General Comments

This study reports the absorption properties, chemical functional bonds, and sources of BrC in six Chinese cities. They were conducted to acquire comprehensive BrC datasets with higher resolution and more species and provide insight into more specified source identification. Overall, the combination and intercomparison of BrC in six Chinese cities is a valuable study of the BrC measurement. I recommend publication after the following issues are addressed.

Response to the Editor and Reviewer

We greatly appreciate editor and anonymous reviewer for their constructive comments and suggestions, which greatly assist to improve the quality of our manuscript. We have responded to all of the points accordingly. The original comments are in black and our responses are in blue. Major changes are highlighted in the revised paper. We hope you and the reviewers will find the revised version meets the standard of the journal.

P7 Line 188

As far as I know, "Elser et al., 2016" reported the AMS data in China, the result is about BBOA is the major source for OA in Xi'an, it was not included any results for the brown carbon. Please revise it.

Response: Suggestion taken. The sentence was revised as:

Lines 200-202:

Biomass burning was revealed to be the dominant source of BrC in these cities during winter (Cheng et al., 2016; Shen et al., 2017; Sun et al., 2017; Cheng et al., 2022).

Reference:

Cheng, Y., Cao, X. B., Liu, J. M., Yu, Q. Q., Wang, P., Yan, C. Q., Du, Z. Y., Liang, L. L., Zhang, Q., and He, K. B.: Primary nature of brown carbon absorption in a frigid atmosphere with strong haze chemistry, Environ Res, 204, 112324, https://doi.org/10.1016/j.envres.2021.112324, 2022.

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

Shen, Z., Zhang, Q., Cao, J., Zhang, L., Lei, Y., Huang, Y., Huang, R. J., Gao, J., Zhao, Z., Zhu, C., Yin, X., Zheng, C., Xu, H., and Liu, S.: Optical properties and possible sources of brown carbon in $PM_{2.5}$ over Xi'an, China, Atmos. Environ., 150, 322-330, http://dx.doi.org/10.1016/j.atmosenv.2016.11.024, 2017.

Sun, J., Shen, Z., Cao, J., Zhang, L., Wu, T., Zhang, Q., Yin, X., Lei, Y., Huang, Y., Huang, R. J., Liu, S., Han, Y., Xu, H., Zheng, C., and Liu, P.: Particulate matters emitted from maize straw burning for winter heating in rural areas in Guanzhong Plain, China: Current emission and future reduction, Atmos. Res., 184, 66-76, http://dx.doi.org/10.1016/j.atmosres.2016.10.006, 2017.

P11 Line 265-280

In Figure 4, there are the big differences between cities at the peak of 1385 cm-1, why?

What are the insights on the difference?

Response: Previous studies have found a sharp peak near 1385 cm^{-1} with particularly high intensity in the FT-IR spectra of atmospheric BrC samples, which may be related to O−H bond deformation and C−O stretching of phenolic groups (Mukherjee et al., 2020; Zhang et al., 2020). In this study, we found the similar peak at 1385cm^{-1}, thus we inferred that the same phenolic functional groups may also exist in the BrC samples in our study. In addition, previous researches have pointed out the presence of peak at 1385 cm^{-1}, which suggests that the contribution of biomass burning source to BrC. Since fine smoke aerosol contain thermally altered lignin derivatives, such as aromatic phenols (e.g., siringyl and guaiacyl derivatives) (Duarte et al., 2007; Mukherjee et al., 2020). The same peak was observed in the FT-IR spectra of BrC samples derived from the combustion of biomass materials (Fan et al., 2016). In our study, we noted that the abundance at 1385 cm^{-1} varies greatly among six cities, which was significantly higher in HrB, XA and WH than other cities. We speculated that this is due to the different contribution of biomass burning among cities, and the higher contribution occur in HrB, XA and WH. Therefore, we revised these sentences in the manuscript as following:

Lines 285-293:
Moreover, the peak at 1385 cm^{-1} was generally considered to be derived from the O–H bond deformation and C–O stretching of phenolic groups (Fan et al., 2016; Mukherjee et al., 2020; Zhang et al., 2020), and the same peak was observed in the FT-IR spectra of BrC samples derived from the combustion of biomass materials (Fan et al., 2016). These observations indicated the contribution of biomass burning to BrC; this was because that biomass burning can release heat-modified lignin derivatives such as aromatic phenols (e.g., syringyl and guaiacyl) (Duarte et al., 2007; Fan et al., 2016; Zhao et al., 2022). It was noted that the abundance of this peak was different among six cities, and was significantly higher in HrB, XA and WH, which indicated biomass burning contributed differently to BrC in six cities, and higher contribution was occur in HrB, XA and WH than those in other cities.

Reference:

Duarte, R. M. B. O., Santos, E. B. H., Pio, C. A., and Duarte, A. C.: Comparison of structural features of water-soluble organic matter from atmospheric aerosols with those of aquatic humic substances, Atmos. Environ., 41, 8100-8113, https://doi.org/10.1016/j.atmosenv.2007.06.034, 2007.
Fan, X., Wei, S., Zhu, M., Song, J., and Peng, P. a.: Comprehensive characterization of humic-like substances in smoke $PM_{2.5}$ emitted from the combustion of biomass materials and fossil fuels, Atmos. Chem. Phys., 16, 13321-13340, https://doi.org/10.5194/acp-16-13321-2016, 2016.
Mukherjee, A., Dey, S., Rana, A., Jia, S., Banerjee, S., and Sarkar, S.: Sources and atmospheric processing of brown carbon and HULIS in the Indo-Gangetic Plain: Insights from compositional analysis, Environ. Pollut., 267, 115440, https://doi.org/10.1016/j.envpol.2020.115440, 2020.
Zhang, Q., Shen, Z., Zhang, L., Zeng, Y., Ning, Z., Zhang, T., Lei, Y., Wang, Q., Li, G., Sun, J., Westerdahl, D., Xu, H., and Cao, J.: Investigation of primary and secondary particulate brown

carbon in two Chinese cities of Xi'an and Hong Kong in wintertime, Environ. Sci. Technol., 54, 3803-3813, https://dx.doi.org/10.1021/acs.est.9b05332, 2020.
Zhao, R., Zhang, Q., Xu, X., Wang, W., Zhao, W., Zhang, W., and Zhang, Y.: Light absorption properties and molecular compositions of water-soluble and methanol-soluble organic carbon emitted from wood pyrolysis and combustion, Sci. Total. Environ., 809, 151136, https://doi.org/10.1016/j.scitotenv.2021.151136, 2022.

P12 Line 292-308
My concern is related to the results of PMF. PMF is a commonly used receptor model for source apportionment. From the shown factor profiles in Figure S4. The results of PMF are highly associated/influenced by the sample number (not many here), chemical components (could be enlarged here), and the suggested factors (4, 5, 6, or even more). There are only 30 (or 31?) samples in each city and different profiles in each city. It could be more careful. And here needs more evidence.

Response: Suggestion taken. In order to extract four to six factors, the PMF of six cities were run multiple times during building of PMF models. Solutions with fewer or greater number factors were also investigated, but these solutions were less defined and factor merging was often observed. Finally, according to the highest correlation coefficient between the constructed $PM_{2.5}$ concentration and the measured $PM_{2.5}$ concentration, the characteristic factors used for source identification were consistent with the literature to determine the optimal model for each site, and thus to reduce the influence of the limited number of samples and chemical species on the PMF results. we provided additional evidences to show the plausibility of the PMF model results:

Line 314-319:
A good correlation was observed between the measured and PMF-reconstructed $PM_{2.5}$ mass concentrations in all sites (BJ: r = 0.99; HrB: r = 0.90; XA: r = 0.97; CD: r = 0.97; GZ: r = 0.94; WH: r = 0.95), theoretical Q_{true} and Q_{robust} displayed a <5% difference, and the scaled residuals for final model solutions were generally normally distributed, falling into the recommended range of −3 to 3. These evidences demonstrating the validity and robustness of our PMF solutions (Borlaza et al., 2021b; Tao et al., 2021).

Reference:
Borlaza, L. J. S., Weber, S., Uzu, G., Jacob, V., Cañete, T., Micallef, S., Trébuchon, C., Slama, R., Favez, O., and Jaffrezo, J.-L.: Disparities in particulate matter (PM_{10}) origins and oxidative potential at a city scale (Grenoble, France) – Part 1: Source apportionment at three neighbouring sites, Atmos. Chem. and Phys., 21, 5415-5437, https://doi.org/10.5194/acp-21-5415-2021, 2021b.
Tao, Y., Sun, N., Li, X., Zhao, Z., Ma, S., Huang, H., Ye, Z., and Ge, X.: Chemical and Optical Characteristics and Sources of $PM_{2.5}$ Humic-Like Substances at Industrial and Suburban Sites in Changzhou, China, Atmosphere, 12, https://doi.org/10.3390/atmos12020276, 2021.

Also, there are some studies about the source apportionment of BrC, which directly input the MAE365 of BrC to the data matrix. Did the author try this solution? How about the results?

Response: We thank the reviewer's suggestion. We tried to run the PMF model by putting BrC b_{abs365} into the data matrix to get the BrC source resolution results directly. However, the correlation between the measured value and the constructed value of b_{abs365} was low, and there was a great difference between the theoretical Q_{true} and Q_{robust}, which indicated that the PMF model results have great uncertainty and low credibility (Borlaza et al., 2021a; Tao et al., 2021). We speculated that this may be caused by the fact that our samples are not suitable for the PMF model. As a bilinear factor analysis method, PMF is widely used for source assignment (Cao et al., 2012; Lei et al., 2018; Li et al., 2021; Shen et al., 2010; Tao et al., 2017). However, atmospheric processes are nonlinear in nature, the interaction between sources cannot be ignored (Borlaza et al., 2021b), which may be the reason why this linear fitting is not suitable for our study. The artificial neural network (ANN) based multilayer perceptron (MLP) model could extract trends from non-linear data, making it an interesting and competitive innovative analytical approach for many scientific disciplines (Borlaza et al., 2021b; Elangasinghe et al., 2014). Therefore, we decided to use a combination of PMF and ANN-MLP model to assign source contributions to BrC.

Reference:

Borlaza, L. J. S., Weber, S., Uzu, G., Jacob, V., Cañete, T., Micallef, S., Trébuchon, C., Slama, R., Favez, O., and Jaffrezo, J.-L.: Disparities in particulate matter (PM_{10}) origins and oxidative potential at a city scale (Grenoble, France) – Part 1: Source apportionment at three neighbouring sites, Atmos. Chem. and Phys., 21, 5415-5437, https://doi.org/10.5194/acp-21-5415-2021, 2021a.

Borlaza, L. J. S., Weber, S., Jaffrezo, J.-L., Houdier, S., Slama, R., Rieux, C., Albinet, A., Micallef, S., Trébluchon, C., and Uzu, G.: Disparities in particulate matter (PM_{10}) origins and oxidative potential at a city scale (Grenoble, France) – Part 2: Sources of PM_{10} oxidative potential using multiple linear regression analysis and the predictive applicability of multilayer perceptron neural network analysis, Atmos. Chem. Phys., 21, 9719-9739, https://doi.org/10.5194/acp-21-9719-2021, 2021b.

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Elangasinghe, M. A., Singhal, N., Dirks, K. N., and Salmond, J. A.: Development of an ANN–based air pollution forecasting system with explicit knowledge through sensitivity analysis, Atmos. Pollut. Res., 5, 696-708, https://doi.org/10.5094/APR.2014.079, 2014.

Lei, Y., Shen, Z., Wang, Q., Zhang, T., Cao, J., Sun, J., Zhang, Q., Wang, L., Xu, H., Tian, J., and Wu, J.: Optical characteristics and source apportionment of brown carbon in winter $PM_{2.5}$ over Yulin in Northern China, Atmos. Res., 213, 27-33, https://doi.org/10.1016/j.atmosres.2018.05.018, 2018.

Li, X., Zhao, Q., Yang, Y., Zhao, Z., Liu, Z., Wen, T., Hu, B., Wang, Y., Wang, L., and Wang, G.: Composition and sources of brown carbon aerosols in megacity Beijing during the winter of 2016,

Atmos. Res., 262, https://doi.org/10.1016/j.atmosres.2021.105773, 2021.
Shen, Z., Cao, J., Arimoto, R., Han, Y., Zhu, C., Tian, J., and Liu, S.: Chemical Characteristics of Fine Particles (PM_1) from Xi'an, China, Aerosol. Sci. Tech., 44, 461-472, https://doi.org/10.1080/02786821003738908, 2010.
Tao, J., Zhang, L., Cao, J., Zhong, L., Chen, D., Yang, Y., Chen, D., Chen, L., Zhang, Z., Wu, Y., Xia, Y., Ye, S., and Zhang, R.: Source apportionment of $PM_{2.5}$ at urban and suburban areas of the Pearl River Delta region, south China - With emphasis on ship emissions, Sci. Total. Environ., 574, 1559-1570, http://dx.doi.org/10.1016/j.scitotenv.2016.08.175, 2017.