Response to reviewers' comments on "Brown carbon aerosol in rural Germany: sources, chemistry, and diurnal variations" (egusphere-2024-1848)

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 #2

Review of Jiang et al. Brown carbon aerosol in rural Germany: sources, chemistry, and diurnal variations. This manuscript presents results from concurrent measurements of aerosol chemical composition and light absorption from black carbon and light-absorbing organic aerosols (aka brown carbon) at a rural site in Germany during one month in winter 2021. The absorption apportionment and chemical speciation of brown carbon aerosols in both gas and particle phases are reported. The sources of brown carbon in rural Germany were identified based on its diurnal variability and regression analysis of brown carbon with emission tracers. In general, this study adds to the literature on the characteristics of brown carbon aerosols in rural Germany, but for the reasons outlined below I cannot recommend publication of this manuscript in its current form.

General comments

1. Overall, I am not convinced that the 178 molecules identified by FIGAERO-CIMS are representative of the brown carbon aerosols, not only because they contributed to a very small fraction (2%) of total organic mass as well as brown carbon absorption (11%), but also the correlation between the molecule mass and brown carbon absorption is not so good. There are a lot of scatters in Figure S6 which means most of the brown carbon absorption cannot be explained by the identified molecules. The authors also did not provide details in how these compounds are identified as brown carbon molecules rather than referencing to an earlier publication from the same group. In several places throughout the manuscript the authors simply refer the 178 molecules as particle-BrC and the 31 molecules as gas-BrC (e.g. Figure 1, Figure S6 and related text), which is not accurate given the reasons provided above.

From the 1500 molecules we observed we assigned 178 as potential BrC molecules according to a method published by Lin et al., (2018). They correlated the number of double bond equivalents with the number of carbon atoms per molecule. A few studies used this method to assign brown carbon molecules. For example, there are good correlations ($r = 0.9$) between mass absorption efficiency at 365 nm and potential brown carbon molecules of larger molecular weight (Tang et al., 2020). Xu et al., (2020) used this method to assign 149 nitrogen-containing potential BrC chromophores in the Tibetan Plateau and we used this method to assign potential BrC molecules in downtown Karlsruhe (Jiang et al., 2022). It is not unusual that only a small mass fraction of absorbing molecules can dominate the aerosol absorption (Mohr et al., 2013). We consider the correlation of the BrC absorption at 370 nm with the estimated BrC mass of 0.7 ± 0.1 shown in figure S6 as relatively good considering the underlying assumptions.

To better point this out we changed “BrC molecules” to “potential BrC molecules” throughout the manuscript and added additional explanations on the method in sections 2.3 and 3.2 as follows:

Section 2.3:

“Lin et al., (2016, 2018) employed high-resolution mass spectrometry to analyze biomass burning organic aerosol. They assigned potential brown carbon compounds according to the correlation of double bond equivalents (DBE) with the number of carbon atoms per molecule (FigureS12). We used this method to assign 178 potential BrC molecules (including 7 NACs) in the particle phase and 31 potential BrC molecules (including 4 NACs) in the gas phase, as shown in Figure 1 in the corresponding mass spectra. A few other studies used this method also to assign more brown carbon molecules. For example, good correlations (r = 0.9) between mass absorption efficiency at 365 nm and potential brown carbon molecules of larger molecular weight were found by Tang et al., (2020). Xu et al., (2020) used this method to assign 149 nitrogen-containing potential BrC chromophores at the Tibetan Plateau and we used this method to assign potential BrC molecules in downtown Karlsruhe (Jiang et al., 2022). The potential BrC molecules we assigned according to this method for the particle and the gas phase are listed in Tables S2 and S3.”

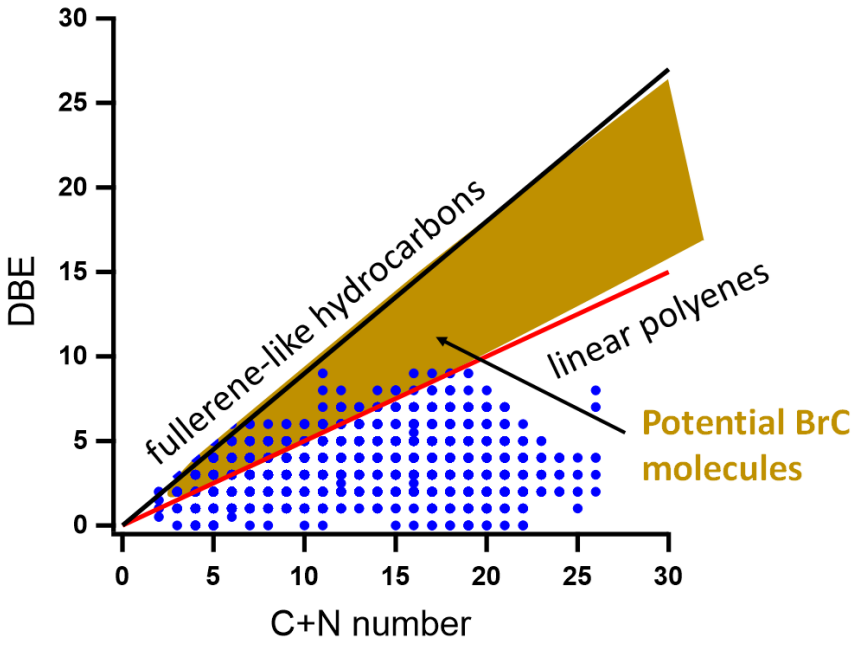

Figure S12. Plot of the double bond equivalent (DBE) vs numbers of carbon and nitrogen atoms according to our measurements following the procedure described by Lin et al., (2018). The lines indicate DBE reference values of linear conjugated polyenes (red solid line) and fullerene-like hydrocarbons with DBE=0.9*C (black solid line). Data points inside the yellow shaded area are potential BrC molecules. (cf. Lin et al., 2018).

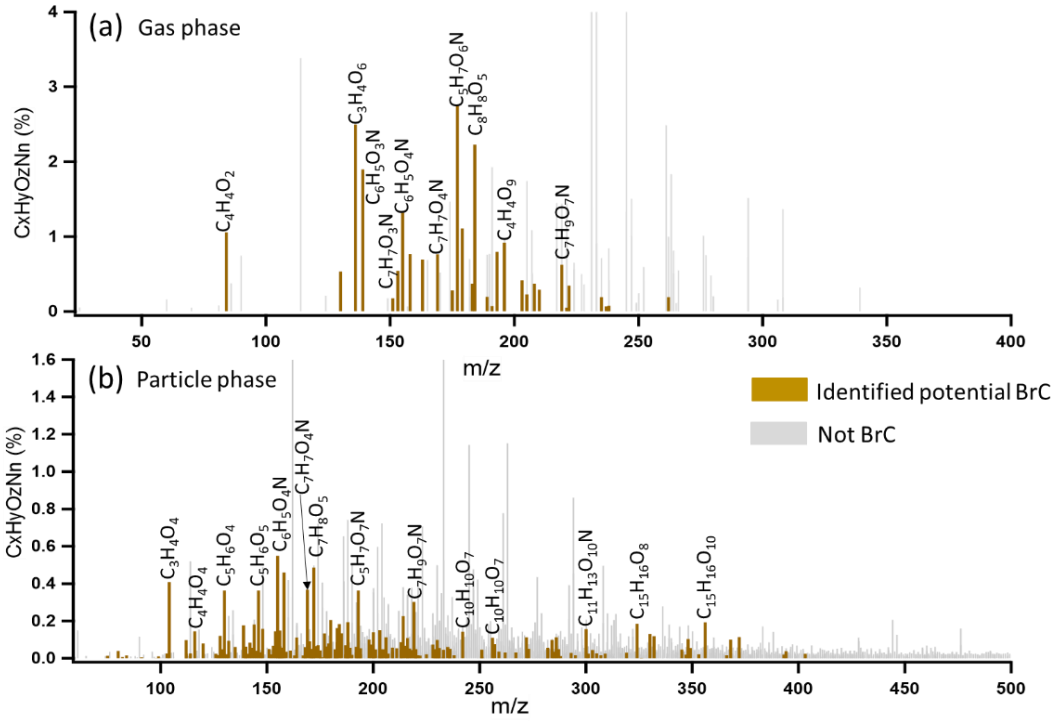

Figure 1. CIMS mass spectra of organic aerosol measured by FIGAERO-CIMS for a biomass burning event on March 1st, 2021, a: gas phase, b: particle phase. The CI source employs reactions of I^- ions, which convert analyte molecules into $[M+I]^-$ ions. Legends above MS features correspond to neutral molecules. The brown peaks in the mass spectra were assigned as potential BrC molecules while the gray peaks refer to the other organic molecules.

Section 3.2:

"We identified 178 potential BrC molecules according to the method developed by Lin et al., (2018) (cf. section 2.3.). The mass of these molecules shows a good correlation (r=0.7 ± 0.1) with the absorption at 370 nm (b_{BrC370}) of BrC (sf. Figure S6). "

2. There is lack of a discussion on the uncertainties related to absorption measurement by the aethalometer and calculations deriving BC and BrC absorption, as well as BrC source apportionment in Line 302-303. In Line 190-191, the authors stated that "During this winter campaign, the BrC absorption accounted for ~40% of total absorption caused by BC and BrC." I could not trace back to how this number (40%) was derived, nor did the authors provide information about which absorption wavelength the calculation is based on.

BC and BrC absorption measurements by aethalometers have the filter-based lensing effect (Moschos et al. 2021). According to previous studies, the lensing effect for BC and BrC measurement were 8%-27% and 6%-20%, respectively (Moschos et al. 2021). We adopted an AAE_{BC} value of 1 in this study. However, this assumption introduces an uncertainty in the estimations of BC and BrC light absorptions. According to previous studies, the AAE_{BC} shows a range of 0.8-1.4 (Lack and Langridge 2013). This range, although maybe not fully applicable to

our measurement location, potentially causes relatively large uncertainties in splitting between BrC and BC absorption (Duan et al. 2024).

We added following sentences to make the reader aware of this problem:
"The absorption measurements by aethalometer have the filter-based lensing effect (Moschos et al. 2021). According to previous studies, the uncertainty from lensing effect for BC and BrC measurement were 8%-27% and 6%-20%, respectively (Moschos et al. 2021). We assumed an AAE_{BC} value of 1.0 in this study. However, this assumption introduces an uncertainty in the estimations of BC and BrC light absorptions. According to previous studies, the AAE_{BC} ranges between 0.8-1.4 (Lack and Langridge 2013). This range although maybe not fully applicable to our measurement location, potentially causes relatively large uncertainties of up 81% (at 370nm) in splitting between BrC and BC absorption (Figure S13) (Duan et al. 2024). Despite these potentially large uncertainties on absolute absorption values, we consider this method still useful. Our assumption of AAE_{BC} = 1.0 is reasonable for our location as based on previous measurements and it should still allow to discuss the relative evolution of BC and BrC absorption."

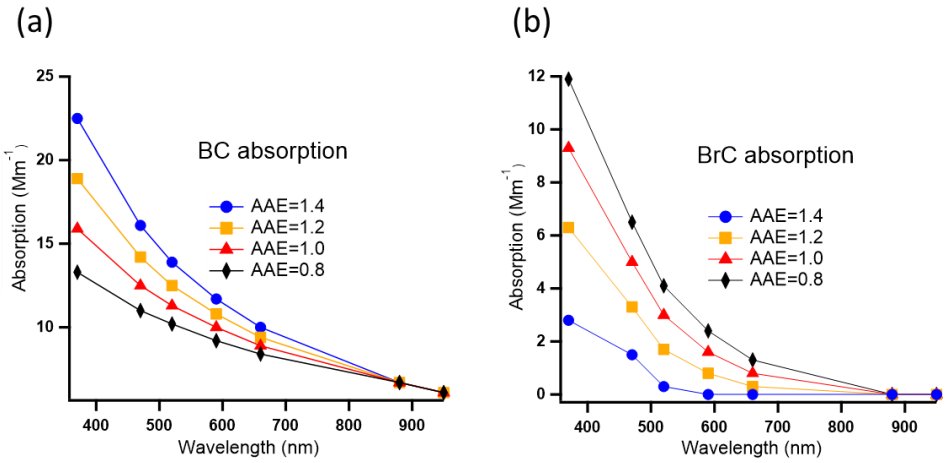

Figure S13. Light absorption of BC (a) and BrC (b) under different assumptions regarding the AAE_{BC}. The blue, yellow, red, and black makers represent light absorption of BC and BrC when AAEBC is 1.4, 1.2, 1.0, and 0.8, respectively.

"The uncertainty of the splitting between BrC from biomass burning and of secondary origin is mainly based on the levoglucosan concentration for which we have included the calibration. Based on this we estimated the uncertainty of the BrC source splitting to ±35%."

We explained that we calculated the BrC absorption contribution for a wavelength at 370 nm and indicated this in the manuscript as follow:

"During this winter campaign, the BrC absorption accounted on average for ~40% of total absorption caused by BC and BrC at 370 nm."

3. The authors also tend to draw causal relationship based on correlation. For example, in Line 200, the authors stated "The levoglucosan had a good correlation (r=0.7) with BC. This also indicates that BC was mainly emitted from biomass burning during the winter campaign." This statement is not supported by evidence. Having a r =0.7 means levoglucosan can explain less than half of the variability in BC concentration. Similar statement is in Line 322-324 "In addition, the O/C ratio of BrC had a positive correlation (r=0.8) with ozone. This indicates that the BrC was photo-oxidized leading to an increase of the O/C ratio of BrC."

Thank for pointing to this. It wasn't our intention to draw causal relationship based on correlations.

We reformulated the sentence in line 200 as follows:

"The levoglucosan showed a good correlation (r = 0.7) with BC. This is in line with the large fraction of biomass burning contributing to BC during the winter campaign. Biomass burning BC accounted for (71 ± 40)% of total BC as we discussed above."

We reformulated the sentence in line 322-324 as follows:

"The O/C ratio of the potential BrC molecules increased during daytime and decreased at nighttime. This is an indication for an impact of photo-oxidation on BrC either during formation or aging leading to an increase of its O/C ratio. Consequently, the O/C ratio of the potential BrC molecules shows a positive correlation (r=0.8) with ozone, another product of photo chemistry."

Specific comments:

4. In Figure 2, the contribution from nitro-aromatics absorption is only plotted at 370 nm. I wonder if the absorption profile of these compounds were measured, and if so, it would be interesting to show absorption contribution from the nitro-aromatics across the whole spectrum.

The absorption spectra of several nitro-aromatic compounds is known in the literature. It would therefore be possible to show their contribution in the spectrum. However, the wavelength dependence is generally decreasing steadily (Xie et al. 2017) with increasing wavelength, except for 4-nitrocatechol, and would hence show a similar behavior as given for all potential BrC molecules.

5. Figure S3: second panel from top: no color differentiation for the two AAE parameters plotted.

We included a color differentiation.

6. Figure S8. The correlation of gas-phase BrC and temperature is based on exponential fit (y=e(0.15*x)). How is the correlation between temperature and particle phase BrC like? The authors stated "Figure S8 shows that BrC in the gas phase had a good correlation (r=0.4) with temperature." I recommend changing "good" to "moderate".

There is no significant correlation between temperature and particle phase BrC (0.02). Particle phase BrC appears to be dominated by low volatile compounds.

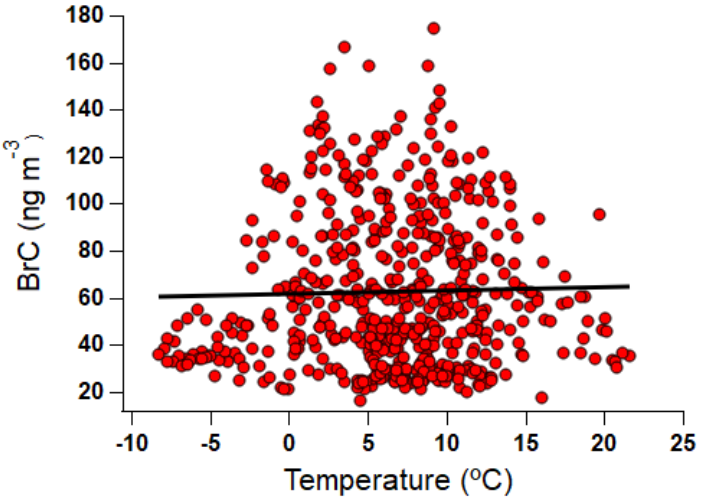

Figure. Correlation between particle phase BrC and temperature.

We changed the sentence on the gas-phase BrC as follows:

Figure S8 shows that BrC in the gas phase had a moderate positive correlation with temperature.

References:

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