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Comment on acp-2022-483

Anonymous Referee #2

Referee comment on "Concurrent photochemical whitening and darkening of ambient brown carbon" by Qian Li et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-483-RC2, 2022

The manuscript entitled "Concurrent photochemical whitening and darkening of ambient brown carbon" investigates the contribution of BC and BrC to aerosol absorption, deploying up-to-date chemical and microphysical aerosol characterization techniques in a suburban area of Beijing. The analysis of primary and secondary BrC absorption daily variability is used to derive conclusion on aerosol darkening and bleaching processes, but this part of the analysis is only weakly supported by experimental results.

Main comments:

The identification of OA sources with PMF analysis could be improved. The authors could analyze how the factor mass spectra identified in the present study correlate with previous results. A library with existing profiles can be found here: https://cires1.colorado.edu/jimenez-group/HRAMSsd/. In addition the mass spectra can be compared to unit mass resolution reference spectra from https://cires1.colorado.edu/jimenez-group/AMSsd/. In addition, COA in previous works usually shows a peak at noon, while in this study the lunch peak is barely visible. The author should discuss this discrepancy. Finally, the authors claim the use of external tracers to identify the PMF factors, but for COA an internal tracer was used instead, which makes the attribution risky, especially considering the correlation in time with HOA factors (based on the diurnal profile).

This study identifies organic nitrate using ATR-FT-IR, integrating the spectra area around the characteristic absorption peaks at 860 cm^{-1} and 1640 cm^{-1}, in agreement with Liu et al. (2012). Nevertheless previous studies showed that the region between 1600 and 1700 cm^{-1} shows typically a strong absorption signal due to the carbonyl group of ketones and carboxylic acid (Maria et al., 2002; Russell et al., 2009), which would lead to an overestimation of the NO2 absorption at 1640 cm^{-1}.

The discussion about the bleaching and darkening of BrC is based on the analysis of diurnal profiles of primary and secondary BrC , both absolute absorption coefficient and fractional contribution in figure 4. The text reports: "Fig. 4b showed the decrease of primary BrC absorption tended to be more rapid than the HOA and BBOA mass (even a slight increase for HOA), which indicated the likely photobleaching process", but this decrease is difficult to discern in the figure. In addition, the attribution of secondary BrC to local photochemical production is based on the comparison between the fraction of secondary BrC diurnal profile and solar radiation, but if local photochemistry triggered secondary BrC formation I would expect to see a correlation between secondary BrC absorption (reported in fig.4 c) and solar radiation. On the contrary, secondary BrC absorption shows a peak in the morning, when photochemistry is expected to be lower.

Minor comments:

Line 34-36. Please revise this sentence. Saleh et al. 2014 reported that the OA to BC ratio is higher during the smoldering phase, but do not compare the absorption efficiency of BrC produced during smoldering and flaming. Similarly, Chakrabarty et al. observed an increase in the absorption angstrom exponent of aerosol particles during smoldering, due to the larger OA contribution, but did not report differences in the imaginary part of the BrC refractive index during smoldering and flaming.

The authors classify the sampling period based on the analysis of back-trajectories (see figure S1). The sampling site is located in a suburban area of Beijing where local and nearby pollution sources are likely affecting the observed PM trend, rather than synoptic scale circulation. If the author wants to discriminate the sampling period into cluster, I would suggest to use local meteorology, including temperature, relative humidity, and wind speed/direction. For example, figure S1 shows an increase in the concentration and relative contribution of nitrate when relative humidity is higher, suggesting the relevance of local processes. Furthermore, wind speed and direction might help to spot the time when the impact of the urban Beijing area is higher.

Line 77: the authors derived BC MAC based on the Mie theory. Liu et al 2018 showed that the Mie theory holds for spherical particles, but fails in reproducing the absorption of fractal particles. The author should discuss the uncertainty derived from it.

Line 105: How do the primary absorption to rBC concentration ratios compared with previous studies?

Line 141-142: Inorganic nitrate usually dominates nitrate signal in the AMS measurements (Farmer et al., 2010). Please, revise this sentence or estimate organic nitrate from AMS signal and compare it with inorganic nitrate.

Technical comments:

Line 83: corrected instead of excluded

Line 181: constant instead of consistent

Figure1: the author might want to change the order of factors in the figure and report OOA1 before OOA2.

Figure 3: If possible, the author might want to use horizontal lines instead of circles as markers in fig 3e to clarify that the FTIR data correspond to a time range of 24 hours. The horizontal lines should start and end at the beginning and end of the corresponding sampling period.

Figure 3: panel b shows a day dominated by secondary BrC at the end of the field experiment (likely May 7), while in fig 3c the secondary BrC absorption during the same day is not reported.

Line 226: accounted for instead of occupied

References:

Farmer et al., 2010, Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry, PNAS, 107 (15): 6670-6675

Liu et al., 2012, Hydrolysis of Organonitrate Functional Groups in Aerosol Particles, JGR, https://doi.org/10.1029/2003JD003703.

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