



Supplement of

Contrasting nighttime heterogeneous and daytime photochemical aging drive the optical evolution of black carbon

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S1 PMF analysis

Positive matrix factorization (PMF), a widely used multivariate receptor model, operates under the assumption that chemical species exhibiting similar temporal trends likely originate from common sources. Owing to this principle, PMF has been extensively applied in aerosol source apportionment studies, particularly for resolving the mass contributions of individual components (Polissar et al., 1998; Reff et al., 2007).

Beyond mass concentration analysis, PMF has also proven effective in processing particle-type data obtained from mass spectrometry, offering valuable insights into emission characteristics and secondary transformation processes (Healy et al., 2015; Zhang et al., 2021). In the present study, we applied the U.S. EPA PMF 5.0 model to classify BC-containing particles based on their chemical signatures. Specifically, 11 ion markers from all detected EC particles were grouped using 60-minute averaged relative peak areas (RPAs) as input. It is worth noting that our application of PMF was not aimed at identifying distinct emission sources; instead, the goal was to cluster chemically similar markers for further interpretation.

Solutions with 2–6 factors were tested, and the results are summarized in TableS1. Across all solutions, Q_{robust} was slightly lower than Q_{true} . The 4-factor solution was ultimately selected because it exhibited high correlations between measured and predicted species concentrations ($R^2 = 0.42\text{--}0.96$) and because the factors were the most physically interpretable. The residuals for this solution ranged from -3 to 3 . F_{peak} values ranging from -1.5 to 1.5 were evaluated, and analysis of the Q values indicated that an F_{peak} of 0 provided the optimal results.

Table S1. Q values for PMF analysis with different number of factors.

# of factors	R^2 between observed and predicted species	Q_{true}	Q_{robust}
2	0.35–0.80	17173.9	13402.1
3	0.37–0.93	9657.3	8638.5
4	0.42–0.96	7061.8	6538.2
5	0.44–0.96	5344.1	4927.0
6	0.56–0.98	3521.1	3431.6

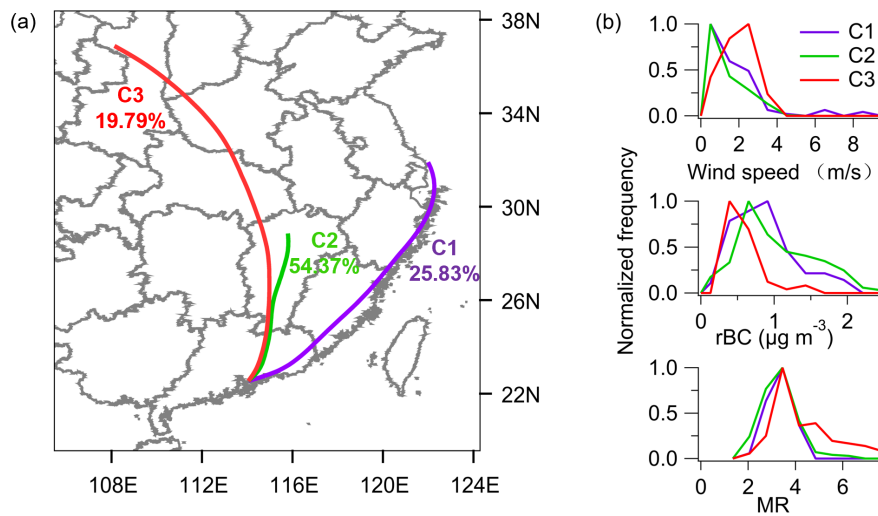


Figure S1. (a) The HYSPLIT 72-hr backward trajectory clusters ending in Shenzhen at 00:00 local time on 9 December 2021, from a height of 100 m. (b) Histograms of wind speed, rBC mass concentration and mixing ratio (MR) for each classified air mass category.

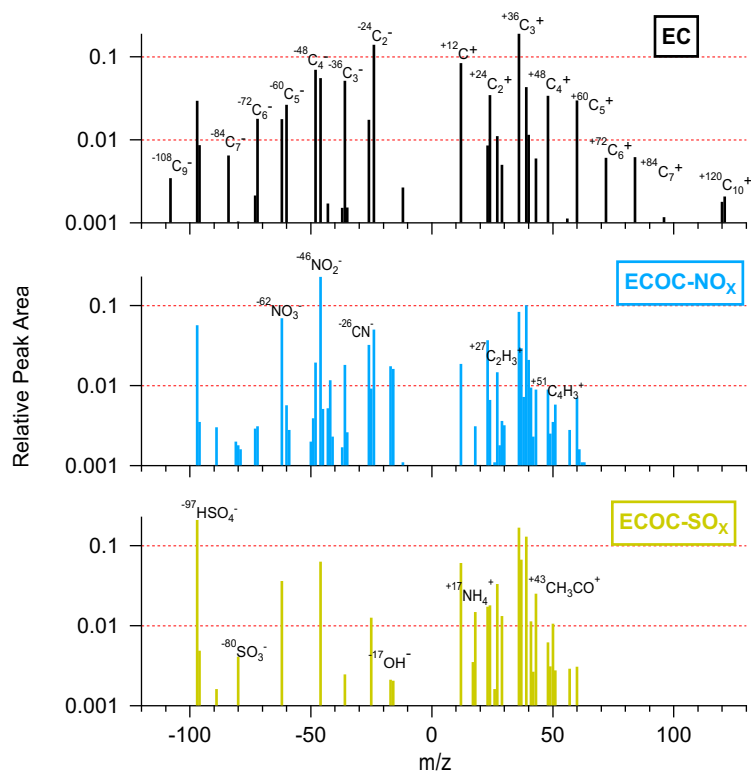


Figure S2. Averaged mass spectra for different BC-containing types of particles.

The cluster-averaged mass spectra of individual BC-containing particles are shown in Fig. S2. The EC group exhibits strong signals for elemental carbon (C_n^- and C_n^+), accompanied by relatively high signals for organic carbon (m/z 27 [$C_2H_3^+$] and m/z 29 [$C_2H_2^+$]). The ECOC- NO_x and ECOC- SO_x groups exhibit similar mass spectral patterns in terms of chemical composition, with more ion peaks than the EC group. The primary distinction between them lies in the relative intensities of the sulfate (m/z -97 [HSO_4^-]) and nitrate (m/z -46 [NO_2^-] and m/z -62 [NO_3^-]) signals.

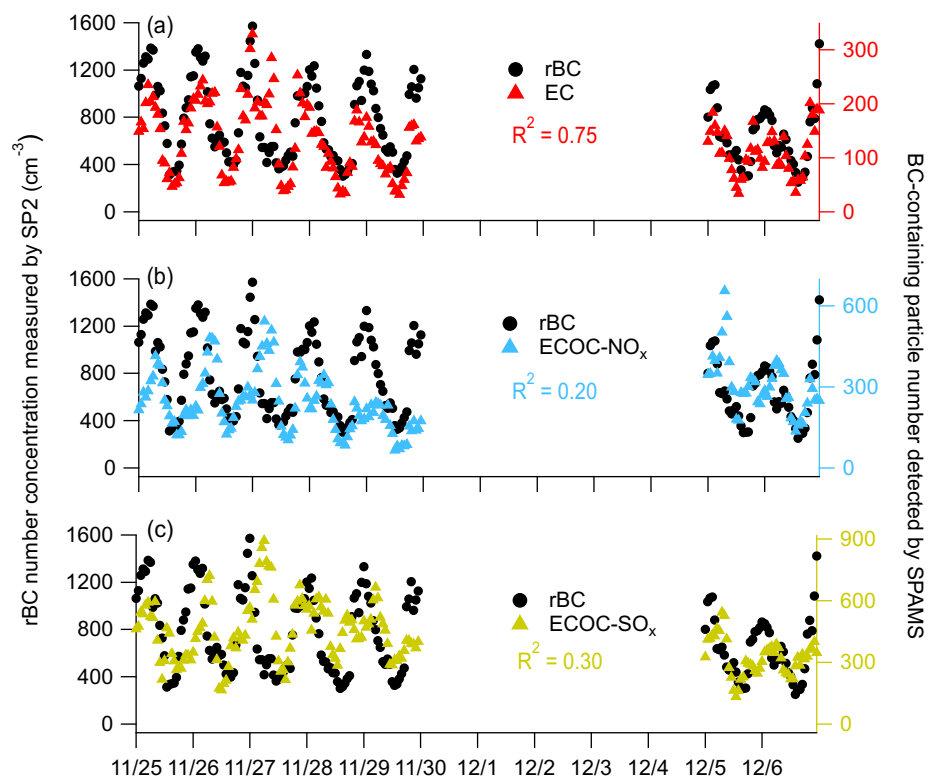


Figure S3. The comparison of SP2-detected rBC number concentration and SPAMS-detected BC containing particle number.

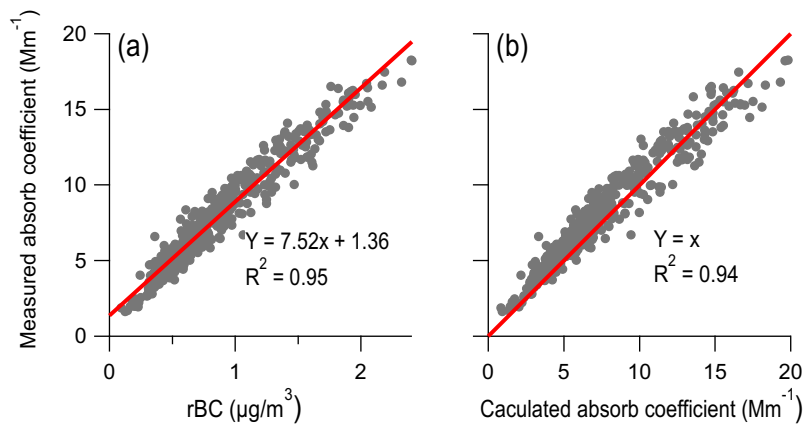


Figure S4. Relationships between the absorption coefficient measured by PAX and (a) the rBC mass concentration, and (b) the absorption coefficient calculated from SP2-measured D_c and D_p using the core-shell Mie model.

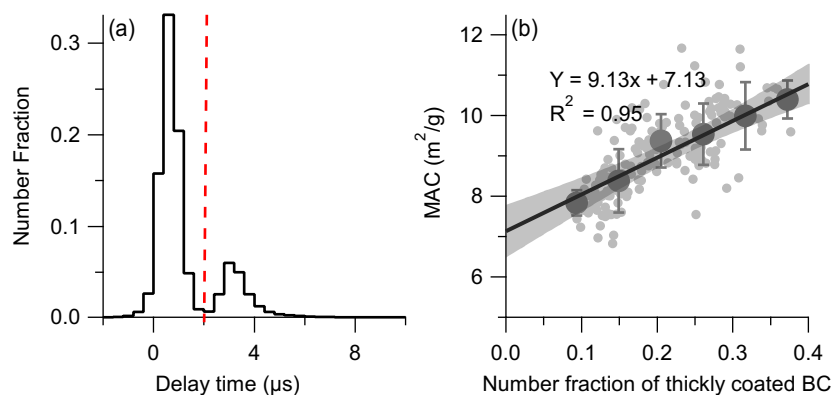


Figure S5. (a) Frequency distribution of the time lag between peak incandescence and scattering signals for individual rBC particles measured by the SP2. (b) Scatter plot showing the correlation between the fraction of thickly coated rBC particles (defined as lag time $> 2 \mu\text{s}$) and the MAC at 532 nm.

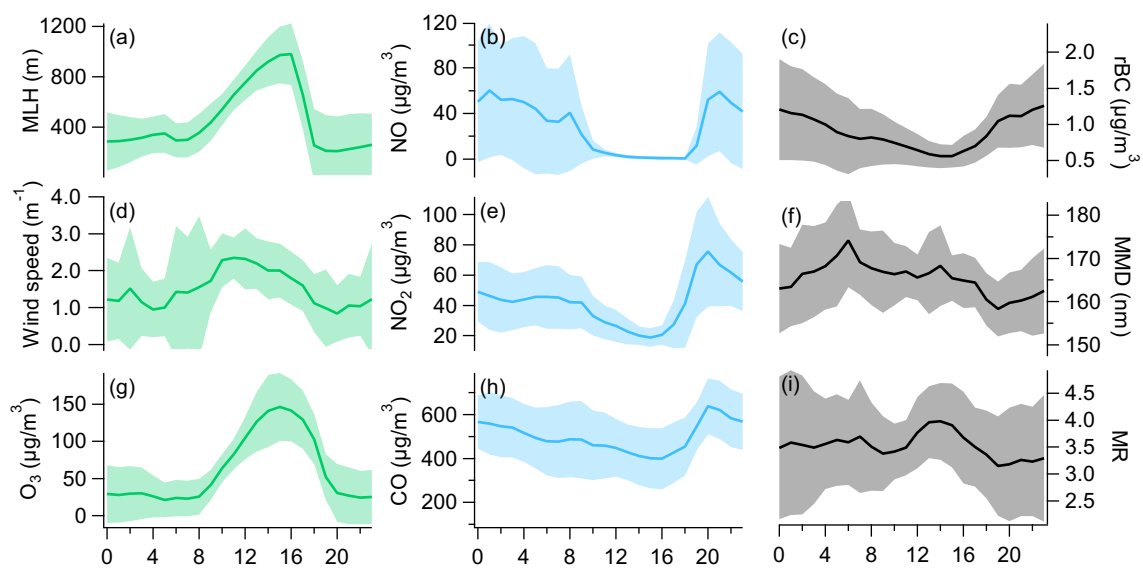


Figure S6. The diurnal variations of (a) MLH, (b) NO mass concentration, (c) rBC mass concentration, (d) wind speed, (e) NO₂ mass concentration, (f) MMD, (g) O₃ mass concentration, (h) CO mass concentration, and (i) MR. Data points denote hourly mean values, and the shaded areas represent ± 1 standard deviation.

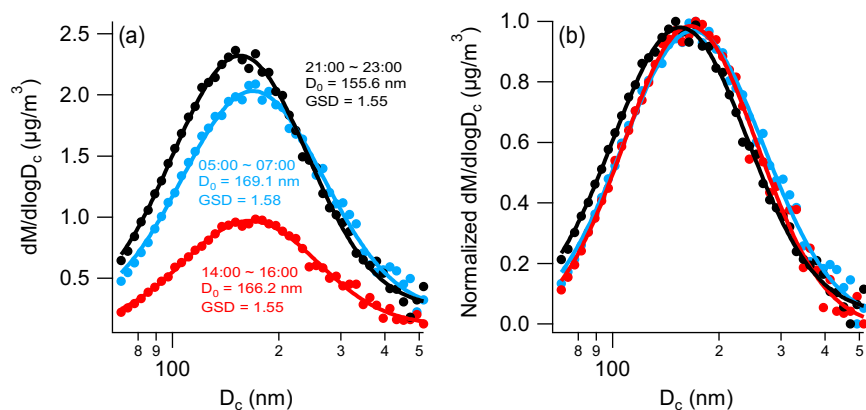


Figure S7. Measured mass size distributions of rBC cores derived from SP2 measurements. Solid lines represent lognormal fits to the observed distributions. Different colors denote different time periods: (a) Absolute mass concentrations. (b) Normalized distributions to facilitate comparison of shifts in MMD and distribution shape across time periods.

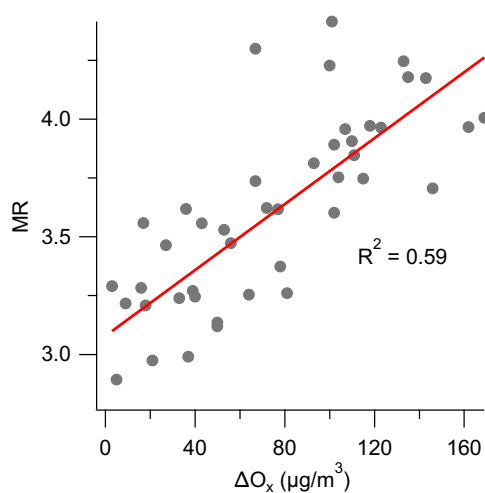


Figure S8. Correlations between MR and ΔO_x .

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