Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC3
https://doi.org/10.5194/acp-2022-465-RC3, 2022

Comment on acp-2022-465

Anonymous Referee #3

Referee comment on "Chromophores and chemical composition of brown carbon characterized at an urban kerbside by excitation–emission spectroscopy and mass spectrometry" by Feng Jiang et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-465-RC3, 2022

General comments

Brown carbon (BrC) compounds are important constituents of atmospheric aerosols. Although in the past decades, BrC aerosols have been a subject of extensive researches in the atmospheric scientific community, their formation pathways, optical properties, and climatic effects are not well investigated yet. This study provides a comprehensive report on the optical properties, chemical composition, and major BrC chromophores collected at a kerbside at different seasons in a typical urban environment in western Europe. This manuscript fits the scope of ACP and well written, but the authors may want to address the following issues before publication. Please see my comments in detail below.

1. BrC defined in this manuscript is dissolved in methanol, however, only a part of BrC is methanol-soluble, and even some highly-absorbing BrC is not soluble in any solvent. I suggest to replace BrC to methanol-soluble BrC (MS-BrC) where needed throughout the manuscript.

2. In Sec.3.3, the authors compared their methanol-soluble fluorophores with many water-based studies. I believe that even for a single chemical species, there might be some differences between its water-based and methanol-based EEMs, in other words, they may not be comparable. The authors may want to discuss this issue.

Specific comments

1ã□□ Please reduce words in the abstract and a single paragraph is recommended.

2ã□□ L85-87. Meaning of this sentence is not clear.

3ã□□ L97. Earlier references need to be cited here. For instance, Lin et al., Molecular Characterization of Brown Carbon in Biomass Burning Aerosol Particles, DOI: 10.1021/acs.est.6b03024.

4ã□□ L167. Why was different duration time applied for FIGAERO-CIMS analysis?

5ã□□ Eq.3. I suggest to use a power-law regression to calculate AAE, instead of use the information of only two single wavelengths. Eq. 3 here is usually used for techniques with limited wavelengths, like aethalometer.

6ã□□ L199. Why did the authors use different emission wavelength increments for summer and winter samples? With different data size, how did the authors assemble data in the PARAFAC model?

7ã□□ L206. The authors used methanol-based solution rather than water-based, why did you use water Raman peak to normalize the fluorescence intensity? Please explain it or

cite proper literatures.
8ã□□ Figure 2a,b. There is a shoulder peak at ~300 nm for summer sample, it is not usually see for aerosol samples. Could the authors put some words on that?
9ã□□ L281. The maximum EM wavelengths of C3 is ~400 nm, not significantly above.
10ã□□ L288. In Chen et al., 2016, C4-like chromophore was partially assigned to phenol- and naphthalene-like substances. Are they possible assignment for C4 chromophore in this manuscript?
11ã□□ L328. What is used to do the correlation analysis between AMS and PARAFAC components? Relative contributions or absolute intensities?
12ã□□ L344-355. In L340, the authors mentioned sampling artifacts for the samples with shorter sampling time. How did the diurnal variation of chromophores can be inferred from unreliable samples?
13ã□□ L357. In my opinion, higher NFV of samples #5 and #6 may not only due to sampling contamination. Species in these samples with higher fluorescence efficiency may also lead to this phenomenon. For instance, in Fig. 5b, samples #5 and #6 have higher fraction of LV-OOA1.
14ã□□ L380. I am confused here. The authors showed that major 5 NACs concentration in their samples was 1.6 ± 0.9 ng m-3 on average. It is one magnitude lower than 10-20 ng m-3.
15ã□□ L394. How did the authors calculate the mass fraction of potential BrC?
16ã□□ Figure 6a. Only 8 samples were analyzed by FIGAERO-CIMS? Which samples were selected?
17ã□□ L396 (Table S8). Are those molecules commonly appeared in all 8 samples? Or all potential BrC molecules detected in every sample. if later one is the case, n values of correlative analysis should be noted as well.
18ã□□ Table S8. The correlation coefficient is calculated between Abs365 and what parameter for potential BrC molecules?
19ã□□ Sec. S3. L37-38. I do not understand here. Without standards, how can the authors derive the mass concentrations of 321 potential BrC molecules?
20ã□□ Sec. S3. In earlier studies, relative fluorescence of PARAFAC components were correlated with relative intensities of each MS peak, not mass concentration fractions. The authors may want to take a look at this paper: Stubbins et al., What's in an EEM? Molecular Signatures Associated with Dissolved Organic Fluorescence in Boreal Canada, 2014, dx.doi.org/10.1021/es502086e.
21ã□□ Table S11. Molecular weight and O/C are intensity weighted or arithmetic mean, should be clarified.
22ã□□ Fig. 7. What are bubble sizes mean? Peak intensities? Needs to be clarified.
23ã□□ Sec. 3.5.3. The discussion of molecular characteristics of molecules assigned to each fluorescence components may needs to be in more detail. Double bond equivalent, aromaticity index, carbon oxidation state and so on, all these metrics are also worth to show.