# Response to reviewers' comments on "Chromophores and chemical composition of brown carbon characterized at an urban kerbside by excitation-emission spectroscopy and mass spectrometry" (acp-2022-465)

The authors kindly thank the reviews for the careful review of the manuscript, and the helpful comments and suggestions, which improve the manuscript a lot. All the comments are addressed below point by point, with our responses in blue, and the corresponding revisions to the manuscript in red. All updates of the original manuscript are marked in the revised version.

## Reviewer #1

This work reported the pollution characteristics and molecular composition of atmospheric chromophores in a certain city. Especially, based on previous studies, some conclusions were obtained in the study of organic aerosols by using EEMs and MS method. Generally speaking, it is interesting and can be considered for publication after dealing with the following problems.

### General comments

1. Abstract: The content describes the results too much and summarizes the conclusions or significance too little.

We agree to have a better balance between results and conclusions in the abstract. Therefore, we deleted the correlation coefficient values, because these details are not so important for the abstract. Furthermore, we directly added some conclusions to highlight brown carbon molecule importance for aerosol absorption. We have revised the abstract as follows:

"The statistical analysis of PARAFAC components and PMF factors showed that LO-HULIS chromophores were most likely emitted from biomass burning in winter. HO-HULIS chromophores could be less volatile oxygenated organic aerosol from regional transport and oxidation of biogenic volatile organic compounds (VOC) in summer." …

"This indicates that a small fraction of brown carbon molecules dominates the overall absorption."

2. L85: Chen's series of studies have promoted the application of EEM methods in the field of atmosphere, and his recent studies have also combined typical sources and molecular substances with EEM (2021). The author should objectively confirm the use of these work in this study. In addition, EEM method is a comprehensive characterization method, and its advantage lies in its systematicness and integrity. Mass spectrometry and EEM methods can be complementary.

We agree to give more credit to the work by Chen et al., and have added more references.

"Chen et al., (2020, 2021) investigated chromophore sources and species in different aerosol samples (combustion source samples, secondary organic aerosols, and ambient aerosols) by using EEM spectroscopy, different chemical analysis, and the PARAFAC model"

3. L06: unscientific expression of "~".

We agree and have updated. We deleted the "~" and added around.

4. L26: I noticed that the observation time was almost a month, but the high-resolution mass spectrometry results did not see so much data.

We corrected the actual measurement periods to "July 6th – 26th 2019" and "February 26th to March 25th, 2020". Figure 1 shows the AMS data for this time period. In addition, we also changed the measurement time in Fig. S4 and S5, which is consistent with high-resolution aerosol mass spectrometer (AMS) measurements.

5. L138: The height of the sampling point is a little low, so it is easy to be affected by the ground or a small range.

We agree that the sampling at 3.7 m above ground level allows influence of nearby and ground level emissions (see figure S1). According to $PM_{2.5}$ variations shown in Fig. 1, and Fig. S3 and S4, there are many spikes that reflect ground traffic emission. Song et al. (2022) have shown for this location and the same inlets that particle composition can be affected by different factors, e.g. regional transport, location emissions, and secondary formation during these measurements.

6. L162: What is the collection efficiency of CIMS? How to calibrate?

The collection of organic compounds on the Teflon filter may depend on the filter loading and the volatility of the different compounds. For particle measurement, the collection efficiency of Teflon filters with 2 µm pore size was estimated to 99.997% by Lopez-Hilfiker et al. (2014). However, the most important issue for a quantitative mass detection efficiency for the chemical ionization mass spectrometer (CIMS) is its varying sensitivity for different chemical species. Since it was not possible for us to calibrate the sensitivities of all organic molecules, we assume the same sensitivity of 22 cps/ppt for all compounds (Lopez-Hilfiker et al., 2016). However, for 5 nitro-aromatic compounds, we did calibration experiments. The calibration results are given in the supporting information (Fig. S2). This information is started in the method section.

7. L197: Why Ex. From 240?

For all Aqualog measurements, we used the excitation values from 239 – 500 nm to have a comparable range as Tang et al. (2020). We modified the manuscript text as follows:

"For all Aqualog measurements, we used an excitation wavelength range from 239 – 500 nm and an emission wavelength range from 247 – 700 nm to have comparable ranges as Tang et al. (2020)."

8. L270: Title too simple.

We agree and have updated the text

"EEM spectra and chromophores of methanol soluble organic carbon".

9. L327: The author did not identify the origin of OA and chromophobe, because LV-OOA and SV-OOA cannot be considered as the source.

LV-OOA and SV-OOA derived from the PMF analysis of AMS-measured OA can be considered as the surrogate factors for SOA (Jimenez et al., 2009). Due to the thermal decomposition inside the AMS, SV-OOA and LV-OOA cannot attribute to specific sources. However, the correlation analysis of SV-OOA and LV-OOA with external tracers can still provide information on their sources. In this study, SV-OOA showed strong correlations with particulate nitrate and production rate of nitrate radicals ($[NO_3] = [NO_2] * [O_3]$) especially during nighttime when the site was mainly influenced by the air masses from rural forested areas in summer. Therefore, SV-OOA was mainly formed from the oxidation of biogenic VOCs by $O_3$ and nitrate radicals during nighttime in summer. LV-OOA1 showed a good correlation with sulfate in summer, suggesting that it was related to the regional transport in summer. While LV-OOA2 had good correlations with $O_x$ and air temperature, indicating that it was attributed to the daytime photochemical oxidation of biogenic VOCs. Please refer to Song et al. (2022) for the results of OA source apportionment. We have added this information to the text:

"Song et al. (2022) found that LV-OOA1 was mainly from regional transport and LV-OOA2 was mainly from oxidation of biogenic VOC in summer."

Furthermore, we have modified the sentence on chromophore identification:

"To potentially identify chromophore sources, we compared the factors from PMF analysis of AMS mass spectra and the components determined by the PARAFAC analysis of the excitation-emission spectra using a Pearson's correlation analysis based on relative abundances, as shown in Figs. S11 and S12."

10. L365: Why did the author not analyze PAHs and OH-PAHs?

A filter inlet for gases and aerosols coupled to a high-resolution time-of-flight chemical ionization mass spectrometer (FIGAERO-CIMS) employing iodide ions for chemical ionization can only measure highly oxygenated organic molecules. Sensitivity of Iodide-CIMS to compounds depends on their polarity and hydrogen bonding capability, and is strongly influenced by molecular geometry and steric factors (Caldwell et al., 1989). Iodide-CIMS is completely insensitive to nonoxygenated compounds, like PAH, and extremely very insensitive (< 0.1 cps/ppt) to mono-alcohols like OH-PAH, due to their weak polarity and bonding, resulting in low binding energies with the Iodide (Lee et al., 2014).

11. L405: Correlation analysis with molecular composition determines that the molecular composition of EEM is one-sided and must be explained in absolute quantities, otherwise the type of chromophores can only be said to be similar substances or sources.

We agree with reviewer's comments and think this is clearly expressed in section 3.5.3 This is a correlation analysis of potential BrC molecules with EEM-PARAFAC components. We did not directly measure the typical chromophore component molecules, because chromophore components can be just resolved by the EEM-PARAFAC model. And then we used the correlation analysis to explain the molecular characteristic of chromophore components. In this manuscript, we did not define component molecules and instead, use "molecules associated with PARAFAC component" to describe this issue.

12. Fig.2: Why MAE and AAE diagrams are made? Aren't they mathematically correct? What is the reason for the higher uncertainty of the red line in the AB diagram?

MAE and AAE diagrams can explain the optical properties of brown carbon. In addition, we would like to compare MAE and AAE from ultraviolet to visible wavelengths in summer and winter. Finally, the graphical representation of BrC classes is also based on AAE and $Log_{10}(MAE_{405}.)$. The shaded color region represents the standard deviation from averaging optical properties of brown carbon in summer and winter. The reason of the large standard deviation is that $MAE_{<350}$ in samples has larger variations in summer than in winter.

13. Fig.3: There are weak signals around Em. = 290 in C3, why?

EEM-PARAFAC model can separate chromophores as different components. However, the chromophoric components cannot be resolved perfectly (see Fig. S3). If we would use the EEM-PARAFAC model to get 6 components, as shown in Fig. 1. The weak signal of component 6 can be considered as a protein-like component. However, component 6 only accounts for 5% of the total fluorescence intensity. The weak signals have relatively high uncertainties and only little influence on the main properties of e.g. component 3. Therefore, we decided to discuss only those 4 components which can clearly be separated.

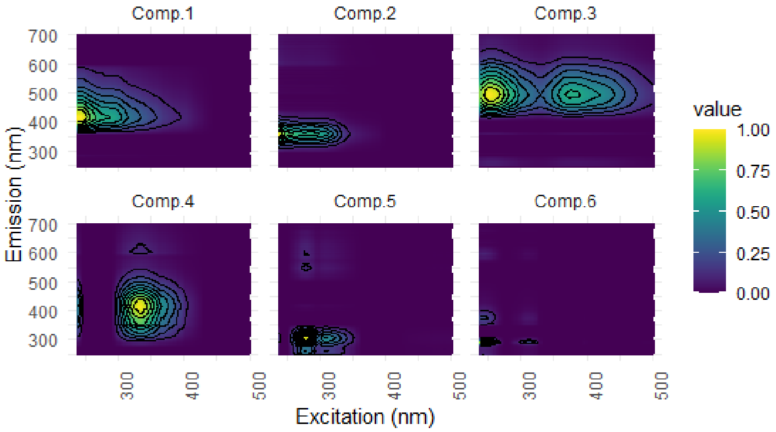

Figure 1. The six components were identified by the PARAFAC model analysis of the excitation-emission spectra from all filter extracts collected in summer and winter.

14. Fig.5: Comparison of recommendations with previous studies.

We agree and have added corresponding information to section 3.4:

"Chen et al. (2016b) also found that the $MAE_{266}$ and NFV values of water-soluble organic matter were positively correlated with $C_2H_4O_2^+$, an ion associated with organics from BBOA."

15. Fig.7: I can't understand what the author wants to express in this figure.

There are more than 2000 organic molecules measured by CIMS during our measurements, and we use a strategic analysis to extract potential brown carbon molecules (Fig. S14). The method was described by Lin et al. (2018). Furthermore, we did a correlation analysis of potential brown carbon molecules with chromophore components from EEM-PARAFAC (Table S10). Then, we generated the van Krevelen plot for the molecule families well associated with each PARAFAC component (Figure 7). Finally, we discuss the characteristics of the molecules associated with the chromophore components.

## References

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## Reviewer #2

Jiang et al., present a study on exploring the optical and chemical composition of brown carbon. Comparing with previous studies, this study combines the optical measurements and chemical measurements (AMS and Fi) and can obtain more information on the sources and chemical processes of chromophores. They found LO-HULIS chromophore was primary with nitrogen-containing molecular and originated from biomass burning at the urban kerbside during winter. However, HO-HULIS chromophores were secondary and could be related with photochemistry during summer. Overall, the results and presentation are reasonable and clear. However, there are many minor issues in the manuscript which should be addressed before publication.

### Major issues

Since the major focus of this manuscript is on BrC and filter measurement, the 2.2 and 3.1 sections could be concise and merged into other section or cited from other parallel publication. In method section, it is also important to describe the data matching between online and offline data.

We think it is important to keep section 3.1 in the main manuscript, because it is important to give the reader an overview of the measurement campaigns. However, we reorganized the method section. The AMS data analysis was moved to section 2 in the supplement. Due to the importance of FIGAERO-CIMS, it has its own section 2.4. Comparison of $PM_{2.5}$ of FIDAS and filter measurement was moved to method section 2.3. $PM_{2.5}$ concentrations by quartz filters and organic molecules concentrations by CIMS have good correlations with online measurements. We have expressed this in section 2.3 and 2.4 as follows:

“We used the online AMS data to calculate major source factors for organic aerosol components employing PMF (Song et al., 2022). Please note that the online NR-$PM_{2.5}$ measured by AMS agrees well with the offline measurements of $PM_{2.5}$ via gravimetric analysis of the quartz filter samples (Song at al., 2022)”

“The sum of the filter deposited particle mass of all molecules detected by CIMS has good correlations (R = 0.6) with organic concentrations measured by AMS.”

The samples described in the method section are unclear. How many filter samples was collected during winter and season, how many samples were collected for one day, morning time or nighttime? What material filter was used? What is the instrument? What is the filter sampling strategy for CIMS analysis? This information should be clearly presented in method section.

We have added a section 2.2 on filter sampling in the method section as follows:

“During the measurement campaigns, the quartz filter samples were collected by a low-volume sampler (LVS, ComdeDerenda GmbH). There were 13 daily filters collected in summer and 21 daily filters in winter. The daily filters were analyzed by a microbalance (Sartorius AG, Germany) for the $PM_{2.5}$ mass concentration. In addition, 3 quartz filters were collected for each morning, afternoon, and nighttime in winter from March 18th to 20th, 2020. The sampling times are shown in Table S4 in the supporting information. During each campaign, 2-3 blank filter samples were collected to correct for the backgrounds. Before sampling, these filters were wrapped in aluminum foil and pre-baked at 450 °C for 5 h. After sampling, they were stored in a freezer at – 20 °C until analysis for optical properties."

Before collecting particles, Teflon filters (polytetrafluoroethylene (PTFE), 1µm, SKC Inc.) were baked at 200 °C for 6 hours to remove potential contamination constitutes from the filter matrix. Only 11 Teflon filters were collected in winter from March 17th to 20th, 2020, including 4 filters in the morning, 4 filters in the afternoon, and 3 filters at night time (cf. Table S3 in the supplement). The sampling flow for particle deposition on the Teflon filter was 6 L min$^{-1}$, and a rotameter was used to keep the total flow of 16.7 L min$^{-1}$ at the $PM_{2.5}$ inlet. In order to avoid any mass loading effects, the deposition time usually varied from about 50 – 270 minutes to obtain similar organic mass loadings based on concurrent AMS measurements (Huang et al., 2019). The sampling tubes and the $PM_{2.5}$ inlet have been described in a previous study (Song et al., 2022). The Teflon filters were stored in a freezer at – 20 °C until analysis for organic composition by FIGAERO-CIMS."

## Minor issues

Line 23-24: present the full name of AMS and more information on the measurement and results (online or offline? How many factors were obtained). In the above, the PARAFAC analysis has present and directly use PARAFAC results.

We have added the following sentence to explain the AMS measurement and data analysis.

"Positive matrix factorization (PMF) analysis of organic compounds detected in real-time by an online aerosol mass spectrometer (AMS) led to five characteristic organic compound classes."

Line 197-210: The results of PARAFAC on winter and summer season are significant different. Is this seasonal process conducted at a combined dataset or separated? It is better to input the combine dataset into the model.

We combined the summer and winter dataset into one EEM-PARAFAC model. To make this clear we have modified the sentence as follows:

"Using all 49 EEMs obtained for summer and winter in the PARAFAC analysis, 4 different components were adopted by comparisons of the residual errors and by visual inspection for the three- to seven-component PARAFAC model (Fig. 3). They were successfully passed the split-half validation with the split style of $S_4C_6T_3$ for the 49 samples (Fig. S3)."

Line 260-263: it is worth to mention the wavelength range of AAE in different studies which can significant influent AAE result.

We agree and have modified the text as follows:

"The absorption Ångström exponent in the range of 300 – 450nm ($AAE_{300–450}$) in summer and winter were 4.7 ± 0.4 and 5.5 ± 1.5, respectively (Fig. 2a). The $AAE_{300–400}$ values show similar values measured at Zurich which are 4.5 and 5.1 in winter and summer, respectively. However, lower values of 3.8 were observed in Magadino during winter (Moschos et al., 2018). Furthermore, comparing $AAE_{300-450}$ and log ($MAE_{405}$), the BrC in summer and winter can be classified as weakly absorptive BrC (W-BrC) and moderately absorptive BrC (M-BrC), respectively (Fig. 2c)."

Line 272-274: this information is already in method section.

We agree and deleted the double information.

lines 287-288, Change to "shorter excitation wavelength (< 250 nm) and shorter emission wavelength (< 350 nm)".

Changed accordingly.

line 289, Change "left" to "right".

Changed accordingly.

Line 308-309: the abbreviation of aerosol mass spectrometer should be consistent in the main text.

Changed accordingly.

In section 3.3, the authors discussed the fluorophores only in MSOC, but the papers cited by the authors when determining the fluorescence components mostly about fluorophores in WSOC. See the previous papers where there are clear differences in the water-soluble and methanol-soluble fractions. https://doi.org/10.5194/acp-20-2513-2020

Thank you for pointing this out. Tang et al. (2020) used water to extract the filters and then freeze-dried and extracted the same filter with methanol. This way brown carbon can be separated as water-soluble BrC and methanol-soluble (water-insoluble) BrC. Therefore, the fluorophores characteristics show clear differences. However, during our measurement, we directly used methanol to extract the filters. This way we had methanol soluble but also water-soluble components in our solutions. Therefore, we can compare our methanol-soluble BrC also with other water-soluble BrC, because the solution contains water-soluble and water-insoluble organic carbon. In addition, Chen et al. (2019) also determined PARAFAC components of methanol-soluble organic carbon according to fluorophores in water-soluble organic carbon. However, to avoid misunderstandings we have added the following sentences to the method section 2.5:

"Please note that the MSOC contains methanol-soluble but also water-soluble compounds since also water-soluble compounds are partially soluble in methanol. We did this direct methanol extraction in order to dissolve a maximum number of compounds facilitating a good comparison with the mass spectrometric analysis in which there is no differentiation between different solubilities. However, this has to be kept in mind when comparing our results with studies that separated the water and methanol soluble fractions."

lines 321-322, "two different types of LV-OOA were observed LV-OOA1 and LV-OOA2", what is the difference between LV-OOA1 and LV-OOA2? The sources of C2 and C3, which are respectively associated with LOOA1 and LOOA2 are both simply classified as a less volatile oxygenated organic aerosol in this study.

In summer, LV-OOA1 and LV-OOA2 show different temporal variations as pointed out in a previous study (Song et al., 2022). LV-OOA1 showed a fair correlation with sulfate (R = 0.53), suggesting that LV-OOA1 was related to the regional transport. In contrast, LV-OOA2 showed a better correlation with $O_x$ ($O_x = NO + O_3$, R = 0.57), a photochemical indicator, suggesting that LV-OOA2 was related to photochemical oxidation processes. Furthermore, LV-OOA2 showed an exponential relationship with air temperature, which was related to the biogenic VOC emissions enhanced by the temperature. Please see more results on the source apportionment of OA in our previous study (Song et al., 2022) To point this out we have added the following sentence to the manuscript:

"HO-HULIS-1 component (C2) had a strong correlation (r = 0.9, $p < 0.01$) with LV-OOA1 which is related to regional transport in summer. In addition, the HO-HULIS-2 component (C3) showed a significant correlation with LV-OOA2 (r = 0.7, $p < 0.01$) which is related to oxidation of biogenic VOC in summer. Therefore, the HO-HULIS could be the less volatile oxygenated organic aerosol from regional transport and oxidation of biogenic VOC in summer."

Section 3.4: It is common to definite SV-OOA and LV-OOA to LO-OOA and HO-OOA, respectively. For the elemental ratio calculation, it is better to mention the method for this calculation.

The SOA factors resolved from the PMF analysis of OA can be named as LO-OOA and HO-OOA based on their oxygenation degree or SV-OOA and LV-OOA based on their assumed volatility and correlations with external tracers like nitrate and sulfate (Zhang et al., 2007; Jimenez et al., 2009). Generally, LO-OOA has semi-volatile nature and a good correlation with nitrate, while HO-OOA has lower volatility and a good correlation with sulfate. In many European field measurements, SV-OOA and LV-OOA were widely resolved by the PMF analysis of AMS-measured OA (Crippa et al., 2014). To keep the consistency with our previous study (Song et al., 2022), we adopt SV-OOA and LV-OOA as SOA factor labels in this study. We have added the description of the elemental ratio calculation method as follows.

"Large ion masses had a low signal-to-noise ratio. The elemental ratios of organics including oxygen-to-carbon and hydrogen-to-carbon ratios (O/C and H/C) were calculated from the V mode data based on the 'Improved-Ambient (I-A)' method (Canagaratna et al., 2015; Song et al., 2022)."

Line 340-341: The explanation on PLS is not convinced. This factor could be primary or secondary. Phenolic compounds have similar EEM feature with this factor. In addition, is there blank filter during sampling? If it is, it can be used comparison?

We agree with the comment and changed the name of factor C4 to phenol- and naphthalene-like substances. All filter samples were already subtracted by blank filters. Fig. S12 shows the time series and a reasonable correlation efficient (R = 0.7) of phenol and factor C4 relative abundance (%), indicating that the factor C4 could be from primary or secondary phenolic compounds.

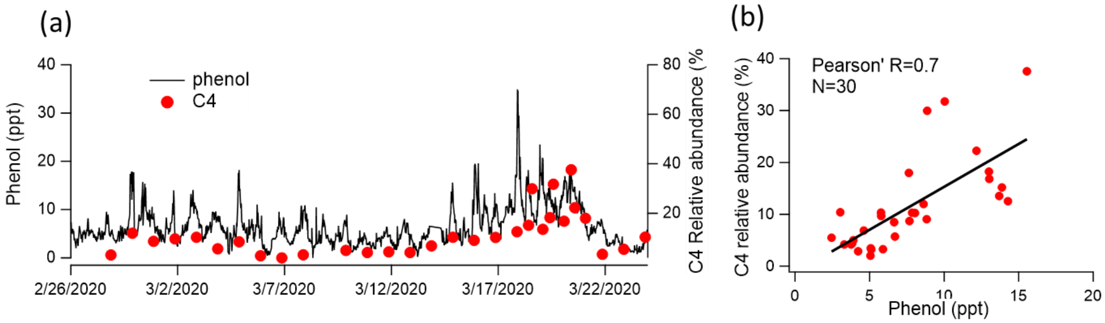

Figure S13. Time series of phenol in gas phase (PTR-MS, Song et al., 2022) and component 4 (C4) in particle phase (a). Correlation analysis of C4 and phenol (b).

"As shown in Fig. 5a, the phenol- and naphthalene-like component C4 had higher contributions to total fluorescence intensity for samples ID 33 to 41 (from March 18th to 20th, 2020). Phenol in the gas phase also showed higher concentrations (Fig. S13) during this period. Furthermore, as shown in Fig. S13, the phenol- and naphthalene-like components had a good correlation (R = 0.7) with phenol which is most likely originating from biomass burning and fossil fuel combustion (Sekimoto et al., 2013; Laskin et al., 2015). Therefore, the phenol- and naphthalene-like component C4 may be related to biomass burning and fossil fuel combustion."

line 356, how to calculate "NFV"? NFV data shown in Figure 5c differs from other literature by several orders of magnitude; please confirm whether the normalization was done using the fluorescence volume integral value (RU-nm2).

The integral fluorescence volume (FV, RU-nm$^2$) of extracts was calculated in the excitation wavelength of 239 – 500 nm and in the emission wavelength of 247 – 700 nm. The normalized fluorescence volume (NFV, RU-nm$^2$ [mg L$^{-1}$]$^{-1}$) was normalized by the organic concentration of the extracts obtained from AMS measurements. The NFV values range between 1500 – 17000 RU-nm$^2$ [mg L$^{-1}$]$^{-1}$ which is a similar level observed in other studies (Chen et al., 2019). We have explained this in section 2.4 as shown below.

"The integral fluorescence volume (FV, RU-nm$^2$) of the methanol extracts was calculated for the excitation wavelength of 239 – 500 nm and in the emission wavelength of 247 – 700 nm. The integral fluorescence volume was normalized by the organic concentration of the extracts obtained from AMS measurements to the normalized fluorescence volume (NFV, RU-nm$^2$ [mg L$^{-1}$]$^{-1}$)."

Line 344-355: It is better to compare the seasonal variation on chemical and chromophore composition using the consistent filter samples. Since some filter samples were collected only during a few hours, these filter should be removed during seasonal comparation. The chemical processing on particulate and gas phase is complicated and cannot be got the conclusion for LO-HULIS and O3 only based on the correlation analysis.

We have updated section 3.4 to account for this. For this part, we mainly discussed the diurnal variations of LO-HULIS and HO-HULIS in the winter. The contribution of LO-HULIS increased during the night. HO-HULIS showed an anticorrelation with this diurnal evolution. Deng et al. (2022) also found that LO-HULIS components contributed more in nighttime and HO-HULIS obviously increased in daytime during the winter in Tianjin, North China. The characteristics of

LO-HULIS are low oxidizing state and high double bond equivalent. However, The HO-HULIS (C2 and C3) have a high oxidation state and low double bond equivalents. Furthermore, LO-HULIS had a negative correlation (R= -0.6) with $O_3$ and HO-HULIS had a positive correlation (R= 0.7) with $O_3$. Therefore, we consider that LO-HULIS may be oxidized into HO-HULIS. This is also consistent with previous studies (Deng et al., 2022; Chen et al., 2021). We changed the paragraph as shown below.

"In contrast, HO-HULIS and phenol- and naphthalene-like chromophores showed an anti-correlation with this diurnal evolution. Deng et al. (2022) also found that LO-HULIS components contributed more at nighttime and HO-HULIS obviously increased in daytime during the winter in Tianjin, North China. The characteristics of LO-HULIS are low oxidizing state and high double bond equivalent. Furthermore, there is a negative correlation (Pearson's R= -0.6) between LO-HULIS and $O_3$ concentrations (Fig. S14a). The HO-HULIS (C2 and C3) have a high oxidation state and low double bond equivalents. They have significant correlations (Pearson's R= 0.7, $p < 0.01$) with $O_3$ in wintertime (Figs. S14b and c). Therefore, we consider that LO-HULIS may be oxidized into HO-HULIS. This is consistent with other studies (Deng et al., 2022; Chen et al., 2021)"

Line 413-415: It is not suitable to cite the result from river chemistry.

We deleted this comparison as it may be misleading.

In Figure 7, although the molecular weight are significant different in each figure, but the O/C and H/C are similar, does this right?

From plotting plot of a double bond equivalent (DBE) vs a number of carbon atoms per molecule (Lin et al., 2018), we assigned 321 potential BrC molecules from the about 2000 oxygenated organic molecules detected in the mass spectra of the FIGAERO-CIMS. According to this plot, the identified potential brown carbon molecules have large ranges (70 – 527 Da) of molecular weights. However, the major identified potential brown carbon molecules have similar O/C ranges of 0.6 – 1.2 and similar H/C ranges of 1.0 – 1.2. Therefore, the molecular weight could be significantly different, and the O/C and H/C are similar. However, the average O/C ratio for LO-HULIS related molecules was lower (0.8) lower than for HO-HULIS-1(0.9) and HO-HULIS-2 (1.0) related molecules.

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# Reviewer #3

## 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.

We agree and modified the manuscript accordingly.

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.

We agree that we should make this point clear to the reader from the beginning. However, our filter samples were directly extracted by methanol in this study. Therefore, our solutions include water-soluble and water-insoluble organic matter and hence can be compared to both. This is in line with studies by Chen et al., (2019, 2020) who also compared methanol-soluble fluorophores with water soluble ones. However, to avoid misunderstandings we have added the following sentences to the method section 2.5:

"Please note that the MSOC contains methanol-soluble but also water-soluble compounds since also water-soluble compounds are partially soluble in methanol. We did this direct methanol extraction in order to dissolve a maximum number of compounds facilitating a good comparison with the mass spectrometric analysis in which there is no differentiation between different solubilities. However, this has to be kept in mind when comparing our results with studies that separated the water and methanol soluble fractions."

## Specific comments

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

We reduced the length of the abstract. Please see lines 25-33 in the modified manuscript.

L85-87. Meaning of this sentence is not clear.

We have modified it as follows:

"However, the combination of these methods doesn't allow identifying specific molecules as the AMS measurement involves strong fragmentation of individual compounds."

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.

We have included Lin et al., 2016 and 2018.

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

The analysis of each filter by FIGAERO-CIMS was done in the same temporal procedure as described in the method section. In order to avoid any mass loading effects, the deposition time was varied from 50 – 270 minutes based on concurrent AMS measurements of organic $PM_{2.5}$ concentration levels to obtain similar organic mass filter loadings (Huang et al., 2019).

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.

We agree and used a power-law regression to calculate AAE for summer and winter. We changed the content as shown below.

"The absorption Ångström exponent (AAE) is an important parameter to characterize the wavelength dependence of light absorption which fits a power law as follows:

$$Abs_\lambda = K \times \lambda^{-AAE} \tag{3}$$

Where K is a concentration- and composition-related constant. In this study, AAE was fitted in the range of 300 – 450 nm."

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?

We agree that this needs to be explained. Due to limited experience with Aqualog data analysis; we set initially a too large wavelength increment for the samples from summer. After analyzing the summer filter samples, we realized this and reduced the wavelength increment for the analysis of the samples from winter. However, the different increment of EEM spectra can be changed by a function (eem_extend2largest) in RStudio staRdom. This function can reduce the larger wavelength increment in the summer samples and ensure the same wavelengths for all samples. This is explained in more detail with the software package: https://cran.r-project.org/web/packages/staRdom/vignettes/PARAFAC_analysis_of_EEM.html (2021 October 8). We have added this information to section 2.5 as follows:

"Please note that after analyzing the summer filter samples we realized that we set initially a too large wavelength increment and reduced the wavelength increment for the analysis of the samples from winter. However, the increments of EEM spectra can be changed by the function (eem_extend2largest) in RStudio staRdom. We used this function to reduce the wavelength increments in the larger samples and ensure the same wavelengths for all samples. This is explained in more detail with the software package: https://cran.r-project.org/web/packages/staRdom/vignettes/PARAFAC_analysis_of_EEM.html (2021 October 8)."

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.

The water Raman area is a unit for fluorescence intensity. It can be used to normalize the fluorescence intensity, even though the solvent is methanol. This was also done in other studies (Tang et al., 2020; Chen et al., 2016a).

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?

Methanol is a strong solvent to dissolve molecules. The small shoulder peak at ~300 nm is most likely due to some molecules from the filter or other contaminations. However, it only occurred in a few filter samples. It does not affect our main results. We added the following explanation to the caption of Figure 2.

"Please note that the small shoulder peak at ~300 nm for the average summer sample (a & b) is most likely due to some contaminations e.g. from the filter. However, it only occurred in a few filter samples and does not affect our main results."

L281. The maximum EM wavelengths of C3 is ~400 nm, not significantly above.

This is correct and we have modified the sentence as follows:

"In contrast to C1, the maximum emission wavelengths of C2 and C3 range above 400 nm."

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?

Thank you for this suggestion. We now assign the C4 component as phenol- and naphthalene-like substances. Fig. S13 shows the time series and good correlation efficient (R=0.7) of phenol and C4 relative abundance (%), indicating that the C4 could indeed stem from primary or secondary phenolic compounds. This is consistent in previous studies (Chen et al., 2016b; Mladenov et al., 2011). We have modified the assignment throughout the manuscript and added Fig. S13. We have added the assignment to section 3.4:

"As shown in Fig. 5a, the phenol- and naphthalene-like component C4 had higher contributions to total fluorescence intensity for samples ID 33 to 41 (from March 18th to 20th, 2020). Phenol in gas phase also showed higher concentrations (Fig. S13) during this period. Furthermore, as shown in Fig. S13, the phenol- and naphthalene-like component has a good correlation (R = 0.7) with phenol which is most likely originating from biomass burning and fossil fuel combustion (Sekimoto et al., 2013; Laskin et al., 2015)."

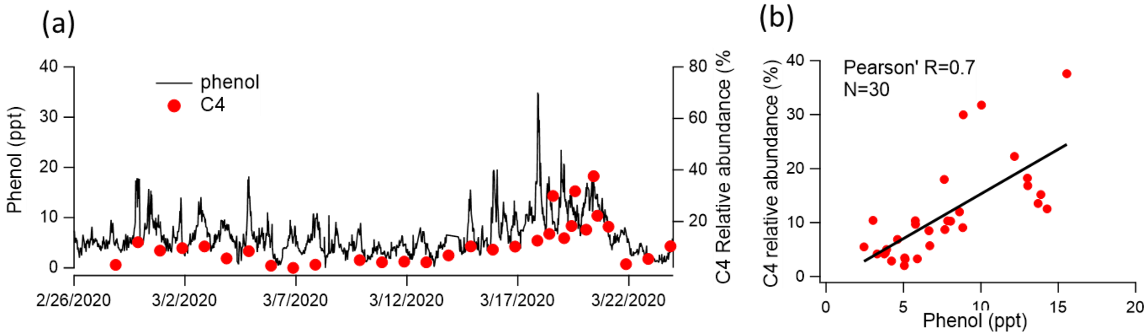

Figure S13. Time series of phenol (PTR-MS, Song et al., 2022) in gas phase and component 4 (C4) in particle phase (a). Correlation analysis of C4 and phenol (b).

L328. What is used to do the correlation analysis between AMS and PARAFAC components? Relative contributions or absolute intensities?

We use relative contributions to do correlations analysis between AMS an PARAFAC components and have modified the sentence as follows to make this clear:

“To potentially identify chromophore sources, we compared the factors from PMF analysis of AMS mass spectra and the components determined by the PARAFAC analysis of the excitation-emission spectra using a Pearson’s correlation analysis based on relative abundances, as shown in Figs. S11 and S12.”

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?

We just wanted to point out that shorter sampling times may imply potentially higher uncertainties but not that these samples are unreliable. With the assignment of C4 as phenol- and naphthalene-like chromophores also the diurnal cycles seem to make sense as expressed in the modified text in section 3.4 of the manuscript:

“In contrast, HO-HULIS and phenol- and naphthalene-like chromophores showed an anti-correlation with this diurnal evolution. Deng et al. (2022) also found that LO-HULIS components contributed more at nighttime and HO-HULIS obviously increased at daytime during the winter in Tianjin, North China. The characteristics of LO-HULIS are low oxidizing state and high double bond equivalent. Furthermore, there is a negative correlation (Pearson’s R= -0.6) between LO-HULIS and $O_3$ concentrations (Fig. S13a). The HO-HULIS (C2 and C3) have a high oxidation state and low double bond equivalents. They have significant correlations (Pearson’s R= 0.7, $p < 0.01$) with $O_3$ in wintertime (Figs. S13b and c). Therefore, we consider that LO-HULIS may be oxidized into HO-HULIS. This is consistent with other studies (Deng et al., 2022; Chen et al., 2021).”

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.

We agree and update.

"The normalized fluorescence volume (NFV) has a high intensity in samples ID 5 and 6 but the $MAE_{365}$ (Fig. 5c) is not significantly enhanced. This could be either due to contamination but also due to specific species in these samples as indicated e.g. by a higher fraction of LV-OOA1."

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.

We agree and updated the text as follows:

Therefore, we conclude that NACs concentrations have levels between 1 – 20 ng $m^{-3}$ in Western Europe, which are substantially lower than in polluted regions.

L394. How did the authors calculate the mass fraction of potential BrC?

We observed typically about 2000 mass peaks corresponding to different oxygenated organic compounds in particles by using FIGAERO-CIMS. We assume an average sensitivity of 22 cps/ppt to calculate molecular mass concentrations (Lopez-Hilfiker et al., 2016), except for 5 nitro-aromatic compounds for which we did individual calibrations with authentic standards. Each of the 2000 molecules were assigned a corresponding double bond equivalent (DBE) and was plotted by DBE vs the number of carbon atoms per molecule. Detailed information about this method is shown in supplement section 3 and Fig. S15. As shown in Fig. S15, if molecules were grouped in the yellow shaded area, they were considered as potential brown carbon molecules (Lin et al., 2018). After this classification of the potential brown carbon molecules from around 2000 molecules, we can calculate their potential mass concentration (Salvador et al., 2021). The total ($PM_{2.5}$) organic aerosol mass concentration was measured by an AMS during the campaigns. Therefore, the mass fraction of potential BrC could be calculated from their mass concentration divided by the total organic aerosol particle mass concentration from AMS (Gao et al., 2022). We have added the following sentence to section 3 of the supplement:

"After this classification of the potential brown carbon molecules from around 2000 molecules, we can calculate their potential mass concentration and mass fraction by assuming an average sensitivity of the CIMS of 22 cps/ppt (Lopez-Hilfiker et al., 2016) and dividing their mass by the total organic aerosol mass from the AMS."

Figure 6a. Only 8 samples were analyzed by FIGAERO-CIMS? Which samples were selected?

The 11 Teflon filters were collected from March 17th to 20th, 2020 (Table S3). There were three Teflon filters and one quartz filter in March 17th 2020. Therefore, three Teflon filters were averaged to represent that day and to be compared with the one quartz filter from March 17th, 2020. Filter 11 was not used due to very low filter loading in the afternoon.

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.

Almost all potential BrC molecules were detected in every sample. We have added the following sentence to Table S8:

“Please note that each sample contained most of the potential BrC molecules.”

Table S8. The correlation coefficient is calculated between Abs365 and what parameter for potential BrC molecules?

The correlation coefficient was calculated between Abs and mass concentration of each potential BrC molecules. We have updated the caption for Table S8:

“Table S8. Assignment of 316 potential brown carbon molecules detected in Karlsruhe, including mass, formula, double bond equivalent (DBE), the ratio of O/C, and correlation coefficients between mass concentration and the absorption of BrC at 365 nm in 8 filter samples. Please note, that each sample contained most of the potential BrC molecules.”

Sec. S3. L37-38. I do not understand here. Without standards, how can the authors derive the mass concentrations of 321 potential BrC molecules?

This has been answered already above (L394) and explained now in section 3 of the supplement.

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.

This is an interesting publication showing an approach quite similar to ours. However, we related estimated potential BrC mass concentrations to the total organic aerosol mass while it is not clear which fraction of the total organic mass was detected by the FTICR-MS (Stubbins et al., 2014).

Table S11. Molecular weight and O/C are intensity weighted or arithmetic mean, should be clarified.

We agree and added the following sentence:

“The molecular weight, O/C, DBE, and modified aromaticity index ($AI_{mod}$) in Table S11 are intensity-weighted mean values.”

Fig. 7. What are bubble sizes mean? Peak intensities? Needs to be clarified.

We agree and updated the text. The size of the circles is the relative contribution to the total brown carbon signals of each compound. We have added this to the figure caption:

“The size of the circles is the relative contribution to the total brown carbon signals of each compound.”

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.

The double bond equivalent (DBE) and modified aromaticity index ($AI_{mod}$) are listed now also in table S11. The carbon oxidation state from the four components was at similar level of 0.6 – 0.8. Therefore, we did not add the carbon oxidation state in table S11.

Table S11. Average properties of molecules associated with four characteristic chromophores in winter

| Average properties | Molecular mass [g $mol^{-1}$] | O/C ratio | DBE | $AI_{mod}$ | Mass fraction of potential BrC [%] | Mass fraction of nitrogen containing molecules [%] |
|---|---|---|---|---|---|---|
| LO-HULIS (C1) | 265 ± 2 | 0.8 ± 0.01 | 5.8 ± 0.04 | 0.23 ± 0.02 | 17 ± 4 | 62 ± 1 |
| HO-HULIS-1 (C2) | 170 ± 1 | 0.9 ± 0.01 | 3.6 ± 0.03 | 0.16 ± 0.01 | 14 ± 2 | 9 ± 0.3 |
| HO-HULIS-2 (C3) | 166 ± 1 | 1.0 ± 0.02 | 3.4 ± 0.02 | 0.10 ± 0.01 | 34 ± 4 | 9 ± 0.3 |
| Phenol- and naphthalene-like (C4) | 163 ± 8 | 0.8 ± 0.03 | 3.8 ± 0.06 | 0.20 ± 0.03 | 5 ± 1 | 32 ± 2 |

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