Zhang et al. conducted a comprehensive analysis on the light absorption of methanol-soluble organic carbon (OC) and its molecular characteristics from residential heating and cooking scenarios using dung and bitumite. The authors found that BrC absorption emission factors were up to 9 times higher for incomplete dung burning than for bitumite combustion. Nitrogen-containing species with high aromaticity and CHO molecules with benzene rings and -COOH are unique markers of dung-fuel BrC. The potential radiative effects of the identified chromophores were also evaluated by calculating the simple forcing efficiency (SFE). Little information on BrC emissions from residential combustion in the Qinghai Tibet Plateau (TPL) is documented in the literature, and the topic of this study is important for connecting BrC emissions, molecular composition, and radiative effects of organic aerosols. However, I agree with the first reviewer that the manuscript needs significant revision before acceptance for publication. Here are my comments.

Response: We thank the reviewer's comments on our manuscript. We have considered each point and responded and revised accordingly.

1. The title is a bit misleading. A question might be raised about "what enhances the optical properties and radiative effects of brown carbon from dung combustion? However, the manuscript is mainly about the light absorption and molecular characteristics of BrC from dung combustion.

Response: We agreed with the reviewer that our manuscript mainly focus on the light absorption and molecular characteristics of BrC from dung combustion. Therefore, we have revised the title to "*Light absorption and molecular characteristics of molecular-specific brown carbon formed in dung combustion in the Tibetan Plateau, China*".

2. The definition and calculation of the molecular absorption coefficient (Mb_{abs}) was not provided in the main text or supplementary information. Therefore, a large part of *Section 3.3* is not understandable.

Response: To make the text in Section 3.3 understandable, the definition of molecular absorption coefficient (Mb_{abs}) was supplied in the revised manuscript as below.

Lines 137-139:

"To determine the relationship between the MSOC b_{abs365} and their detected molecules, the molecular absorption coefficient (Mb_{abs}), which represents the light-absorbing coefficient of individual MSOC molecules at 365 nm, was calculated."

In addition, in response to the first reviewer's comments, the calculation of molecular absorption coefficient (Mb_{abs}) was described in detail and was added to Section 2.4 in the revised manuscript as follows.

Lines 139-143:

"Following the steps applied in our previous studies, the Mb_{abs} for each molecule corresponding to the ion intensity was multiplied by its calibration coefficient (β). The "β" is an integrated reflection of UV–vis absorption and ionization efficiency for individual molecules, which can be determined from the combination of 16 MSOC b_{abs365} data, hundreds of detected molecular formulas, and their ion intensities using partial least squares regression (PLSR) analysis (Mehmood et al., 2019; Rambo et al., 2016; Zeng et al., 2020)."

3. Page 3, lines 67-70. BrC from flame combustion shows higher absorption than that from smoldering combustion.

Response: After our careful checking, the cited reference of Xie et al. (2020) suggested that large molecules of BrC compounds probably generated from flame combustion shows high absorption. Therefore, we have revised the incorrect expressions as follows.

Line 68-71:

"Interestingly, Xie et al. (2020) found that the factors of a variety of fuel types, high relative humidity, and low elemental carbon to organic carbon ratio (i.e., a measurement proxy for burning conditions) involved in flaming combustion probably produce abundant high molecule weight N-containing aromatic compounds and can strongly enhance the light absorption ability of biomass burning BrC."

Reference:

Xie, M., Zhao, Z., Holder, A. L., Hays, M. D., Chen, X., Shen, G., Jetter, J. J., Champion, W. M., and

Wang, Q. G.: Chemical composition, structures, and light absorption of N-containing aromatic

compounds emitted from burning wood and charcoal in household cookstoves, Atmospheric Chem.

Phys., 20(22), 14077-14090, 10.5194/acp-20-14077-2020, 2020.

4. Section 2.2 and Appendix II section 2.2. It seems that the MAC_λ was calculated by dividing b_{abs} by OC concentrations without considering dissolution ability. Since methanol cannot extract all organic materials in particles, the method used in this work may underestimate the MAC_λ value. This should be mentioned and discussed in the last paragraph of Section 3 (Page 7, lines 192-195).

Response: Owing to that for methanol extracts the use of an organic solvent prohibits determining carbon mass, the MSOC was not directly quantified. As the reviewer's comment, the loss of OC during the methanol extraction process has truly existed. Both Chen et al. (2019) and Cheng et al. (2016) have found that the average MSOC mass accounted for 88% and 85% of the total OC mass of near source and ambient OC in China. In response to the first major comment raised by the first reviewer, the discussion of methanol extraction error was mentioned in new Lines 99-102 in the revised manuscript. Also, the discussion of MAE (namely MAC_λ) uncertainties in the revised supplementary materials is as follows.

Supplementary lines 69-74:

"The b_{abs} is the light absorption coefficient of methanol-soluble BrC (Mm^{-1} or 10^{-6} m^{-1}), and OC represents the thermal-OC filter-based concentration which was measured using a Sunset thermal/optical carbon analyzer ($\mu g \cdot mL^{-1}$). In this study, we assumed that OC was completely dissolved during the methanol extraction processes. However, this should have a limitation on the MAE calculation, as previous studies showed that the loss of OC potentially existed within 15% (Chen et al., 2019; Cheng et al., 2016; Zhang et al., 2022). Consequently, the calculated MAE of MSOC would be underestimated."

Also, both the underestimation of MAE and their related descriptions were rephrased in Section 3 in the revised manuscript as below.

Lines 227-229:

"As depicted in Section 2.2 in SI, the underestimation of MAE within 15% might exist in the methanol extracts, thus the primary BrC emissions detected in this study exhibit comparable and even lower MAE values than the mixed primary and secondary BrC polluted urban areas…".

Lines 232-235:

"However, most average BrC MAE and AAE values for ambient aerosols over TPL regions are in relatively low concentration levels (MAE: 0.34-0.77 $m^2 \cdot g^{-1}$; AAE 3.8-6.24) (Kirillova et al., 2016; Wu et al., 2020; Zhang et al., 2017a), suggesting that residential combustion of dung and coal combustion could be an important source of BrC in the atmosphere over the TPL regions."

References:

Chen, D., Zhao, Y., Lyu, R., Wu, R., Dai, L., Zhao, Y., Chen, F., Guan, M.: Seasonal and spatial variations of optical properties of light absorbing carbon and its influencing factors in a typical polluted city in Yangtze River Delta, China. Atmos. Environ., 199, 45-54, 10.1016/j.atmosenv.2018.11.022, 2019.

Cheng, Y., He, K.B., Du, Z.Y., Engling, G., Liu, J.M., Ma, Y.L., Zheng, M., Weber, R.J.: The characteristics of brown carbon aerosol during winter in Beijing. Atmos. Environ., 127, 355–364, 10.1016/j.atmosenv.2015.12.035, 2016.

Kirillova, E. N., Marinoni, A., Bonasoni, P., Vuillermoz, E., Facchini, M. C., Fuzzi, S., and Decesari, S.: Light absorption properties of brown carbon in the high Himalayas, J. Geophy. Res.: Atmos., 121, 9621-9639, 10.1002/2016JD025030, 2016.

Wu, G., Wan, X., Ram, K., Li, P., Liu, B., Yin, Y., Fu, P., Loewen, M., Gao, S., and Kang, S.: Light absorption, fluorescence properties and sources of brown carbon aerosols in the Southeast Tibetan Plateau, Environ. Pollut., 257, 113616, 10.1016/j.envpol.2019.113616, 2020.

Zhang, Q., Li, Z., Shen, Z., Zhang, T., Zhang, Y., Sun, J., Zeng, Y., Xu, H., Wang, Q., and Ho, S. S. H.: Source profiles of molecular structure and light absorption of $PM_{2.5}$ brown carbon from residential coal combustion emission in Northwestern China, Environ. Pollut., 299, 118866, 10.1016/j.envpol.2022.118866, 2022b.

Zhang, Y., Xu, J., Shi, J., Xie, C., Ge, X., Wang, J., Kang, S., and Zhang, Q.: Light absorption by water-

soluble organic carbon in atmospheric fine particles in the central Tibetan Plateau, Environ. Sci.

Pollut. Res., 24, 21386-21397, 10.1007/s11356-017-9688-8, 2017a.

5. Section 3.2, lines 208-211. How did the authors determine the relative intensity of individual groups of compounds? Please provide this information in the methods section or in the supplementary information.

Response: In fact, the "relative intensity" concept is an inappropriate expression in the original manuscript. The majority of "relative intensity" in our original manuscript was an inappropriate expression. In response to the second minor comment raised by the first reviewer, the "relative intensity" has been corrected to "ion intensity" in the revised manuscript. The definition of intensity and their assignments for individual molecules were supplied in the revised manuscript as follows:

Lines 123-126:

"During the detection, the ion intensity refers to ion signal response and mass-to-charge ratio (m/z) were both obtained. Both m/z data and ion intensities were processed on the platform of the UNIFI Software 1.9.4 (Waters Corp., Milford, MA, USA) to assign the possible molecular formulae. The lower and upper limitations for a peak intensity of energy detection were set as 80 and 200, respectively."

6. Section 3.3. I suspect that the Mb_{abs} could be simulated by fitting b_{abs365} of aerosol extracts to the identified molecules statistically. Do all the identified CHO, CHON, and CHONS compounds have light absorption at 365 nm? How did the authors quantify individual groups of molecules based on intensity only?

Additionally, UHPLC-Q-ToF MS/MS operated in the ESI⁻ mode cannot identify all organic compounds in methanol extracts of aerosols. ESI is a soft ionization technique, and many organic compounds cannot be ionized and detected, particularly for large molecules. These limitations should be mentioned and discussed.

Response: In fact, the Mb_{abs} for each detected molecule were equal to the ion intensity multiplied by its calibration coefficient (β). Among them, the data of "ion intensity" was directly measured by UHPLC-Q-Tof MS/MS while the "calibration coefficient (β)"

value was obtained from fitting b_{abs365} of aerosol extracts to the identified molecules statistically using the PLSR method. As noted in previous studies, the multivariate regression technique of PLSR can handle high-dimensional data and model complex variable relations (Wehrens and Mevik, 2007; Sujaritha et al., 2019), which is thus suitable for the present work with 16 aerosol extracts and thousands of molecules to obtain β. Therefore, the Mb_{abs} of individual molecules can be calculated from the PLSR method.

To ensure the accuracy and completeness of the Mb_{abs} calculation, three measures including MSOC molecular formula assignments, PLSR model optimization, and BrC compounds selection, were conducted in our study.

① MSOC molecular formula assignments. To quantify individual groups of molecules, two datasets of ion intensity and m/z for each MSOC sample were used. The UNIFI software was used to calibrate and assign the possible molecular formulae for all peaks in the selected mass spectra of the active analysis and has been widely attempted in related studies (Xu et al., 2020; Man et al., 2021). The formulae of all measured m/z values could be calculated through the corresponding mass spectra data. The mass error for the molecular formulae assignment did not exceed ±2 mDa. Therefore, the software can be used independently to obtain molecular formula with high precision. The formula and the corresponding ion intensity for each molecule were acquired from the platform UNIFI software. In response to the 3rd major comment raised by the first reviewer, the data analysis of the UNIFI platform was added to the new lines 124-134 in the revised manuscript.

② PLSR model optimization. It's noted that the determination of the optimal number of components is very critical for the PLSR. In our study, the 5-fold cross-validation method was used. The series of average statistical parameters between the calculation and validation set includes the coefficient of determination for calculation, the coefficient of determination for validation (R^2_{cal} and R^2_{val}), the root mean square error of calibration (RMSEC), and the root mean square error of validation (RMSEV) were calculated (Filgueiras et al., 2014; Sujaritha et al., 2019), which can select the optimized 15th component to obtain the optimal fitting results. In the case of the PLSR

model for 15th components in our study, the mean squared error of the prediction (MSEP) of 1.96 Mm^{-1} is low, and the coefficient of determination (R^2) of 0.999 is high, representing the best-suited number of components for β predictions (Wehrens and Mevik, 2007; Kvalheim et al., 2019). In addition, as depicted in Figure S4, the predicted value of b_{abs} (i.e., the sum of Mb_{abs} for all measured molecules) was highly correlated with the measured methanol-soluble BrC total b_{abs} (slope = 0.51, r^2 = 0.91, p < 0.001). It is noteworthy that over 70% of predicted b_{abs} points displayed more appropriate model performances with increasing measured b_{abs} at full spectrum. Further, the non-zero intercept in Figure S4 was used to indicate a sufficient contribution of other undetected BrC components (i.e., nonpolar or less polar compounds such as saturated hydrocarbons and PAHs), rather than ESI^- selected BrC to the measured absorption (Lin et al., 2018).

③ BrC compounds selection. The identified CHO, CHON, and CHONS compounds discussed in our study can be divided into two categories. One refers to the whole compounds detected using UHPLC-Q-Tof MS/MS, which is only used in the original section 2.3 to obtain their individual Mb_{abs} by fitting the b_{abs365} of MSOC. Certainly, not all detected molecules are BrC that have light absorption at 365 nm. The value of Mb_{abs} was used as a criterion to distinguish whether these measured molecules are BrC compounds or not. In this study, the molecules with high Mb_{abs} ($\geq 10^{-8}$) represent BrC while relatively low Mb_{abs} values ($<10^{-8}$) as non-BrC molecules. Non-BrCs are molecules with negative or extremely low absorptions, which were not discussed in detail in this study because of their negligible absorption contributions. The other category represents the measured CHO, CHON, and CHONS compounds with high Mb_{abs} ($\geq 10^{-8}$), which was identified as BrC molecules and was thoroughly discussed in section 3.2 and 3.3. To avoid misunderstanding, section 2.3 in the original manuscript was divided into two parts of "Section 2.3 Detection of MSOC molecules" and "Section 2.4 Calculation of absorption from individual BrC molecules" in the revised manuscript. In response to the fifth major comment raised by the first reviewer, the related sentences about the classification of discussed BrC molecules were added

to lines 149-151 in the revised manuscript to clarify the identified CHO, CHON, and CHONS compounds.

Furthermore, we totally agreed that the limitations of the molecules' detection exist using negative ESI mode. The polar compounds such as nitro-phenols, aromatic acids, and carboxylic acids can be preferentially ionized by negative ESI mode, while the detection of oxygenated aliphatic and non-polar aromatic compounds (i.e. larger PAHs) can be achieved from positive ESI or atmospheric pressure photoionization (APPI) mode (Cha et al., 2018; Lin et al., 2018). Therefore, as depicted below, these limitations were added to the description of MSOC molecules detection and the interpretation of the slope and intercept for PLSR, respectively.

Line 114-116:

"In this study, the negative ESI UHPLC-Q-TOF MS/MS can measure semi-polar and polar organic molecules with acidic protons, but it is insensitive to non-polar compounds. Therefore, the detected molecules in our study only refer to a part of the MSOC fraction."

Line 153-156:

"The slope here suggests that the model explained nearly 60% of the measured b_{abs} in the full spectrum, and the nonzero intercept in linear correlations indicates a contribution of undetected non-polar or weakly polar organic compounds using a negative ESI source."

References:

Cha, E., Jeong, E. S., Han, S. B., Cha, S., Son, J., Kim, S., Oh, H. B., and Lee, J.: Ionization of gas-phase polycyclic aromatic hydrocarbons in electrospray ionization coupled with gas chromatography, Anal. Chem., 90, 4203-4211, 10.1021/acs.analchem.8b00401, 2018.

Filgueiras PR, Alves JCL, Sad CM, Castro EV, Dias JC, Poppi RJ.: Evaluation of trends in residuals of multivariate calibration models by permutation test. Chemometr. Intell. Lab, 133:33-41, 10.1016/j.chemolab.2014.02.002, 2014.

Kvalheim, O.M., Grung, B., Rajalahti, T.: Number of components and prediction error in partial least

squares regression determined by Monte Carlo resampling strategies. Chemometr. Intell. Lab, 188, 79–86, 10.1016/j.chemolab.2019.03.006, 2019.

Lin, P., Fleming, L.T., Nizkorodov, S.A., Laskin, J., Laskin, A.: Comprehensive molecular characterization of atmospheric brown carbon by high resolution mass spectrometry with electrospray and atmospheric pressure photoionization. Anal. Chem., 90, 12493-12502, 10.1021/acs.analchem.8b02177, 2018.

Man, Y., Stenrød, M., Wu, C., Almvik, M., Holten, R., Clarke, J. L., Yuan, S., Wu, X., Xu, J., Dong, F., Zheng, Y., and Liu, X.: Degradation of difenoconazole in water and soil: Kinetics, degradation pathways, transformation products identification and ecotoxicity assessment. J. Hazard. Mater., 418, 126303, 10.1016/j.jhazmat.2021.126303, 2021.

Sujaritha, M., Kavitha, K., Janet, J.: Comparative analysis of accuracy on partial least squares and principal component regression methods. Indian J. Sci. Technol., 12, 0974-6846, 10.17485/ijst/2019/v12i8/141809, 2019.

Wehrens, R., Mevik, B.H.: The pls package: Principal component and partial least squares regression in r. J. Stat. Softw., 18, 1-24, hdl.handle.net/2066/36604, 2007.

Xu, L., Liu, Y., Wu, H., Wu, H., Liu, X., and Zhou, A.: Rapid identification of chemical profile in Gandou decoction by UPLC-Q-TOF-MSE coupled with novel informatics UNIFI platform. J. Pharm. Anal., 10(1), 35-48, 10.1016/j.jpha.2019.05.003, 2020.

7. The manuscript should be proofread carefully. For example, page 2, line 58, "liner correlations".

Response: Suggestion taken. We have corrected "liner correlations" as "linear correlations".