General comments

The manuscript of Cheng et al. reports the diurnal variations of brown carbon (BrC) investigated during two distinct seasons in the northernmost megacity of China. Authors discussed drivers of diurnal BrC variations observed in two seasons, i.e., a cold winter (January 2021) and an agricultural fire-impacted spring (April 2021), relying on indicators of various sources.

This paper is well written, the experimental part is well presented and, along with citing the relevant literature, the experimental approach is well described. However, my main concern is directed to data presentation, interpretation, and drawing the conclusions as will be indicated later. Considering the importance of the topic that is the focus of this article, my overall assessment is that this paper should be considered for publication in ACP, but after major revision since there are some issues that need to be addressed to improve this work.

Major point

The authors hypothesized on more absorbing BrC at night, based on comparison of mean nighttime and daytime MAE_{365} values in winter. However, I do not see that this difference is statistically significant. Furthermore, authors attempted to explain the drivers of observed "diurnal variations", but have not reached a clear conclusion, which is not surprising since it is double if the diurnal difference even exists. In fact, authors discussed that the predominant influencing factor for MAE_{365} is vehicle emissions, especially those from nighttime HDDTA transport, based on the lower average $R_{S/N}$ observed at night (0.5 ± 0.1) compared to $R_{S/N}$ for the daytime samples (0.7 ± 0.2). The problem here is again that the average $R_{S/N}$ values obtained for the nighttime and daytime samples were not statistically different and such a conclusion is overstated.

The authors should first test the statistical significance of the MAE_{365} difference between night and day in winter. Furthermore, the discussion and conclusions should be based on statistically reliable data, and rigorous arguments need to be added to this paragraph. I suggest rewriting this paragraph, including changing the title.

Diurnal variations of MAE_{365} in spring (averaging 0.98 ± 0.31 and 1.69 ± 0.65 m^2/gC) should also be disused based on statistically proven difference between the day and night samples.

Our responses: We agree with the reviewer that statistical analyses should be performed to support comparisons involved in the manuscript. Thus we conducted *t*-tests and confirmed that: (i) for the winter campaign, the diurnal variations were statistically significant at the 95% confidence level for both MAE_{365} and $R_{S/N}$ (p = 0.004 and 0.000, respectively), and (ii) the diurnal variations of MAE_{365} and LG/OC (p = 0.000) were also statistically significant in spring. In the revised manuscript, *t*-test results were provided alongside descriptions of diurnal or seasonal differences, and were also summarized in a supplementary table. Based on the statistical results, we on one hand confirmed that major conclusions of the original manuscript still held, and on the other hand avoided overstatement **(see lines 167-170, 173-174, 201-203, 239, 263, 295-296, 299, 311, 318, 329, 425, 433-434, and Table S1)**.

Table S1. Summary of *t*-test results for the comparisons involved in the main text. A *p* value of below 0.05 indicates statistically significant difference at the 95% confidence level.

Compared parameters	*p* value of *t*-test	Indication
Winter campaign		
Daytime and nighttime MAE_{365}	0.004	More absorbing BrC at night
Daytime and nighttime LG/OC (LG/EC)	0.001 (0.000)	Increased residential burning emissions at night
Daytime and nighttime $R_{S/N}$	0.000	Increased vehicle emissions at night
Daytime and nighttime SOR in the RH range of 70–80%	0.417	Relatively weak influence of photochemistry on sulfate formation
Daytime and nighttime NOR in the RH range of 70–80%	0.005	Relatively strong influence of photochemistry on nitrate formation
Daytime and nighttime AAE	0.000	Stronger wavelength dependence of BrC absorption at night
Daytime and nighttime sulfate/OC	0.011	Decreased SOC/OC ratios at night
Spring campaign		
Daytime and nighttime MAE_{365}	0.000	More absorbing BrC at night

Daytime and nighttime LG/OC	0.006	Increased agricultural fire emissions at night
Daytime and nighttime $R_{S/N}$	0.000	Increased vehicle emissions at night
Daytime and nighttime SOR	0.489	Insignificant diurnal variations of sulfate formation
Daytime and nighttime NOR	0.083	Insignificant diurnal variations of nitrate formation
r values for typical samples and open burning episodes [derived from linear regression of $\ln(ATN_{\lambda})^{*}$ on ln (λ)]	0.000	Agricultural fire-induced non-linearity for BrC's absorption spectra shown on ln-ln scale
Inter-campaign		
LG/K^{+} in winter and spring	0.000	Different biomass burning ways in the two seasons (i.e., residential and open burning, respectively)
LG/OC in winter and spring	0.000	Stronger impacts of biomass burning in spring
SOR in winter and spring	0.050	——
NOR in winter and spring	0.012	Significant seasonal variations of nitrate formation
Wintertime MAE_{365} and MAE_{365} of typical samples in spring	0.000	Less absorbing BrC in spring with the absence of agricultural fires

Specific points

(1) Lines 240-241. MAE_{365} exhibited a negative dependence on $R_{S/N}$ for nighttime samples? Please explain.

Our responses: Yes, MAE_{365} exhibited a negative dependence on $R_{S/N}$ for the nighttime samples in winter, and their relationship [$MAE_{365} = (–0.57 \pm 0.18) \times R_{S/N} + (1.88 \pm 0.09)$; $r = 0.51$] was comparable with that derived from all the winter samples [$MAE_{365} = (–0.51 \pm 0.09) \times R_{S/N} + (1.84 \pm 0.05)$; $r = 0.61$]. The similar negative correlations suggested that the variation of nighttime $R_{S/N}$ might also be caused by the difference in numbers and/or emissions of heavy-duty diesel vehicles.

(2) Line 325. Please explain how Fig 2b is created. Are there cumulative fire events present for January and April? Please indicate this in the figure caption.

Our responses: Figure 2b was created using latitudes and longitudes of fire hotspots detected throughout the spring campaign. Figure 2a was created similarly. Both figures indicate cumulative fire events. This point was clarified in the revised manuscript **(see lines 769-771)**.

(3) Line 335. Is there any evidence of more frequent/intense nighttime burning from NASA/NOAA Suomi National Polar-orbiting Partnership (S-NPP) satellite, and/or the Fire Information for Resource Management System?

Our responses: The S-NPP satellite passed over Northeast China twice a day, approximately at noon and midnight, respectively. The fire hotspots were mainly detected during the day. However, this does not conflict with our inference on the prevalence of nighttime fires, which resulted in relatively high LG/K^+ levels compared to the daytime fires (1.73 $\pm$0.53 vs. 1.27 $\pm$0.35, p = 0.018). It had been observed that the transition from flaming to smoldering combustion favored the increase of LG/K^+ (Gao et al., 2003), thus the nighttime fires should have relatively low combustion efficiencies and consequently, they were more difficult to be detected by satellites. Cheng et al. (2021) found that the CMAQ air quality model significantly under-predicted OC and $PM_{2.5}$ during low-efficiency fire events, mainly due to the underestimation of open burning emissions by satellite-based inventory. Thus, we think compared to fire hotspots, directly-measured chemical signatures (e.g., LG/K^+ and LG/OC) could reflect the differences between daytime and nighttime fires more reliably.

(4) Lines 390-393. I agree that aromatic compounds with nitro-functional groups are good representatives of BrC related to biomass burning emission. I suggest not referring specifically to methylnitrocatechols, but rather to aromatic compounds with nitro-functional groups in general.

Our responses: Changes were made as suggested, i.e., "$C_7H_7NO_4$" mentioned throughout the manuscript were replaced by "aromatic compounds with nitro-functional groups" **(see lines 34-35, 401-403, 406 and 410)**.

(5) Lines 439-441. Based on my general comment above, please rewrite this part of the conclusion about the higher MAE_{365} observed at night in winter samples.

Our responses: As mentioned in our responses to the major comment, the diurnal variations were statistically significant at the 95% confidence level for both the wintertime MAE_{365} and $R_{S/N}$ (p = 0.004 and 0.000, respectively). Thus we think it should be acceptable to conclude that MAE_{365} were higher at night, accompanied with increased nighttime $R_{S/N}$.

(6) L453-455. Please rewrite the sentence since in its current form one could read that your work also involves chromophore absorption spectra and molecular measurements.

Our responses: This sentence was re-written as "*Aromatic species with nitro-functional groups were a possible class of compounds that were at play*" **(see lines 465-468)**.

Reference

Cheng Y., Yu Q.Q., Liu J.M., Zhu S.Q., Zhang M.Y., Zhang H.L., Zheng B., He K.B. Model vs. observation discrepancy in aerosol characteristics during a half-year long campaign in Northeast China: the role of biomass burning. ***Environmental Pollution***, 2021, 269: 116167.