

Authors' Response to Referee #1

Brown carbon (BrC) is a poorly characterized component of particulate matter that absorbs solar radiation and may contribute significantly to global warming. Some of the factors responsible for the current knowledge gap on BrC are the lack of understanding of its chemical composition, light-absorption properties, and contribution to total particulate mass and light absorption, which are likely subjected to significant spatial and seasonal variations. The measurement report by Dong et al. focused on the physicochemical characteristics and sources of 1BrC in Tianjin, northern China. In particular, the light absorption and excitation emission matrix fluorescence of both water-soluble and water-insoluble but methanol-soluble BrC in PM_{2.5} were measured off-line using a three-dimensional fluorescence spectrometer. The measurements were performed for one year and the seasonal variations were investigated. The results showed clear seasonal differences both in the BrC light-absorption and the type of constituting chromophores, an association with the potential sources, and a significant contribution of BrC to climate warming. The methodology used was appropriated for the described investigation, and the obtained results were well presented and of high relevance to the field of atmospheric science. Therefore, I recommend for publication after the following comments are addressed:

Dear Luis Miguel Feijo Barreira,

Thank you very much for your critical reading of the manuscript, appreciation of our work and comments/suggestions, which helped to further improve the quality of the MS. The MS is revised accordingly, and our point-by-point responses to all the comments are provided below. Please see the revised MS for details of the revisions.

Major comments: 212009

P6L242-The authors claim that “The higher Abs₃₆₅ in winter indicates that the light absorption of BrC in PM_{2.5} may have more significant effect on the climate and the photochemical reactions in the atmosphere over Tianjin in winter than in other seasons”. However, the effect of aerosols on climate are complex and photochemical reactions depend as well on the type and amount of atmospheric oxidants, precursor VOCs, and many other factors. Therefore, these conclusions are difficult to estimate based on a higher light absorption at a specific wavelength.

Response: We agree with the referee’s opinion. We modified this concluding point as: “Such higher abs₃₆₅, particularly in winter, indicates that BrC in PM_{2.5} has a significant effect on light absorption and thus on climate system over the Tianjin region. Please see Page 7, Lines 43-46 in the revised MS.

P7254-In this sentence it is mentioned that the absorption coefficient of WI-MSBrC was always greater than that of WSBrC across the shorter wavelengths. However, In Fig. 2a the absorption coefficient of MSBrC was lower than the one of WSBrC from autumn to spring, except at a wavelength of about 280nm.

Response: To avoid such generalization, we modified our statement by specifying the seasons and wavelength range in the revised MS (see Page 8, Lines 10-13).

P11L301-The results show a higher correlation between Abs₃₆₅ and K⁺ in spring and autumn, especially for WSBrC, which is opposite to what was observed for Cl⁻ where the correlation was higher in winter. Shouldn’t the correlation with K⁺ be higher in winter as well when biomass burning

is usually higher? Is there any reason why biomass burning at the measured site would not be higher in winter?

Response: No, biomass burning is one of the major sources in winter too, but the coal combustion is a dominant source. The poor correlation of Abs_{365} with K^+ was mainly driven by outliers in the K^+ concentration data, which might have been occurred due to unknown biomass burning event(s) at local scale. We noted this point in the revised MS (see Page 9, Lines 13-15).

In fact, concentration of K^+ was higher in winter than in other seasons, but it showed moderate correlation with $\text{PM}_{2.5}$ ($R^2=0.47$), whereas chloride ion (Cl^-) showed high correlation ($R^2=0.71$) with the $\text{PM}_{2.5}$ in winter, indicating that coal combustion is a dominant contributor, compared to that of biomass burning, to $\text{PM}_{2.5}$ (and for BrC as well) in winter (Dong et al., 2023).

P11L303-In this sentence, it is mentioned that the correlation between WSOC and K^+ in autumn was stronger than that between MSOC, confirming that most of the chromophores generated by biomass burning were water-soluble. However, in P7L258 it says that most chromophores, including PAHs from biomass burning, were soluble in methanol. Furthermore, in Sect. 3.4 it is mentioned that “MeOH-soluble OC was much higher than that in WSBrC, which indicated that chromophores were (more?) abundant in WI-MSBrC than in the WSBrC.” Can the authors clarify these differences?

Response: Actually, we mean that the chromophores derived from the biomass burning emissions only, but not all the chromophores, are relatively more soluble in water compared to that in organic solvent (methanol). To avoid such confusion to the reader, we made it clear modifying this sentence in the revised MS (see Page 9, Lines 15-18). Therefore, the other two statements mentioned here in the comment (P7L258 and Sect. 3.4) stand as they are.

P13L342-It is mentioned that the AAE of BrC increases with the polarity of constituents. However, the AAE of MSOC was similar to the one of WSOC. Shouldn't the AAE be higher for WSOC?

Response: Generally, the AAE of BrC is increased with its increasing polarity (Chen et al. 2016). However, it has also been found that the value of $\text{AAE}_{300-600}$ of water extract of biomass burning samples is lower than that extracted into acetonitrile (Lin et al., 2017), indicating that the origin of the BrC is also play an important role. We clarified it by including this point in the revised MS (see Page 11, Lines 24-26).

P14L370-The fluorescent properties of WSBrC are dominantly described this chapter. For example, in the first paragraph of Sect. 3.3.1 the proportion of water-soluble chromophores was presented and discussed contrary to the ones of water-insoluble but methanol soluble chromophores. However, the methanol-soluble chromophores had actually contributed the most to the fluorescence volume of aerosol particles (e.g. Fig. 6). Is there a reason for focusing the discussion of this paragraph on WSBrC when the contribution of MSBrC was much more significant?

Response: Yes, we agree with the referee's view. We removed this paragraph and focused on both the fractions of the BrC equally throughout the text in the revised MS.

P14394- In this paragraph it is mentioned that “the higher molecular weight and aromatic organic compounds contribute more to WSBrC in summer and autumn while the contents of WI-MSBrC (winter > autumn > spring > summer) were opposite”. Can the authors clarify in more detail the results that supported this conclusion?

Response: We substantially improved the discussion about all the three fluorescence indices in the revised MS (see Section 3.3.1).

Minor comments:

P1L33-The word “However” should be replaced by “For example,” since that sentence does not contradict the previous one.

Response: We replaced the word “However” with “For example” in the revised MS (see Page 1, Line 34).

P2L41-Do the authors mean nitrogen-containing aromatic compounds?

Response: We mean that the compounds with polar functional group that consists of nitrogen and/or oxygen. We modified the phrase to make it clear to the reader in the revised MS (see Page 2, Lines 1-3).

P2L48-Automobile exhaust is a consequence of fossil fuel combustion. Could these be combined?

Response: We removed the phrase ‘automobile exhaust’ in the revised MS.

P2L55- Not only ultraviolet spectroscopy but ultraviolet-visible spectroscopy is commonly used to study the light absorption of brown carbon.

Response: We changed “ultraviolet spectroscopy” into “ultraviolet-visible spectroscopy” in the revised MS (see Page 2, Line 27).

P2L67-Can the authors clarify this sentence? In particular, are the authors comparing the sensitivity of EEM with the one from UV-vis spectroscopy? What type of classification are the authors referring to and what “shape of absorption spectra” means in this case?

Response: No, we are only highlighting the advantage of the fluoresce method by referring the absorption spectral measurements. We modified the corresponding phrases to clarify the type (chromophores) of classification and to avoid the confusion about the shape of spectra in the revised MS (see Page 2, Lines 41-43)

P2L73-This sentence could be changed to “quantitative measurement of light-absorbing organic components”. The structural properties of those compounds are also important since they determine both the light-absorption and the potential health effects.

Response: We removed this part of text in the revised MS.

P2L74- There are currently ways to differentiate between light absorption of black and brown carbon. For example, this differentiation has been done using AE33 measurements and employing a method based on the wavelength dependence of AAE (WDA analysis). However, it is true that this separation is challenging since both components absorb light over the entire UV-vis range and some assumptions are made to separate their light absorptions.

Response: Yes, we agree with the referee. However, we removed that part of text in the revised MS.

P4L133-Can the extraction method be described in more detail? For example, was the entire filter used for the extraction or a part of it (1.0 cm by 1.5 cm in size?) was taken for the OC/EC analysis? Were the filters weighted prior and after particle sampling? Where were the quartz filters inserted

during ultrasonic extraction? The PTFE filter was used to remove undissolved particles, right? Currently, it is mentioned that it was used to remove water-insoluble compounds. The majority of those should remain in the extraction vessel/tube for subsequent extraction with methanol. Was the extraction efficiency determined in this study?

Response: Following the referee's suggestion, we improved the method description substantially by including all these details and provided the citations for further details in the revised MS (see Sects. 2.1 and 2.2). Yes, the extracts were filtered through PTFE syringe filter to remove the undissolved particles. We corrected it in the revised MS (see Page 4, Line 20). Since it is a well-established procedure, we didn't check the extraction efficiency in this study.

P4L145-Should this section be part of the chemical analysis? I understand that the used instrument relies on the measurement of a physical property, but it is an analytical chemistry instrument. Or Sect. 2.2. could be changed e.g. to "Physical-chemical analysis".

Response: We agree with the referee's opinion. However, in order to keep the main attention on optical properties, we rephrased the sub-titles and also re-structured the chemical analysis part in the revised MS (see Sects. 2.2 and 2.3).

P4L154-These samples were also analysed by the HORIBA Aqualog optical spectrometer, right? In that case, there is no need to mention "a fluorescence spectrometer" since the blank samples were analysed by the same instrument.

Response: Yes. We removed the phrase: "a fluorescence spectrometer", in the revised MS.

P4L170-The AAE can both indicate that the BrC has a greater or smaller contribution to aerosol absorption, depending on its value. The last part of the sentence can be removed.

Response: As suggested, we removed the last part of the sentence in the revised MS.

P6L219-The units can be removed from the title.

Response: We removed the units from the title in the revised MS.

P6L227-The decomposition of BrC constituents during summer, likely due to photobleaching, is induced both by solar intensity and oxidants present in the atmosphere.

Response: We modified this sentence accordingly in the revised MS (see Page 7, Lines 14-16).

P6L229-This is true, but a decrease in atmospheric oxidation likely plays a role as well.

Response: We included this point in the revised MS.

P7L261-The nitroaromatics compounds do not always contribute 60% to the absorbance. The sentence needs to be rewritten to e.g. "In another study, nitroaromatics have contributed 60 % to the total absorbance in the 300-400 nm range".

Response: We modified it accordingly in the revised MS (see Page 8, Lines 17-19).

P8L282-The authors mean on summer holidays? This paragraph can be combined with the previous one because it continues that discussion.

Response: Yes. We replaced that phrase with summer to avoid any confusion to the reader and combined the two paragraphs in the revised MS (see Page 9, Lines 3-6).

P8L283-And photobleaching as mentioned earlier?

Response: We included the word, 'Photobleaching' in the revised MS (see Page 9, Line 4).

P12L316- The references are missing.

Response: We cited appropriate references in the revised MS (see Page 11, Lines 2-3).

P13L320-Can the authors clarify this sentence?

Response: We mean that unlike the direct measurement of AAE of the particulate matter, which is influenced by factors such as particle size, mixing state and chemical composition, the AAE of the solution depends on only the chemical composition. We made it clear in the revised MS (see Page 11, Lines 10-15).

P13L343-The large MAE365 during winter is a consequence of air pollution. Therefore, the sentence should be modified to "which is a result of severe air pollution in the mentioned period".

Response: We modified this section substantially in the revised MS.

P13L45-This sentence can be deleted or moved to the Methods section.

Response: We moved this sentence to the Methods section in the revised MS.

P13L347-Change to UV-Vis range.

Response: Modified it in the revised MS (see Page 12, Line 40).

P13L350-What were the values for MSBrC?

Response: We included the values of WI-MSBrC in the revised MS (see Page 13, Lines 18-20).

P13L355-Are the presented values the SFE range?

Response: Yes, the values are the SFE range.

P13L359-Change to UV-Vis range.

Response: We changed it to "UV-Vis range" in the revised MS.

P21L514-Can the authors clarify this paragraph? Is this the total FV of SOC (WSBrC+WIBrC) or the correlation of FVs of WSBrC and WIBrC with SOA?

Response: What we meant the total FVs was that the sum of FV of WSBrC and WI-MSBrC. To avoid such confusion to the reader, we modified this phrase in the revised MS (see Page 20, Lines 8-10).

P21L520-The second sentence can be removed/modified since Fig. 10 refer to the NFVs and not to the overall optical properties of the different samples.

Response: We agree with the referee and modified the first and second sentences of this paragraph in the revised MS (see Page 20, Lines 16-18).

P22L540- N-containing substances were soluble in water. but how about in methanol?

Response: Since stable carbon isotope ratios did not show any relations, we removed this part of discussion to avoid any mislead from the drawn conclusions in the revised MS.

P2L5553-Do the authors mean that Tianjin PM2.5 contained more polar BrC than other cities of

China as shown by the higher AAE values?

Response: We removed this phrase in the revised MS.

P23L556-And photobleaching?

Response: We added this phrase in the revised MS (see Page 21, Line 10).

P23L568.The polarity of water is higher than the one of methanol. Since WBrC contributed the most to the fluorescence of aerosols, can the authors conclude that this indicates that there were more polar BrC substances in the collected aerosol samples?

Response: We removed this sentence in the revised MS.

p23L571-How about biomass burning?

Response: Yes, biomass burning and coal combustion emissions are the major sources in winter. We corrected it in the revised MS (see Page 21, Line 17).