Point-by-point response to review comments

Wang et al. report the characteristics and sources of brown carbon (BrC) in the urban atmosphere of Shanghai based on comprehensive multi-instrument measurements combined with positive matrix factorization (PMF) analysis. The authors identify 15 potential BrC sources and investigate their seasonal variations and diurnal pattern. In particular, the study identifies several secondary BrC episodes and discusses their potential formation pathways and products. Overall, the manuscript presents a comprehensive dataset and applies an interesting and potentially valuable analytical approach. However, I have substantial concerns regarding the PMF analysis and, in particular, the interpretation and source attribution of individual PMF factors. The robustness of the PMF solutions and the evidence supporting the identification and formation pathways of several factors are not yet sufficiently established. These issues should be addressed carefully before the conclusions can be fully supported. Therefore, I recommend major revision. My specific comments are provided below.

Response: We thank the reviewer for the insightful comments, which have helped us improve the manuscript. Each of the questions raised by the reviewer has been addressed in detail in our point-by-point response below. Our response text is marked in blue in this document. References cited are placed at the end. Corresponding changes in the main text are also highlighted in blue.

1. *Lines 116–117: More details regarding the sampling setup should be provided, including the particle size cut, the environmental conditions surrounding the sampling site, inlet height, and other relevant information that may affect the representativeness of the measurements.*

   Response: suggestion taken; we've added the relevant information in the revised ms.

   Lines 115-120: "The sampling site is located within a complex urban environment encompassing major roadways, commercial zones, and residential neighborhoods, making it a representative receptor for from both local emissions and regional transport. The sampling inlet was positioned on the eighth floor (approximately 30 m above ground level), where ambient air was drawn through a $PM_{2.5}$ cyclone to collect particles <2.5 μm for subsequent chemical composition analysis."

2. *Line 148: What does WtC represent? Please clearly define this parameter and explain whether the absorption contribution from mineral dust was considered.*

   Response: suggestion taken; we've added the relevant information in the revised ms.

   Lines 155-157: "Where TC, BC, BrC and WtC (white carbon) are the concentrations of TC and its three carbon components. BC and BrC are light-absorbing constituents, while WtC is optically non-absorbing."

   In the BI modelling, the absorption contribution from mineral dust was not considered. As the measurement site is a typical urban site, the absorption contribution from mineral dust should be low compared with that of BC and BrC. This assumption was also supported by previous source apportionment analysis of BrC light absorption in this region (e.g., Xu et al., 2024).

   Lines 166-168: "It should be noted that absorption contribution from mineral dust was not considered in current BI method. However, at our sampling site, dust absorption is expected to be minor compared with that of BC and BrC."

Reference:

Xu, S., Wang, J., Li, Y. E., Zhang, N., Ge, X., & Aruffo, E. (2024). Analysis of the influencing factors and sources of brown carbon light absorption in a typical megacity of the Yangtze River Delta, China. *Atmosphere*, *15*(4), 421.

3. *Lines 149–152: These two parameters are important for the subsequent analysis. Please provide more details on how they were determined, including the analytical procedures, assumptions, and associated uncertainties.*

Response: suggestion taken; we've added the relevant information in the revised ms.

Lines 152-166: "

$$b_{\lambda_i} \sim N\left(MAE_{\lambda_i}^{BC} \times BC + \left(K^{BrC} \times \lambda_i^{-AAE^{BrC}}\right) \times BrC, \sigma_{\lambda_i}^2\right), i = 1,2,3 \ldots,7 \qquad (6)$$

$$(BC, BrC, WtC) \sim Dirichlet(1,1,1) \times TC \qquad (7)$$

$$AAE^{BrC} \sim 1 + \exp(1) \qquad (8)$$

Where TC, BC, BrC and WtC (white carbon) are the concentrations of TC and its three carbon components. BC and BrC are light-absorbing constituents, while WtC is optically non-absorbing. $MAE_{\lambda_i}^{BC}$ is the mass absorption efficiency of BC at wavelength λ_i. K^{BrC} is a sample-dependent constant, and AAE^{BrC} describes the wavelength dependence of light absorption for BrC. We assumed $AAE^{BC} \approx 1$ and $AAE^{BrC} > 1$. The likelihood function is given in Eq6, assuming normally distributed errors. The prior distributions of the three carbon components are shown in Eq7, and scaled by TC concentration. The prior distribution of AAE^{BrC} follows an exponential distribution (Eq8), with a threshold parameter of 1, in line with its physical interpretation. The prior distribution of K^{BrC} is assigned a normal distribution with a mean of 2.7×10^5 and a standard deviation equal to 20 % of the mean, following the parameterization established by previous studies (Li et al., 2026; Liao et al., 2024). Detailed principles of the BI model and its parameter settings are described in Liao et al. (2024)."

4. *Line 173: Since the PMF analysis includes both organic and inorganic species, the term "organic-tracer-based source apportionment" may not accurately describe the approach. Please consider revising the terminology accordingly.*

Response: suggestion taken; we have revised the term to "Molecular and elemental tracer-based source apportionment" to emphasize the importance of molecular and elemental tracers for source apportioning.

Lines 188: "2.3. Molecular and elemental tracer-based source apportionment for BrC by PMF"

5. *Lines 178–185: One of the strengths of this study is the inclusion of a wide range of chemical species measured by different instruments in the PMF analysis. However, this also raises an important issue regarding the construction of the PMF error matrix. Since the input species were measured using different instruments and analytical methods, please explain in detail how the errors for each species were determined and how the uncertainties from different instruments were made comparable. This information should be clearly described in the Methods section. In addition, the authors should carefully evaluate whether some species may be over weighted in the PMF solution. For example, TC includes*

contributions from BC, BrC, and other organic carbon components and may therefore receive relatively high weight in the analysis.

Response: the errors of each species were determined based on initial tests and previous studies, and the uncertainties from different instruments were incorporated by the MDL and EF values, two parameters associated with the measurement uncertainties. Different values were suggested for species measured by different instruments, based on the initial tests and previous publications.

In terms of the over-weight issue, we incorporated the three carbon components (BC, BrC, and WtC), instead of TC, in the PMF model. A relative higher uncertainty was assigned to the three carbon components compared to the individual tracer species. For example, the EF values of 20% for the three carbon components while EF values of 10% for the tracer species were adopted.

We have added the assignment of the uncertainties for the input species in the Methods section in the revised ms.

Lines 203-208: "A total of 551 and 418 ambient samples in spring and summer were incorporated into the PMF model. The uncertainty of input species was calculated as (conc.×EF + 1/3×MDL; Reff et al., 2007), where MDL is the method detection limit and EF is the error fraction. For data below MDL, the uncertainty was set as 5/6 × MDL. Based on initially test and previous work, we adopted final EF values of 10% for elements and inorganic ions, 20% for BrC, BC and WtC, and 10% for polar and non-polar organics (Li et al., 2026)."

References

Reff, A., Eberly, S. I., & Bhave, P. V. (2007). Receptor Modeling of Ambient Particulate Matter Data Using Positive Matrix Factorization: Review of Existing Methods. Journal of the Air & Waste Management Association, 57(2), 146-154. https://doi.org/10.1080/10473289.2007.10465319

Li, Z., Wang, Q., Zhao, Y., Huang, Z., and Liao, K.: Seasonal variability and sources of brown carbon in Wuhan: Insights from Bayesian modeling and organic tracers-based source apportionment, Atmos. Res., 333, 108736, https://doi.org/10.1016/j.atmosres.2025.108736, 2026.

6. *Lines 237–244: The information presented here appears to describe the methodology and would be more appropriately placed in the Methods section. In addition, obtaining a 15-factor solution is relatively complex. The authors should provide stronger justification for selecting 15 factors and demonstrate that this solution is statistically and physically robust.*

Response: suggestion taken; we've moved the related content to the method section.

By inclusion of multiple high-time-resolution organic and elemental tracers, it is possible to separate more specific source categories, which cannot be resolved using offline coarse-time resolution data. The reason of selecting 15 factors in this study was based on the variations of Q/Q_{exp} and the interpretation of the factor profiles. The variation of Q/Q_{exp} suggested a minimum number of 12 factors, while the factor profiles suggested an optimum number of 15 factors which produced the most reasonable factor profiles. The BS and DISP error estimation of the 15-factor solutions indicated the robustness of the results, with >90% of factor mapping and no factor swaps. We've added the related information in the revised ms.

Lines 209-223: "Five to eighteen factors were initially tested, and a fifteen-factor PMF solution was selected for both seasonal datasets. Specifically, variations of Q/Q_{exp} suggested a minimum factor number of 12, beyond which changes in Q/Q_{exp} values diminished (Figure S1). The factor profiles suggested that the fifteen-factor solution showed most reasonable factor profiles. The 13-factor and 14-factor solutions failed to resolve secondary cooking from biomass burning, whereas the 16-factor solution produced an unexplained factor with various low-abundant species. To evaluate the stability of the PMF solution, bootstrapping (BS) and displacement (DISP) analysis were performed. A BS mapping frequency exceeding 80% (with a correlation coefficient $R \geq 0.6$ between the BS factors and the base-run factors) is considered indicative of stable factor assignment. The DISP results are deemed acceptable when no significant decrease in the scaled residual Q (i.e., %dQ < 1%) and no factor swapping are observed. The error estimation results of the PMF runs (summarized in Tables S3&S4) indicated that the selected 15-factor solution passed the BS and DISP tests, with >90% of factor mapping and no factor swaps, confirming robust solutions. The PMF-predicted BrC mass agreed well with measured values, with slope of 0.82 and R_p of 0.91 (Figure S2)."

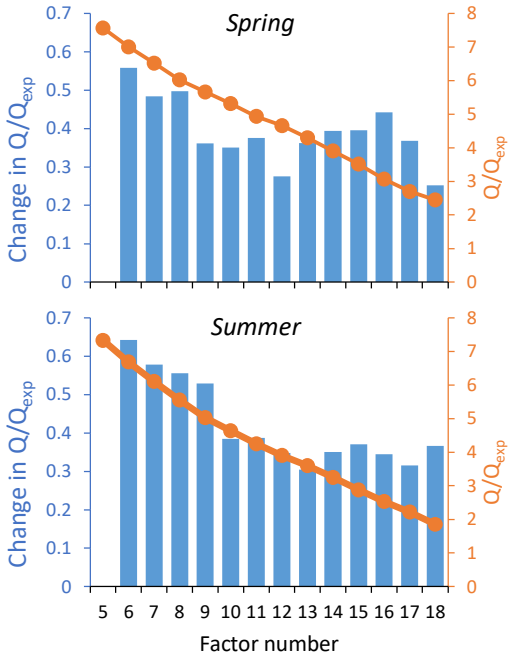

Figure S1. Change of Q/Q_{exp} values from 5-factor to 18-factor run for PMF with spring and summer data as input.

7. *Lines 253–263: More evidence is needed to support the attribution of these factors to specific sources. A factor should not be assigned to a particular source based on a single characteristic or tracer alone. Multiple independent lines of evidence, such as factor profiles, temporal variations, correlations with external tracers, meteorological dependence, and/or comparison with source profiles, would provide stronger support for the source attribution. In particular, what is the likely source of biomass-burning emissions in the urban area of Shanghai? Please provide additional discussion and, if possible, supporting observations or references.*

Response: suggestion taken; the establishment of indicative source tracers has been validated by previous laboratory studies of source profiles and they have been widely used as tracers for source identification in receptor modeling. In this study, the allocation of each source factor was based on

tracer species, diurnal variations of the source contributions, and correlations with the supportive data including meteorological parameters and gas pollutants. However, direct comparison of the entire source profiles from PMF with laboratory results is unattainable, as the PMF-resolved factor profiles represent the combined effect of source emissions and atmospheric processing. We've added the discussion in the revised ms.

As biomass burning is restricted in urban Shanghai, the observed source contributions likely originate from regional transport from the peripheral districts of Shanghai and some neighboring areas (Cheng et al., 2014). Indeed, both secondary and primary biomass burning showed moderate correlations with CO in both seasons, suggesting their regional feature (R_p: 0.44-0.60; Table S5). These explanations have been added in the revised ms.

Lines 278-331: ".... The factor profiles of the fifteen-factor solutions are shown in Figure 3a&c, and the diurnal variations of each factor's percentage contributions to BrC are shown in Figure 3b&d. Temporal trends and diurnal variations of individual factor contributions are presented in Figures S3-S4. Factor identification was based on established organic and elemental tracers and is generally consistent with results from laboratory studies and field observations in this region (Wang et al., 2018; Zhu et al., 2021). However, direct comparison of the entire source profiles from PMF with laboratory results is unattainable, as the PMF-resolved factor profiles represent the combined effect of source emissions and atmospheric processing.

Briefly, the secondary nitrate and sulfate formation process factor was identified by high loadings of sulfate, ammonium and nitrate (Figure 3a). This factor was enriched in Se and Pb, elements primarily emitted from coal-fired industrial sources that also release SO_2 and NO_x, key precursors of sulfate and nitrate formation. Their presence in this factor may suggest the importance of industrial sources in sulfate and nitrate aerosol formation. BrC associated with this factor reflects formation pathways similar to those of secondary inorganic aerosols. This factor exhibited higher contributions during nighttime hours, with more pronounced contributions in spring (Figure 3b). It showed highest correlation with CO (R_p: 0.48-0.50; Table S5), suggesting its regional feature. Among SOA factors, we resolved aromatic SOA factor, α-pinene SOA, isoprene SOA and β-caryphyllene SOA based on their respective tracers, which have been demonstrated in laboratory experiments to form from oxidation of the corresponding volatile organic compound (VOC) precursors (Table S2). Laboratory studies have demonstrated the oxidation of toluene, naphthalene, terpenes and sesquiterpene in the presence of NO_x or NH_3 can generate light-absorbing SOA (Lambe et al., 2013; Li et al., 2021; Updyke et al., 2012). Formation of light-absorbing oligomers during reactive uptake of isoprene epoxydiol onto acidified sulfate aerosols were also observed in laboratory studies (Lin et al., 2014). Distinct diurnal patterns were observed for these SOA factors (Figure 3b). Aromatic SOA showed comparable seasonal contributions with higher daytime values. α-Pinene SOA peaked at late afternoon hours (16:00-20:00) and was substantially enhanced in summer. β-Caryphyllene SOA contributed more in spring overall, but with higher afternoon contributions in summer. Isoprene SOA showed increased contributions in summer, with higher values in early morning. The four SOA factors exhibited moderate correlations with T, RH, and O_3 in summer (R_p: 0.39-0.61; Table S5), consistent with their secondary formation characteristics. The oxygenated cooking OA factor was identified by azelaic acid, which was the main oxidation products of unsaturated fatty acids such as oleic acid (Wang and Yu, 2021). This factor showed clear noontime and dinner-time peaks, with slightly higher contributions in summer (Figure 3b). During dinner hours (20:00-22:00), average contributions reached 15-20% of total BrC. Secondary biomass burning was identified by NACs, and it showed comparable seasonal contributions with slightly higher daytime values. Biomass burning was identified by saccharides and it contributed more during

nighttime hours, with higher contributions in spring. As biomass burning is restricted in urban Shanghai, the observed source contributions likely originate from regional transport from the peripheral districts of Shanghai and some neighboring areas (Cheng et al., 2014). Indeed, both secondary and primary biomass burning showed moderate correlations with CO in both seasons, suggesting their regional feature (R_p: 0.44-0.60; Table S5). The cooking emission factor was identified by fatty acids, and this factor showed higher contributions in spring, with apparent noontime and dinner-time peaks. Vehicle exhaust factor was identified by high loadings of hopanes, while tire wear was characterized by high loadings of Mn and Fe, typical non-exhaust emission tracers (Wang et al., 2018). Both factors displayed clear morning rush-hour peaks (Figure 3d), and correlated well with NO_x (Figure S5), confirming their traffic origins. The two factors showed higher contributions in spring. Re-suspended road dust was identified by Ca and Ba and it showed bimodal distributions with higher daytime contributions, indicating the resuspension of road dust caused by passing vehicles (Wang et al., 2022). This factor showed comparable seasonal contributions and moderate correlations with T and RH (R_p: 0.47-0.50; Table S5). Coal combustion, identified by PAHs, showed higher contributions in spring and nighttime hours (Figure 3d). Power plant combustion, identified by Cr, Zn and Se, exhibited higher contributions in summer. The two factors showed moderate correlations with CO (R_p: 0.38-0.60; Table S5), indicating their regional feature. Residual oil combustion was identified by Ni, with higher contributions in spring and nighttime hours."

Table S5. Correlation of the PMF factor contributions with the meteorological conditions and gas pollutants.

	Temp	RH	wind speed	O_3	CO	SO_2	NO_x
spring							
secondary nitrate and sulfate formation processes	0.094	0.166	0.170	0.038	**0.480**	0.079	0.144
aromatic SOA	**0.597**	0.022	0.072	**0.352**	**0.357**	0.023	0.037
α-pinene SOA	**0.458**	0.237	0.110	0.069	**0.393**	0.003	0.134
β-caryophyllene SOA	0.180	0.018	0.017	0.037	0.069	0.187	0.123
isoprene SOA	**0.338**	0.174	0.063	0.007	0.222	0.012	0.058
oxygenated cooking OA	0.180	0.141	0.271	0.234	**0.555**	0.081	**0.508**
secondary biomass burning	0.232	0.023	0.092	0.035	**0.596**	0.216	0.333
biomass burning	0.146	0.261	0.171	0.277	**0.432**	0.137	0.302
cooking emission	0.008	0.001	0.088	0.066	0.313	0.139	0.301
vehicle exhaust	0.076	0.162	0.293	0.388	0.389	0.229	**0.623**
tire wear	0.298	0.144	0.145	0.065	**0.576**	0.243	**0.620**
re-suspended road dust	**0.503**	**0.465**	0.170	0.316	0.198	0.117	0.052
coal combustion	0.054	0.106	0.071	0.176	0.437	0.062	0.208
power plant combustion	0.355	0.081	0.145	0.009	**0.596**	0.184	**0.435**
residual oil combustion	0.248	0.229	0.182	0.110	0.247	0.048	0.213
summer							
secondary nitrate and sulfate formation processes	0.016	0.028	0.282	0.144	**0.503**	0.126	0.105
aromatic SOA	**0.612**	**0.391**	0.003	**0.428**	0.061	0.268	0.052
α-pinene SOA	**0.421**	**0.402**	0.016	**0.441**	0.214	0.241	0.063
β-caryophyllene SOA	**0.474**	**0.384**	0.013	**0.420**	0.263	0.296	0.106
isoprene SOA	**0.442**	0.190	0.119	0.058	0.259	0.425	0.179
oxygenated cooking OA	0.011	0.181	0.219	0.240	0.138	0.080	0.239
secondary biomass burning	**0.412**	0.285	0.092	0.318	**0.441**	0.271	0.196
biomass burning	0.062	0.242	0.249	0.253	**0.393**	0.101	0.257
cooking emission	**0.345**	0.187	0.096	0.098	0.194	0.203	0.090

vehicle exhaust	0.014	0.155	0.108	0.256	0.296	0.157	**0.346**
tire wear	0.265	0.226	0.078	0.136	0.358	0.279	**0.553**
re-suspended road dust	**0.478**	**0.501**	0.037	0.360	0.216	0.385	0.361
coal combustion	0.203	0.180	0.076	0.071	0.377	0.138	0.012
power plant combustion	**0.450**	0.323	0.068	0.252	**0.522**	**0.421**	0.189
residual oil combustion	0.012	0.159	0.183	0.204	0.052	0.266	0.354

References:

Cheng, Z., Wang, S., Fu, X., Watson, J. G., Jiang, J., Fu, Q., Chen, C., Xu, B., Yu, J., and Chow, J. C.: Impact of biomass burning on haze pollution in the Yangtze River delta, China: a case study in summer 2011, Atmos. Chem. Phys., 14, 4573–4585, https://doi.org/10.5194/acp-14-4573-2014, 2014.

Lambe, A. T., Cappa, C. D., Massoli, P., Onasch, T. B., Forestieri, S. D., Martin, A. T., Cummings, M. J., Croasdale, D. R., Brune, W. H., Worsnop, D. R., and Davidovits, P.: Relationship between Oxidation Level and Optical Properties of Secondary Organic Aerosol, Environ. Sci. Technol., 47, 6349–6357, 2013.

Li, Y., Zhao, J., Wang, Y., Seinfeld, J. H., and Zhang, R.: Multigeneration Production of Secondary Organic Aerosol from Toluene Photooxidation, Environ. Sci. Technol., 55, 8592–8603, https://doi.org/10.1021/acs.est.1c02026, 2021.

Lin, Y., Budisulistiorini, S. H., Chu, K., Siejack, R. A., Zhang, H., Riva, M., Zhang, Z., Gold, A., Kautzman, K. E., and Surratt, J. D.: Light-Absorbing Oligomer Formation in Secondary Organic Aerosol from Reactive Uptake of Isoprene Epoxydiols, Environ. Sci. Technol., 48, 12012–12021, 2014.

Updyke, K. M., Nguyen, T. B., and Nizkorodov, S. A.: Formation of brown carbon via reactions of ammonia with secondary organic, Atmos. Environ., 63, 22–31, 2012.

8. *Lines 286–287: Is the reported fraction calculated separately for each season?*

Response: yes, the values are the seasonal average values. We've added the statement in the revised ms.

Lines 344-345: "Overall, 58% (0.92 μg/m^3) and 51% (0.89 μg/m^3) of the BrC mass was attributed to primary emissions in spring and summer, respectively."

9. *Lines 338–342: Does NOx exhibit a corresponding variation during this period? Additional evidence is needed to support this conclusion. Furthermore, could the observed increase in concentration be affected by variations in planetary boundary layer (PBL) height? Changes in PBL dynamics can substantially influence surface pollutant concentrations, and this possibility should be considered and discussed.*

Response: yes, during this event we also observed a clear increasing trend in NOx concentrations, supporting the importance of NO_x-evolved oxidation. We've added the information in the revised ms.

Lines 396-402: "The elevated BrC can be attributed to enhanced formation of NACs, such as 4-nitrocatechol, through nitration of phenolic VOCs emitted by biomass burning via gas-phase or aqueous-phase pathways (Mayorga et al., 2021). Notably, secondary nitrate and sulfate formation processes were the main sources of secondary BrC during this event. These processes share NO_x as a

common precursor with NACs formation, suggesting a concurrent formation regime. Indeed, NO_x concentrations increased steadily from 21.9 to 51.3 ppb throughout the event, corroborating the importance of NO_x-involved oxidation chemistry."

About the interference from the variation of planetary boundary layer (PBL) height, the reviewer's concern is valid. Variations in PBL height may introduce uncertainties into the analysis, potentially masking cases when meteorological effects outweighed changes in source emissions. Nevertheless, we observed distinct changes in source contributions across different events in this study, indicating that source contribution variations were substantially stronger than meteorological influences during the investigated secondary BrC increment episodes. Therefore, this factor does not compromise our major conclusions. More accurate quantification of each source contribution would require accounting for meteorological effects. We've added the discussion in the revised ms.

Lines 439-445: "Variations in planetary boundary layer (PBL) height may introduce uncertainties to the above analysis, potentially masking cases when meteorological effects outweighed changes in source emissions. Nevertheless, we observed distinct changes in source contributions across different events in this study, indicating that source contribution variations were substantially stronger than meteorological influences during the investigated secondary BrC increment episodes. Therefore, this factor does not compromise our major conclusions. More accurate quantification of each source contribution would require accounting for meteorological effects."

10. *Line 352: Please check whether there is a typographical error here.*

Response: the value (108%) is valid. In this case, the aromatic SOA contribution showed a noticeable decrease at the end of the episodic period (-0.12 μg/m^3), which resulted in the oxygenated cooking OA contribution exceeding 100%. We've added the information in the revised ms.

Lines 411-414: "Oxygenated cooking OA was the predominant contributor, contributing to 108% of the total increment, because the marked decrease in aromatic SOA during the final hour of the episode (–0.12 μg/m^3) drove its contribution above 100%."

11. *Figures 1–4: The presentation of these figures could be improved. The current horizontal layout makes the information relatively difficult to follow, particularly when comparing multiple factors. A vertical arrangement may improve readability. For Figures 3 and 4, I suggest considering a more compact presentation in which the factor spectrum and the corresponding diurnal variation are displayed side by side. This would facilitate a more direct comparison between the chemical characteristics and temporal behavior of individual factors.*

Response: suggestion taken; Figure 2 has been re-organized to vertical distribution for improved visualization. Figures 3 and 4 have been combined as one figure with factor profiles and diurnal variation pattern of individual factor shown side-by-side for better comparison.

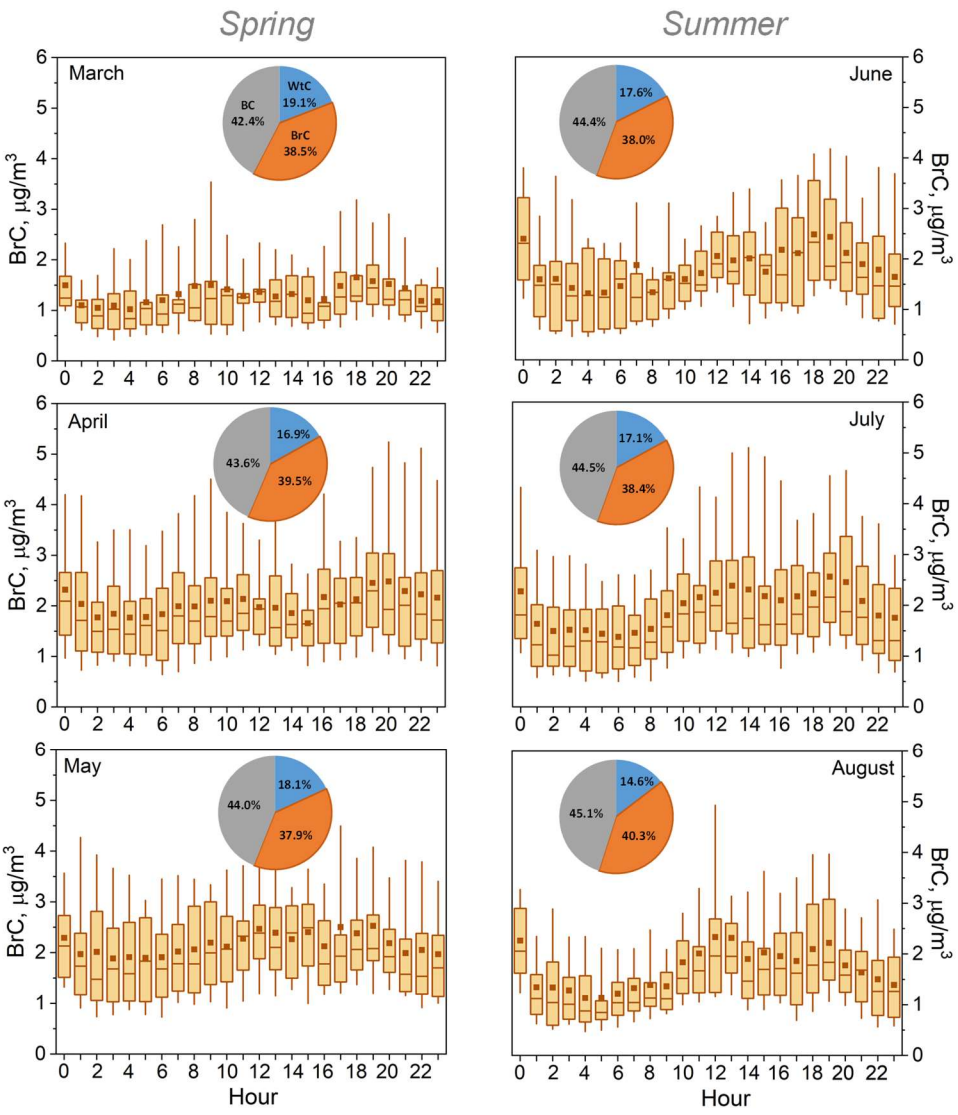

Figure 2. Monthly diurnal variations of BrC during the study period from 1/3/2020-31/8/2020 in Shanghai (squares and solid lines correspond to mean and median values, respectively; box indicates the 25th and 75th percentiles, and whiskers are the 10th and 90th percentiles). The insert pie chart shows the fraction of the three carbon components (i.e., BC, BrC and WtC).

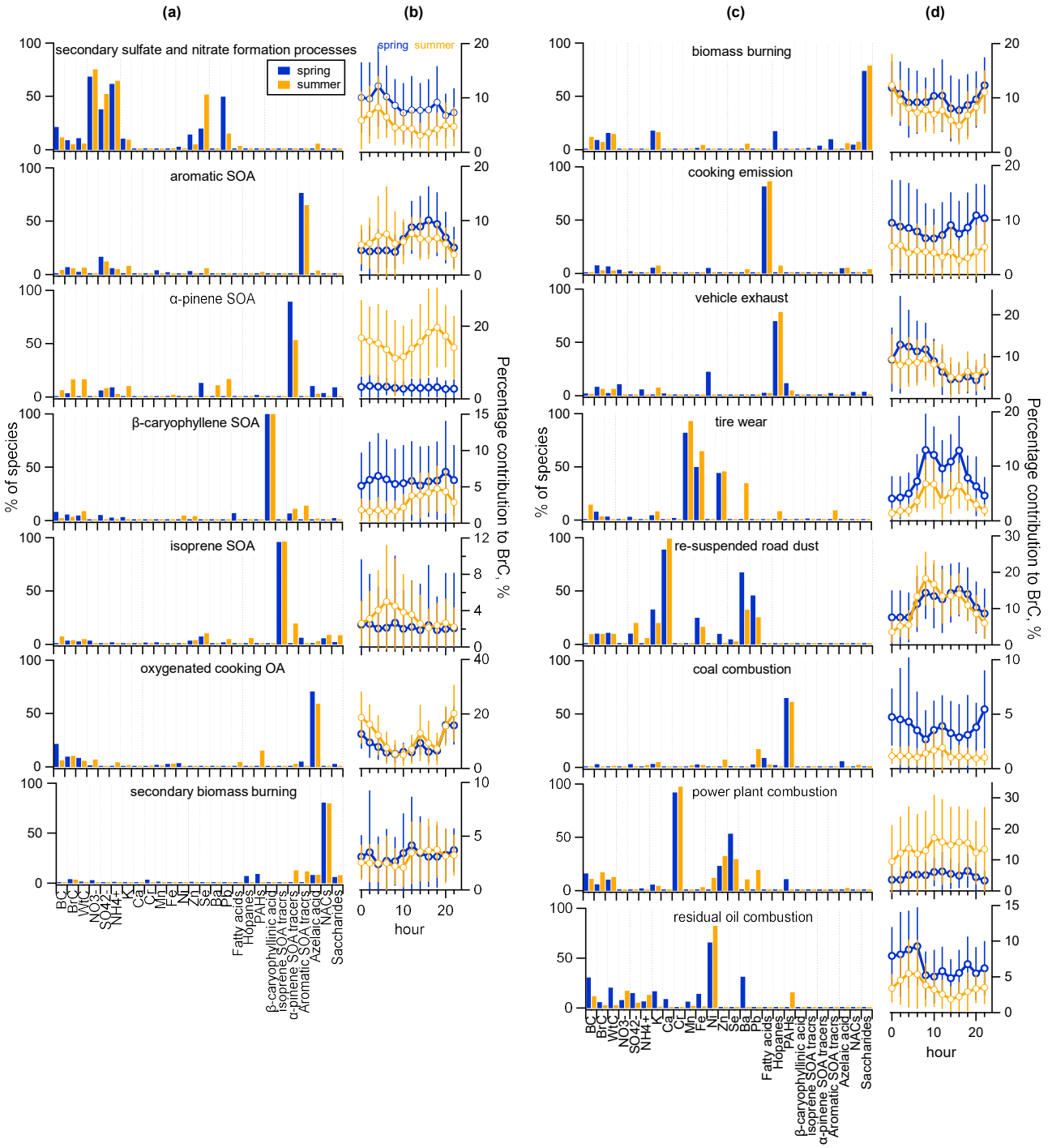

Figure 3. Source profiles (percentage of species) (a&c) and diurnal variations of percentage contribution to BrC (b&d) of individual factors resolved by PMF model using measurement data in spring (March-May) and summer (June-August). Spring results are shown in blue while summer results are in orange color. Means are shown as points and standard deviations as error bars (b&d).