rBC,i}}$$

Here, $m_{rBC,i}$ denotes the rBC mass of the single particle, and $F_{C-S-like}$ represents the fraction of total rBC mass associated with particles classified as core–shell-like. The MR > 3 threshold was used only for particle classification, while $F_{C-S-like}$ represents the quantitatively calculated fraction of total rBC mass carried by particles within this highly coated regime. As shown in Fig. 6b, the $F_{C-S-like}$ increased from 0.32 to 0.35 during the night, decreased to 0.32 following the morning rush hour, and subsequently rose to 0.40 after daytime photochemical aging. Notably, the magnitude of this diurnal change is substantially larger than the observed day–night variation in bulk MAC.

10. The manuscript would benefit from a concise uncertainty paragraph summarizing the main uncertainties in the derived quantities: rBC mass calibration, coating thickness, MR, BrC correction, fresh-BC MAC baseline, and inferred enhancement rates. I do not necessarily expect a comprehensive uncertainty propagation, but the manuscript should include a clearer qualitative or semi-quantitative discussion of the dominant uncertainties affecting the SP2-derived coating thickness/MR and the inferred MAC enhancement rates.

Response: We thank the reviewer for this helpful suggestion. A sensitivity analysis has been added to the revised manuscript (Fig. 9). The apparent MAC enhancement rates were recalculated using different values of MAC_{fresh}, coating density, and MR threshold:

The coating thickness and MR derived from the SP2 LEO-fit analysis should be regarded as model-dependent estimates rather than directly measured quantities. The assumed rBC refractive index (m = 2.26 + 1.26i at 1064 nm) is used specifically for the SP2 scattering retrieval and is distinct from the optical parameters used for the 532 nm measurements. The retrieved coating thickness is sensitive to assumptions regarding the refractive indices of the rBC core and coating, while the calculated MR additionally depends on the assumed core and coating densities. Deviations from the idealized concentric core–shell morphology may introduce further uncertainty. Consequently, these assumptions may affect the absolute values of the retrieved coating thickness, MR, and the classification of particles close to the operational MR = 3 threshold. These uncertainties should therefore be considered when interpreting the quantitatively derived coating properties. The parameter sensitivity was further evaluated by varying the MR threshold, coating density, and MAC_{fresh}. For each parameter combination, $MAC_{C\text{-}S\text{-}like}$ and $F_{C\text{-}S\text{-}like}$ were recalculated, and the daytime and nighttime rates were derived. As shown in Fig. 9, the derived rates varied with the MR threshold, coating density, and MAC_{fresh}. The nearly vertical contours in the daytime panels indicate a stronger sensitivity to MAC_{fresh}, reflecting the larger daytime variation in $F_{C\text{-}S\text{-}like}$. In contrast, the nighttime rates were more sensitive to coating density, likely because density-induced changes in MR resulted in stronger reclassification of particles near the prescribed threshold. The sensitivity results are summarized in the boxplots (Fig. 9d and h), with daytime and nighttime $R_{MAC,C\text{–}S\text{-}like}$ values of 0.51 ± 0.11 and 0.36 ± 0.05 m2 g^{-1} h^{-1}, respectively.

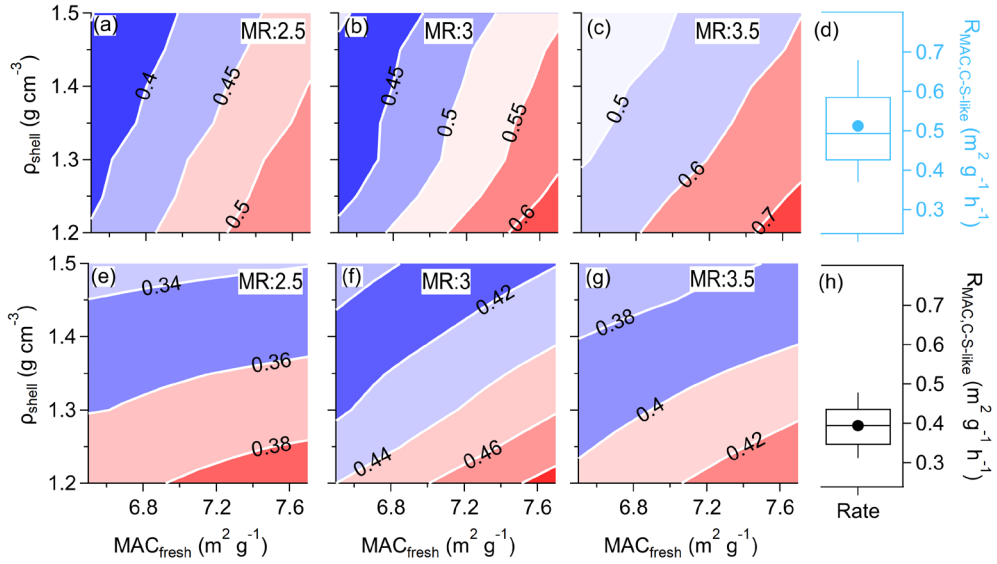

(a)
MR:2.5
0.4
0.45
0.5
(b)
MR:3
0.45
0.5
0.55
0.6
(c)
MR:3.5
0.5
0.6
0.7
(d)
(e)
MR:2.5
0.34
0.36
0.38
(f)
MR:3
0.42
0.44
0.46
(g)
MR:3.5
0.38
0.4
0.42
(h)
Rate
ρshell (g cm-3)
MACfresh (m2 g-1)
RMAC,C-S-like (m2 g-1 h-1)

Fig .9

Anonymous Referee #2

This manuscript presents integrated SP2, SPAMS, and PAX observations to examine diurnally contrasting black-carbon aging pathways and their optical consequences in urban Shenzhen. The topic is important, the combined single-particle physical and chemical measurements are valuable, and the attempt to quantify separate nighttime and daytime MAC enhancement rates under ambient conditions is a clear strength. Overall, the study is scientifically valuable and largely convincing. I suggest that the authors make a minor revision to better quantify the uncertainty of the optical interpretation, clarify several methodological details, and slightly temper a few mechanistic statements. These revisions would improve the robustness and broader usefulness of the manuscript without changing its main conclusions.

Response: We sincerely thank the reviewer for the constructive and insightful comments on our manuscript and for recognizing the value of this work. We have carefully considered each comment and revised the manuscript accordingly, with particular attention to the uncertainties associated with the optical interpretation, methodological clarification, and the wording of mechanistic interpretations. Our point-by-point responses and the corresponding revisions are provided below:

1. The daytime and nighttime MAC enhancement rates are important and useful. Because the calculation depends on the fresh-BC MAC, MR > 3 threshold, f_{coated}, and the regression method used to separate aging from fresh emissions, please provide a brief discussion on uncertainty or sensitivity analysis. This does not need to be extensive, but it would make the reported 0.34 and 0.59 $m^2\ g^{-1}\ h^{-1}$ rates more useful for comparison with other studies.

   Response: We thank the reviewer for this helpful suggestion. We agree that the apparent MAC enhancement rates should be interpreted with the assumptions involved in their derivation. We have therefore added a sensitivity analysis in the revised manuscript (Fig. 9) to evaluate the influence of several key parameters on the derived apparent MAC enhancement rates. Specifically, we recalculated the rates using alternative values of the empirical MAC_{fresh} baseline, coating density, and the operational MR threshold used to classify highly coated BC particles. The coating-density assumption affects the derived MR and consequently the calculated fraction of highly coated BC.

   The coating thickness and MR derived from the SP2 LEO-fit analysis should be regarded as model-dependent estimates rather than directly measured quantities. The assumed rBC refractive index (m = 2.26 + 1.26i at 1064 nm) is used specifically for the SP2 scattering retrieval and is distinct from the optical parameters used for the 532 nm measurements. The retrieved coating thickness is sensitive to assumptions regarding the refractive indices of the rBC core and coating, while the calculated MR additionally depends on the assumed core and coating densities. Deviations from the idealized concentric core–shell morphology may introduce further uncertainty. Consequently, these assumptions may affect the absolute values of the retrieved coating thickness, MR, and the classification of particles close to the operational MR = 3 threshold. These uncertainties should therefore be considered when interpreting the quantitatively derived coating properties. The parameter sensitivity was further evaluated by varying the MR threshold, coating density, and MAC_{fresh}. For each parameter combination, $MAC_{C\text{-}S\text{-}like}$ and $F_{C\text{-}S\text{-}}$

$_{like}$ were recalculated, and the daytime and nighttime rates were derived. As shown in Fig. 9, the derived rates varied with the MR threshold, coating density, and MAC_{fresh}. The nearly vertical contours in the daytime panels indicate a stronger sensitivity to MAC_{fresh}, reflecting the larger daytime variation in $F_{C\text{-}S\text{-}like}$. In contrast, the nighttime rates were more sensitive to coating density, likely because density-induced changes in MR resulted in stronger reclassification of particles near the prescribed threshold. The sensitivity results are summarized in the boxplots (Fig. 9d and h), with daytime and nighttime $R_{MAC,C\text{–}S\text{-}like}$ values of 0.51 ± 0.11 and 0.36 ± 0.05 $m^2\ g^{-1}\ h^{-1}$, respectively.

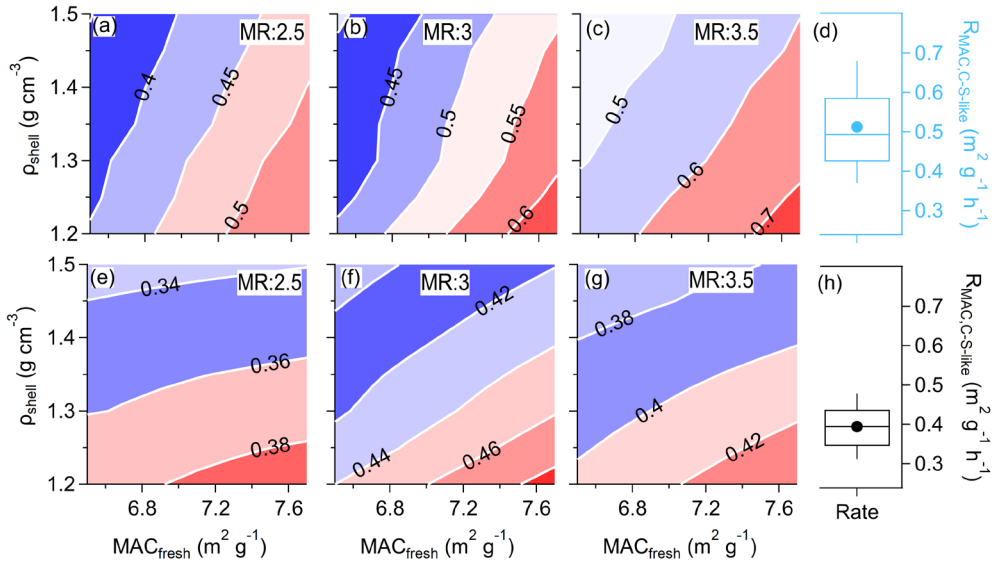


Fig .9

2. The manuscript states that MAC values were adjusted to reduce BrC influence, with details in the Supplement. Since the optical result is central to the paper, please briefly summarize the correction method and its likely magnitude in the main text. If the BrC contribution is small during the selected period, a simple quantitative statement would be sufficient.

Response: We thank the reviewer for this helpful suggestion. We have therefore expanded Section 2.4 to summarize the BrC correction method, the magnitude of the correction, and its diurnal characteristics.

Given that some BrC is known to absorb at 532 nm (Zhai et al., 2025) and measurements at longer wavelengths were unavailable, we adopted the method proposed by Cappa et al. (2019) to isolate the BrC contribution from the total absorption. First, the relative coating thickness of individual rBC particles was inferred based on the time lag between the peaks of the incandescence and scattering signals recorded by the SP2. Particles exhibiting a lag time greater than 2 μs were classified as thickly coated (Fig. S5a). Assuming that freshly emitted BC corresponds to a thinly coated population under ambient conditions, the intercept of the MAC obtained by extrapolating to a zero fraction of thickly coated particles was interpreted as the MAC of fresh BC (Lan et al., 2013), yielding a value of 7.13 $m^2\ g^{-1}$, with a 95% confidence interval of 6.57–7.78 $m^2\ g^{-1}$ (Fig. S5b). The apparent absorption enhancement for each hourly interval was calculated as:

$$b_{abs,BrC} = b_{abs,obs} - b_{abs,BC} = b_{abs,obs} - MAC_{BC,fresh} \cdot E_{abs}(MR) \cdot [rBC]$$

where $b_{abs,BrC}$, $b_{abs,obs}$, and $b_{abs,BC}$ are the absorption by BrC, the observed absorption, and the estimated absorption for coated BC particles, respectively. The resulting $b_{abs,BrC}$ estimates were subsequently averaged by hour of day to obtain a mean diurnal profile (Fig. 1b). When calculating the MAC of rBC, the mean $b_{abs,BrC}$ over the predefined daytime period was subtracted from the observed absorption during the corresponding daytime hours, after which the MAC was recalculated using the adjusted absorption coefficient. During daytime, the estimated BrC contribution accounted for 2–9% of the measured absorption, corresponding to a MAC correction of 0.25–1.15 $m^2 g^{-1}$. In contrast, because high rBC concentrations dominate the optical absorption at night and yield physically meaningless negative $b_{abs,BrC}$ values (Fig. 1b), the BrC contribution was not further corrected during nighttime. These negative values indicate that the nighttime BrC contribution could not be robustly resolved and was likely minor relative to BC absorption. This treatment does not imply the absence of nighttime BrC absorption, and the daytime correction should be regarded as a model-dependent adjustment. All optical and single-particle measurements were averaged to the same hourly time resolution before regression analysis and diurnal averaging.

3. BC absorption enhancement remains a major source of uncertainty in aerosol radiative forcing estimates, while recent modeling studies have made important progress in constraining BC optical properties in global models. For example, Chen et al. (2023, https://doi.org/10.1029/2022MS003501) developed an aerosol optical module with observation-constrained BC properties for global climate models. Given the observational enhancement rates reported here, the authors may briefly discuss whether and how these results could inform numerical model optimization, such as constraints on aging timescales, coating-dependent MAC enhancement, or diurnal parameterizations of BC optical properties.

   Response: We thank the reviewer for this constructive suggestion. We agree that our observations may provide useful constraints for evaluating and improving model representations of the evolution of BC mixing state and optical properties. We have therefore added a brief discussion of the potential implications of our results for numerical modeling, with reference to recent observation-constrained modeling efforts such as Chen et al. (2023).

   We emphasize, however, that the daytime and nighttime enhancement rates reported here are campaign-specific apparent rates that reflect the combined influence of atmospheric aging, emissions, dilution, transport, boundary-layer dynamics, and removal processes. They should therefore not be directly prescribed as universal kinetic aging rates in models. Instead, the observed diurnal evolution of BC coating state and MAC, together with their characteristic timescales and coating-dependent optical changes, may serve as observational benchmarks for evaluating whether models can reproduce the magnitude and timing of BC optical evolution under urban conditions. We have added the following discussion to the revised manuscript:

BC optical properties evolve nonlinearly as particle morphology and composition change during atmospheric aging (Wang et al. 2021a). These observations may also provide useful constraints for evaluating model representations of BC aging and optical evolution. Recent modeling studies have incorporated observation-constrained BC mixing-state and optical properties to improve estimates of BC radiative effects (Chen et al., 2023). In this context, the observed diurnal evolution of BC coating state and MAC can provide benchmarks for evaluating whether models reproduce the characteristic timescales and magnitude of BC optical changes under urban atmospheric conditions. In particular, the contrasting daytime and nighttime evolution highlights the potential importance of representing temporally varying aging environments rather than assuming a single constant aging timescale. The observed relationship between BC coating state and optical enhancement may also help evaluate parameterizations linking BC mixing state to MAC.

4. The claim that BC specifically promotes sulfate formation is interesting but needs stronger support. Since SPAMS relative peak areas are semi-quantitative and detection efficiencies vary across particle types, please discuss whether the enhanced sulfate variability in BC-containing particles could be influenced by sampling or ionization biases.

   Response: We thank the reviewer for this important comment. The SPAMS relative peak areas are semi-quantitative and may be affected by particle size, matrix effects, sampling efficiency, and composition-dependent ionization efficiency. Therefore, the stronger sulfate signals observed in BC-containing particles cannot be interpreted as direct evidence that BC surfaces promote sulfate formation. We have softened the relevant statement and clarified that the observations only indicate preferential sulfate accumulation on BC-containing particles, while potential sampling and ionization biases cannot be fully excluded:

   This distinct enhancement indicates that BC-containing particles exhibited stronger sulfate signals, suggesting preferential sulfate accumulation on these particles and possibly reflecting the influence of BC-involved photochemistry.

5. Clarify whether all optical and single-particle data are averaged to the same time resolution before regression and diurnal analysis.

   Response: We thank the reviewer for this helpful comment. We have clarified in the revised Methods section that all optical and single-particle datasets were averaged to the same hourly time resolution before the regression and diurnal analyses. The revised text reads as follows:

   All optical and single-particle measurements were averaged to the same hourly time resolution before regression analysis and calculation of the diurnal averages.

6. Several wording issues should be corrected, for example 'exhibt', 'that that', 'removing processes', and 'changes in the MR provides'.

   Response: Thank you for pointing out these wording issues. We have corrected all the wording issues noted. Specifically, the typo “exhibt” was corrected and the sentence was rephrased, the

duplicated “that that” was removed, “removing processes” was replaced with “removal processes”, and “changes in the MR provides” was corrected to “changes in the MR provide”.

7. The conclusion should state more explicitly that the reported rates mainly apply to thickly coated BC under the selected urban episode.

   Response: We thank the reviewer for this helpful comment. The conclusion has been revised to clarify that the reported rates apply specifically to BC classified as core--shell-like using the prescribed MR threshold during the selected urban episode. Accordingly, the rate is now denoted as $R_{MAC,C-S-like}$, rather than as a general MAC enhancement rate for the entire BC population. We also emphasize that these values are episode-specific apparent rates and should not be interpreted as universal aging rates.

   The evolving mixing state exerted profound influences on BC optical properties, with the MAC at 532 nm increasing by ~0.8 m^2 g^{-1} overnight and ~1.0 m^2 g^{-1} during the daytime. By classifying BC particles according to the MR threshold, we tracked the MAC evolution of core–shell-like BC during the nighttime and daytime periods. The corresponding $R_{MAC,C-S-like}$ values were 0.36 ± 0.05 and 0.51 ± 0.11 m^2 g^{-1} h^{-1}, respectively. The mean daytime rate was approximately 1.4 times the nighttime rate, indicating faster optical evolution during the daytime period. These values represent campaign-specific apparent rates for core–shell-like BC during the selected urban episode. Although photochemical aging proceeds significantly faster, the comparable magnitudes of the total nocturnal and diurnal MAC increments indicate that the rapid daytime coating accumulation was partially offset by the dilution and removal of aged particles during mixing layer expansion.

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