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Brown carbon in Tianjin, China

Anonymous Referee #2

Referee comment on "Measurement report: Optical properties and sources of water-soluble brown carbon in Tianjin, North China – insights from organic molecular compositions" by Junjun Deng et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-1045-RC2, 2022

This paper reports on measurements of PM2.5 water-soluble BrC and fluorescent properties of these aerosol particles extracted from filters. Measurements of other species, including PM2.5 organic carbon, elemental carbon, water-soluble organic carbon and a number of specific organic species are used to determine the sources of the BrC. The measurements are made in a large city in China, Tianjin, and contrasts are made between winter and summer. There are a number of limitations and confusing aspects that should be clarified. First, it should be made very clear in the abstract and throughout the paper that the BrC discussed is light absorption of species in the water extract of filters collecting PM2.5 particles and that no consideration is given to conversion from solvent absorption to aerosol particle absorption (particle size effects on light absorption) and that insoluble BrC species are not included. Thus, the measurements and the analysis of BrC are not comprehensive and light absorption coefficients are not those of actual aerosol particles, which affects the calculations of the radiative effects and associated comparisons with BC. The utility of the fluorescence measurements in relation to BrC is not clear. Even on its own, why is fluorescence of interest; I assume it is to identify sources and processing of the aerosol? The authors seem to assert that there are specific organic species that absorb light and are fluorescent, which they refer to as BrC fluorophores, or fluorescent BrC. This may be so, but the data does not prove this since it is only based on a correlation analysis, whereas a single particle analysis is needed to show individual particles, or species with individual particles, have this property. I believe the authors are saying that high correlation between measurements of BrC and fluorescents provides insights on the sources and processing of species that contribute to BrC, but their discussion and terminology is confusing. These Issues should be addressed before publication.

Specific Comments:

In the Abstract state how this BrC was determined. That is, the BrC is only the water-soluble fraction and is measured in a solution extract, which is not aerosol BrC.

In the Introduction the assertion that BrC has a large effect on the global radiation balance is based on some highly speculative modeling studies. One might consider studies based more on actual measurements.

Regarding the radiative forcing calculations, what is the limitation of assuming what is measured only at the surface can be used to predict top of atmosphere radiative properties? For example, can this prediction actually be compared to a model or measurements that considered BrC throughout the whole atmospheric column? Is there no light absorbing aerosol above the boundary layer? Also, only water-soluble BrC in a solution was measured, which is not comprehensive and not necessarily the same as BrC in the aerosol particles. Discuss how these various factors affect the prediction on the radiative importance of BrC (seems like they will result in a significant underestimation of BrC direct radiative effects). Also, in section 3.2, make sure the data being compared from this work to that of others involves the same approximations as used here (e.g., only water-soluble species considered, BrC of solution not aerosol, only BrC in the boundary layer). Overall, the direct radiative effects presented will likely not accurately estimate the actual impact of BrC species on TOA forcing.

Line 179, change liner to linear.

Line 313 states: "To explore the possible sources and controlling factors of fluorescent BrC", Are the authors really looking at specific organic species that both absorb light and are fluorescent? For example, below this line it states that there is a strong correlation between fluorescent intensities and EC. Does that mean EC contains organic fluorescent compounds? The line "a majority of light-absorbing BrC aerosols were fluorescent (Figure S5a)" is not proven by a correlation and terms like fluorescent BrC and BrC chromophores are very confusing, and in my view not accurate. Also, why does one care about these species? It seems the main reason for the interest in the fluorescent properties is that it provides information on the BrC, and other species, sources. But that is not what line 313 states, which gives the impression the authors are looking specifically at organic species that absorb and are fluorescent, but which the data cannot prove exist. To summarize, I do not see proof for the existence of so-called BrC fluorophores. I do agree that one can find both of these types of species in a group of organic compounds, like HULIS, but that does not mean they are the same organic species. The authors should clarify this throughout and the whole section, (3.4 Fluorescent Components of BrC), which should be reviewed carefully and modified.

Ling 415 states: Besides primary emissions from combustions, bioaerosols, which contain various particle types such as bacteria, algae, pollen, fungal spores, plant debris and biopolymers, are also important sources of BrC aerosols (Andreae and GelencseÌ□r, 2006; PoÌ□hlker et al., 2013). Is this really that important for PM2.5, many of these species are most likely in the coarse mode? Are these source of water-soluble BrC (I doubt, pollen, spores and plant debris are soluble), which is important since the authors are measuring

only water-soluble BrC. Same questions apply to the discussion after the line copied above. The authors should clarify if they are mostly talking about BrC of coarse or fine particles here and are they water-soluble.

Regarding the factor analysis, it is not clear what the difference is between F1 and F5. Is F5 more primary anthropogenic emissions and F1 secondary anthropogenic emissions? The confusion is partly due to calling one anthropogenic and the other fossil fuel emissions – what is the difference between these two at this location.

The last line: The larger contributions of secondary BrC may also partly explain the lower MAE in summer (Table 1), since atmospheric aging processes would weaken light absorption (Zhong and Jang, 2014; Liu et al., 2016). In the summer there is also more sources of WSOC, such as biogenic SOA, that are not brown, which along with aging, would lower the MAE.