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.

Editor

Please carefully respond to the new referee reports. There are several comments raised by the reviewers that need your attention. It seems both of the reviewers suggest moving this to a Measurement Report style due to the large uncertainties in the presentation of the data. I agree with this suggestion from the reviewers. If you agree as well, we will make this change before publication would occur. In any case, I would like to request that you carefully review their new comments and provide a point-by-point response and track changes version of the manuscript that considers these comments.

We agree to publish this manuscript as a Measurement Report with following title:

Measurement report: Brown carbon aerosol in rural Germany: sources, chemistry, and diurnal variations

We also added dataset DOI links in the manuscript.

"The data related to this article are accessible at KIT open data (https://doi.org/10.35097/d0prpzkxqkq2t09y, Jiang et al., 2024).

Reviewer #1

The authors have largely addressed the points raised in my original review. Thank you. I have a few additional minor points to raise:

1. Provide units for the new "sensitivity factors".

We changed the sensitivity factors into sensitivity with units of cps ppt^{-1} throughout the manuscript and supplement.

2. Provide the wavelength in Table S5 for the MAC value.

We added the wavelength as given below:

Nitro aromatic compounds in particle phase detected at KIT Campus Nord, including chemical formula, mass absorption coefficient (MAC) at 365 nm, concentration range, and average concentration (mean ± standard deviation).

3. Double check the new text in the paper, as there are a couple of typos and wording problems in it.

We double checked the manuscript for typos and wording.

4. Add the dates at which the calibrations were done. If the calibrations were not close in time to the field campaign, then a comment indicating the associated uncertainty should be included.

First calibrations for nitro aromatic compounds (NACs) were done directly after the field campaign. However, due to technical problems during the first calibration, it was repeated in August 2024. We added this information as follows:

"First calibrations for nitro aromatic compounds (NACs) were done directly after field campaign. However, due to technical problems, the calibration of 4-nitrophenol, 4-nitrocatechol, 2-methyl-4-nitropehnol, and 4-methyl-5-nitrocatechol was repeated in August 2024. These results are shown in Figure S9. Despite the large time between measurements and second calibration, we have indications from repeated measurements of formic acid that the sensitivity of the instrument didn't change substantially over this time period. Please note that this leads to an additional uncertainty of about 20%."

5. Overall, this paper provides coupled absorption and mass spectrometry measurements related to BrC in Germany. There is merit to publication because the measurements are new. The absorption measurements are fine, especially now that the aethalometry approach has been better described. However, I still feel that this work is "semi-quantitative" with respect to BrC molecule quantification. For example, I feel it is not appropriate to have statements such as the following in the Abstract: "The 178 potential BrC molecules only accounted for 2.6 ± 1.5% of the total organic mass, but can explain 14 ± 13% of the total BrC absorption at 370 nm" In particular, by calibrating only a few nitrophenols, I do not believe that one can claim to make a statement about closure between BrC absorption and the species giving rise to that absorption. Moreover, the organic aerosol mass was not measured.

We agree that there are large uncertainties from CIMS sensitivity, mass absorption cross-section for nitro-aromatics, and estimated organic matter concentrations. Therefore, we deleted the absorption results and discussions from potential BrC molecules in section 3.3. In addition, we deleted this statement of "The 178 potential BrC molecules only accounted for 2.6 ± 1.5% of the total organic mass, but can explain 14 ± 13% of the total BrC absorption at 370 nm" in abstract and conclusion.

Since we calibrated the NACs sensitivity of CIMS and known the mass absorption cross-section of NACs (Xie et al., 2017). We calculated the absorption contribution of seven NACs for total BrC absorption, as shown in new Figure 3.

We add a new statement in the abstract:

"The average light absorption of seven NACs in the particle phase was 0.2 ± 0.2 Mm^{-1}, contributing to 2.2 ± 2.1% of total BrC absorption at 370 nm."

We add new statements to the results and discussion section 3.3:

"We calculated the average light absorption of seven nitro aromatic compounds (NACs) by using the mass absorption coefficients (MAC_{365}, Xie et al., 2017), given in Table S5 and the average concentrations measured. Based on this, the mean light absorption of the sum of the seven NACs was calculated to be 0.2 ± 0.2 Mm^{-1}. The absorption of the seven NACs contributed to 2.2 ± 2.1% of total BrC absorption at 370 nm (Figure 3b)."

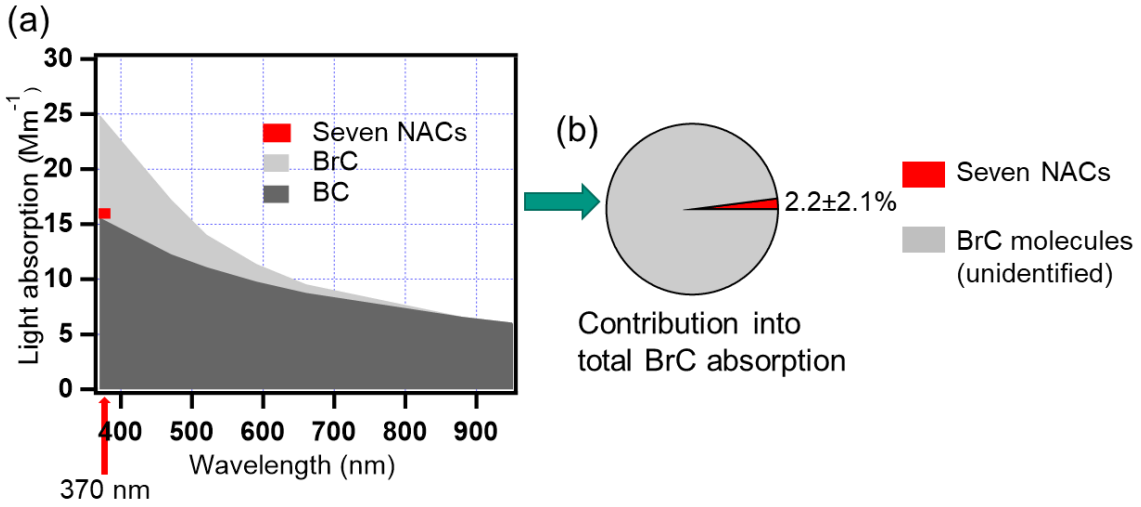

Figure 3. (a) A stacked plot showing the main contributions to aerosol absorption from brown carbon and black carbon based on the seven wavelengths measured by the aethalometer AE33. The contribution of seven NACs to the total aerosol absorption is indicated in red at 370 nm. (b) Average absorption contribution of seven NACs to total absorption by BrC. The red: seven NACs; the gray: unidentified-BrC molecules.

6. Also, I am still puzzled by the following statement in the paper: "Please note that the sensitivity of CIMS for different organic compounds varies by a few orders of magnitude. Sensitivity uncertainties were taken into account in the calculation of the overall uncertainties of CIMS concentrations (±60%) …" If CIMS sensitivities can vary by orders of magnitude (which I agree with), then how can the overall uncertainties in the CIMS concentrations be ±60%? This doesn't make sense.

We deleted this sentence.

7. My advice would be to remove such statements about absorption closure (such as that in the Abstract) from the paper, because I don't believe they are quantitatively justified.

We deleted this statement of "The 178 potential BrC molecules only accounted for 2.6 ± 1.5% of the total organic mass, but can explain 14 ± 13% of the total BrC absorption at 370 nm" in abstract, results, and conclusion.

References:

Xie, M., Chen, X., Hays, M. D., Lewandowski, M., Offenberg, J., Kleindienst, T. E., and Holder, A. L.: Light Absorption of Secondary Organic Aerosol: Composition and Contribution of Nitroaromatic Compounds, Environ. Sci. Technol., 51, 11607– 11616, https://doi.org/10.1021/acs.est.7b03263, 2017.

Jiang, F., Saathoff, H., Ezenobi, U., Song, J., Zhang, H., Gao, L., and Leisner, T.: Dataset for the publication: Brown carbon aerosol in rural Germany: sources, chemistry, and diurnal variations, Karlsruhe Institute of Technology [data set], https://doi.org/10.35097/d0prpzkxqkq2t09y, 2024.

Reviewer #2

General comments

1. After reviewing the revised manuscript and author's response, I am not convinced by the quantitative conclusions drawn from this study based on numerous assumptions. The study used too many empirical or averaged parameters (e.g. CIMS sensitivity, mass absorption cross-section for nitro-aromatics, organic matter concentrations) that could lead to a very large error bar on any of the quantities derived from the analysis. In fact, the mass concentrations of the identified brown carbon compounds and their contribution to organic mass and brown carbon absorption changed significantly in the revised manuscript without proper explanation.

We agree that we used to many assumptions to estimate the potential absorption of the 178 potential BrC molecules. Therefore, we deleted the absorption results and discussions from potential BrC molecules in section 3.3. In addition, we deleted this statement of "The 178 potential BrC molecules only accounted for 2.6 ± 1.5% of the total organic mass, but can explain 14 ± 13% of the total BrC absorption at 370 nm" in abstract and conclusion.

In the revised manuscript we use mass concentrations of the nitro aromatic compounds based on a calibration of our CIMS instead of an estimated average sensitivity. Together with literature values (Xie et al., 2017) of their mass absorption cross sections, we can quantify their contribution to BrC absorption, as show in new Figure 3.

We add a new statement in the abstract and conclusion:

"The average light absorption of seven NACs in the particle phase was 0.2 ± 0.2 Mm^{-1}, contributing to 2.2 ± 2.1% of total BrC absorption at 370 nm."

We add new statements to the results and discussion:

"We calculated the average light absorption of seven nitro aromatic compounds by using the mass absorption coefficients (MAC_{365}, Xie et al., 2017), given in Table S5 and the average concentrations measured. Based on this, the mean light absorption of the sum of the seven NACs was calculated to be 0.2 ± 0.2 Mm^{-1}. The absorption of the seven NACs contributed to 2.2 ± 2.1% of total BrC absorption at 370 nm (Figure 3b)."

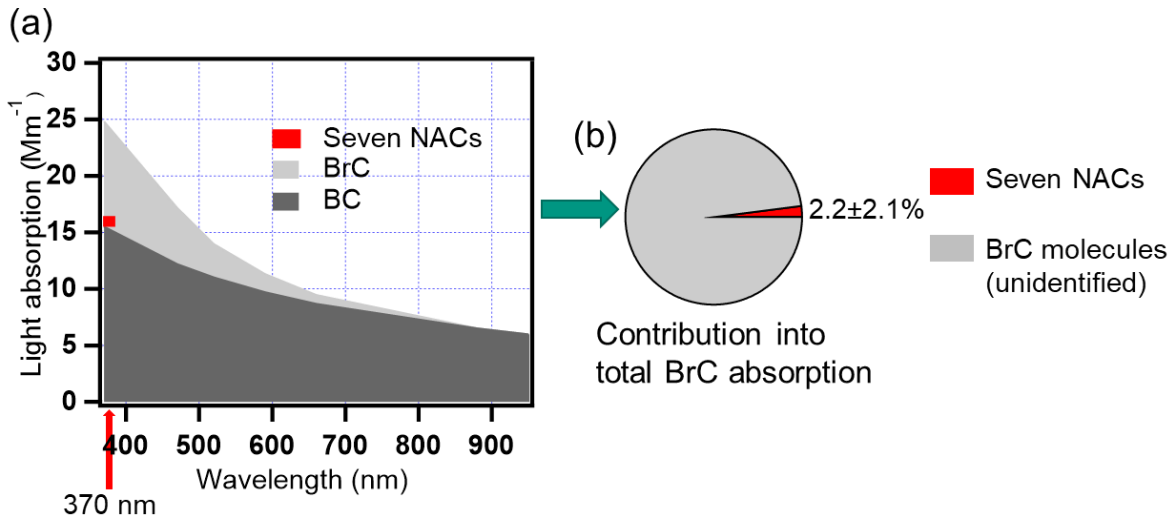

Figure 3. (a) A stacked plot showing the main contributions to aerosol absorption from brown carbon and black carbon based on the seven wavelengths measured by the aethalometer AE33. The contribution of seven NACs to the total aerosol absorption is indicated in red at 370 nm. (b) Average absorption contribution of seven NACs to total absorption by BrC. The red: seven NACs; the gray: unidentified- BrC molecules.

References:

Xie, M., Chen, X., Hays, M. D., Lewandowski, M., Offenberg, J., Kleindienst, T. E., and Holder, A. L.: Light Absorption of Secondary Organic Aerosol: Composition and Contribution of Nitroaromatic Compounds, Environ. Sci. Technol., 51, 11607– 11616, https://doi.org/10.1021/acs.est.7b03263, 2017.