This study compares the extraction of ambient $PM_{2.5}$ samples applying different solvents and the subsequent light absorption and determination of brown carbon (BrC). Authors find that the traditional approaches using MeOH or water extraction underestimate BrC absorption due to the insolubility of OC possessing larger chromophores and DMF exhibits the highest extraction efficiency among all the tested solvents. They suggest that using DMF instead of MeOH for BrC extraction and incorporate the results into receptor model will generate distinct source apportionment results. After PMF analysis, they conclude that the contributions of BrC from unburned fossil fuels and polymerization of aerosol organics are underestimated particularly. I do appreciate the interesting work and the information provides new insights into the radiative forcing of BrC. The work is well drafted, and I recommend publication in ACP before a few comments to be addressed as below.

**1.** Line 146-147. In the sampling setup, PUF is attached after two quartz filters to collect the gas phase polar and non-polar organic compounds. However, we do not see the subsequent treatment of the gas phase samples. Also, the absorption of vapors to quartz filter is substantial. In this regard, the sampling artifacts of this experimental design may be great concern and should be addressed.

*Reply:*

The adsorbent samples were analyzed for gas-phase organic molecular markers (OMMs), not BrC absorption. Details on the measurements and sampling artifacts of gas- and particle-phase OMMs have been provided in our previous studies (Gou et al., 2021; Qin et al., 2021). Similar to Xie et al. (2022), total concentrations (gas + particle phases) of OMMs were input for PMF modeling to avoid the influence of gas-particle partitioning. The total concentrations of individual OMMs were calculated as the sum of concentrations in $Q_f$, $Q_b$, and adsorbent samples, and were not impacted by the adsorption of organic vapors on quartz filters. In the original manuscript, we mentioned that

"The input bulk components and organic molecular marker (OMM) data for PMF analysis were obtained from Xie et al. (2022) and are summarized in Table S3." (Lines 231–233)

To make this clear, we added the following statements in the revised manuscript.

"The measurement results of gas- and particle-phase organic compounds were provided by Gou et al. (2021) and Qin et al. (2021)." (Lines 177–179)

"The total concentration data ($Q_f$ + $Q_b$ + adsorbent) of organic compounds have been used to apportion the light absorption of MeOH-soluble OC to specific sources (Xie et al., 2022), so as to avoid the impacts of gas-particle partitioning. In this work, the input particulate bulk components and total organic molecular marker (OMM) data for PMF analysis were obtained from Xie et al. (2022) and are summarized in Table S3." (Lines 265–270)

Additionally, the OC adsorbed on $Q_b$ and its light absorption were used to address positive sampling artifacts in *Section 2.3*. As shown in Table S6, the average $Abs_{365}$ of $Q_b$ samples is less than 10% of $Q_f$ samples. The light-absorbing properties of DMF extractable OC after $Q_b$ corrections are shown in Table 3 and Figure 2.

**2.** Session 3.3 PMF analysis. Current discussion about the PMF is brief, and the following key information should be included, either in the main text or the SI. (1) the stability test of the final solution, as it indicates the robustness of the solution. A solution fails the robustness test is meaningless. (2) The change of the $Q_{robust}/Q_{exp}$ with factor numbers should be examined.

*Reply:*

In comparison to the source apportionment performed by Xie et al. (2022), the input data set of this study only replaced the light absorption of water extracts with DMF extracts ($Abs_{365,d}$). Considering that the light absorption of aerosol extracts in water, MeOH, and DMF was intercorrelated ($r > 0.80$), these two studies are expected to have similar PMF error estimation results and $Q/Q_{exp}$ values. Xie et al. (2022) provided summaries of BS, DISP, BS-DISP error estimation diagnostics and $Q/Q_{exp}$ values for 4- to 10-factor PMF solutions as follows

| | 4-factor | 5-factor | 6-factor | 7-factor | 8-factor | 9-factor | 10-factor |
|---|---|---|---|---|---|---|---|
| **BS diagnostics** | | | | | | | |
| Lowest %BS mapping | 76 | 64 | 44 | 27 | 40 | 27 | 30 |
| Highest % unmapped | 16 | 32 | 53 | 49 | 58 | 67 | 66 |
| | | | | | | | |
| **DISP diagnostics** | | | | | | | |
| Error Code: | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Largest Decrease in Q: | 0 | -0.23 | -1.25 | -1.40 | -0.21 | -11.7 | -1.65 |
| %dQ: | 0 | -0.0015 | -0.010 | -0.013 | -0.0022 | -0.14 | -0.022 |
| Highest swaps by factor: | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | |
| **BS-DISP Diagnostics** | | | | | | | |
| Number of cases accepted | 85 | 88 | 79 | 66 | 69 | 69 | 53 |
| % of cases accepted | 85% | 88% | 79% | 66% | 69% | 69% | 53% |
| Largest decrease in Q | -73.7 | -174 | -758 | 1996 | 1894 | -320 | 1182 |
| %dQ | -0.41 | -1.16 | -6.12 | 18.4 | 20.0 | -3.83 | 16.1 |
| Number of decreases in Q | 14 | 10 | 19 | 11 | 19 | 14 | 14 |
| Number of swaps in best fit | 0 | 1 | 0 | 11 | 4 | 5 | 13 |
| Number of swaps in DISP | 1 | 1 | 2 | 12 | 8 | 12 | 20 |
| Highest swaps by factor: | 0 | 2 | 0 | 10 | 3 | 8 | 11 |
| | | | | | | | |
| **Q/Qexp** | 3.52 | 2.94 | 2.49 | 2.18 | 1.97 | 1.78 | 1.63 |

In the revised supplementary information, we added a section (Text S2) describing the preparation of the input data set and the determination of the final factor number, including robustness analysis and $Q/Q_{exp}$ changes.

"*Text S2. PMF data preparation and factor number determination*

Similar to Xie et al. (2022), 102 observations of 9 $PM_{2.5}$ bulk components ($NH_4^+$, $SO_4^{2-}$, $NO_3^-$, $Ca^{2+}$, $Mg^{2+}$, OC, EC, WSOC and MEOC) and 50 OMMs (22 *n*-alkanes, 14 PAHs, 5 steranes and hopanes, C5-alkanetriols, 2-methyltetrols, levoglucosan, and 6 sugar and sugar alcohols) were selected to apportion the light absorption of aerosol extracts in methanol ($Abs_{365,m}$) and the solvent with the highest extraction efficiency (η) to sources. The measurement results of the bulk components in $PM_{2.5}$ and total OMMs (gas + particle phase) are summarized in Table S3. Uncertainty fractions of bulk components and aerosol extract absorption were set to their ARPD values of collocated $Q_f$-$Q_b$ data (Yang et al., 2021; Xie et al., 2022; Figure 1). The uncertainties of OMM concentrations were calculated as (Zhang et al., 2009; Xie et al., 2016, 2019; Liu et al., 2017)

$$\text{Uncertainty}=\sqrt{(20\%\times\text{ concentration})^2+(0.5\times\text{detection limit})^2} \qquad (3)$$

Missing values and measurements below detection limits (BDL) were replaced by the geometric mean of all observations and half of the detection limit, respectively. Their accompanying uncertainties were set to four times the geometric mean and five-sixths the detection limit (Polissar et al., 1998).

Because the identified sources for BrC absorption are essential, interpretability is the primary basis for determining an appropriate factor number and is defined by how PMF apportioned specific source-related OMMs (Shrivastava et al., 2007). Furthermore, the change in $Q/Q_{\mathrm{exp}}$ with varying factor numbers is also a typical indicator of factor number selection (Liu et al., 2017; Wang et al., 2017, 2018). Specifically, $Q/Q_{\mathrm{exp}}$ is expected to change less dramatically when the factor number increases to a certain value. The EPA PMF5.0 tool can evaluate the robustness of individual base-case solutions with three built-in error estimation methods, including bootstrapping (BS), displacement (DISP), and BS-DISP (Norris et al., 2014; Paatero et al., 2014; Brown et al., 2015). In this work, 100 BS runs were conducted with a minimum *r* value of 0.8 (default 0.6) to map the BS run to base run factors. Once the error code or swap counts at dQmax=4 of DISP analysis were not 0, the base case solution was considered invalid. All input species were included for BS-DISP analysis.

In Table S4, $Q/Q_{\mathrm{exp}}$ changes by 9.14% from 8- to 10-factor solutions, less significant than the value (10.0%–15.1%) for factor numbers varying from 4 to 8, indicating that a factor number of eight is needed to explain the input data. When examining the factor profiles, the 8-factor solution had the most interpretable factor profiles by identifying a lubricating oil combustion factor (Figure S6). The 9-factor solution resolved an unexplainable factor characterized by a mixture of anthropogenic and natural source markers (e.g., steranes, $Ca^{2+}$, and saccharides). In comparison to the input data set for PMF analysis in Xie et al. (2022), this work replaces the light absorption of water extracts with DMF extracts at 365 nm ($Abs_{365,d}$). The error estimation results of these two studies were similar. Although the factor matching rate of the BS runs decreased as the factor number increased, the BS matching rate of the 8-factor solution was larger than 50% when the default minimum *r* value (0.6) was used. Furthermore, no DISP swap was observed and the acceptance rates of BS-DISP analysis were higher than 50% for 4- to 10-factor solutions. Therefore, the resulting base-case solutions are valid and interpretable, and an 8-factor solution was finalized to explain the sources of aerosol extract absorption."

We also mentioned this information in the main text of the revised manuscript.

Lines 272–273

"More information on input data preparation and the factor number determination are provided in supplementary information (Text S2 and Table S4)."

Lines 421–423

"A final factor number of eight was determined based on the interpretability of different base-case solutions (four to ten factors), the change in $Q/Q_{exp}$ with factor numbers, and robustness analysis (Text S2 and Table S4)."

**3.** Figure S5 UV-VIS spectra of 4-nitrophenol and 4-nitrocatechol. There is a strong light absorption at around 450 nm using DMF, which is not observed in other samples. It looks that unknown reactions occur, and the products introduce the unexpected light absorption. Considering that 4-nitrophenol and 4-nitrocatechol are representative tracers for biomass burning, readers may concern that DMF extracts would cause significant bias when investigate the BB BrC.

*Reply:*

Referring to existing studies, 4-nitrophenol and 4-nitrocatechol are strong light-absorbing chromophores coming from several sources, including biomass/biofuel burning (Lin et al., 2016, 2017; Xie et al., 2019), fossil fuel combustion (Lu et al., 2019), and photochemical reactions of aromatic VOCs with $NO_X$ (Xie et al., 2017). Therefore, these two species are not uniquely linked with biomass burning.

The strong light absorption of 4-nitrophenol and 4-nitrocatechol in DMF at 450 nm was not observed in other solvents, and was likely caused by unknown reactions. Then the solvent effect introduced by DMF might overestimate the light absorption of low-molecular-weight (LMW) nitrophenol-like species at > 400 nm in source or ambient aerosols. However, evidence shows that BrC absorption is dominated by large molecules with extremely low volatility (Saleh et al., 2014; Di Lorenzo and Young, 2016; Di Lorenzo et al., 2017), and LMW nitrophenol-like species have small contributions to particulate OM (e.g., < 1%) and aerosol extract absorption (e.g., <10%) (Xie et al., 2019, 2020; Li et al., 2020). The shapes of the light absorption spectra of aerosol extracts in DMF were similar to other solvents (Figure S4) and PAH solutions (Figure S6g-l), and no elevation in light absorption appeared at 400–500 nm (Figure S4). Thus, the overestimated absorption of LMW nitrophenol-like species in DMF might not substantially impact the overall BrC absorption of aerosol extracts.

These discussions have been added to the revised manuscript.

"In Figure S6, the absorbance spectra of 4-nitrophenol and 4-nitrocatechol in water shift toward longer wavelengths compared to their MeOH solution. This is because neutral and deprotonated forms of 4-nitrophenol and 4-nitrocatechol may have different absorbance spectra, and these two compounds are deprotonated at pH ≈ 7 (Lin et al., 2015b, 2017). The strong light absorption of 4-nitrophenol and 4-nitrocatechol in DMF at 450 nm was not observed in other solvents, and was likely caused by unknown reactions. Then the solvent effect introduced by DMF might overestimate the light absorption of low-molecular-weight (LMW) nitrophenol-like species at > 400 nm in source or ambient aerosols. Evidence shows that BrC absorption is dominated by large molecules with extremely low volatility (Saleh et al., 2014; Di Lorenzo and Young, 2016; Di Lorenzo et al., 2017), and LMW nitrophenol-like species have very low contributions to particulate OM (e.g., < 1%) and aerosol extract absorption (e.g., <10%) (Mohr et al., 2013; Zhang et al., 2013; Teich et al., 2017; Xie et al., 2019a, 2020; Li et al., 2020). The shapes of the light absorption spectra of aerosol extracts in DMF were similar to other solvents (Figure S4) and PAH solutions (Figure S6g-l), and no elevation in light absorption appeared at 400–500 nm. Thus, the overestimated absorption of

LMW nitrophenol-like species in DMF might not substantially impact the overall BrC absorption of aerosol extracts." (Lines 353–370)

**4.** Line 317-318. The authors propose that the low-volatility OC fractions are possibly featured with PAH skeleton and DMF has higher dissolubility for those compounds than MeOH. Nevertheless, no light absorbance difference is observed in Figure S5 g-l.

*Reply:*

In this work, we showed the difference in light absorption of ambient aerosol extracts across five solvents. However, the difference might be partly ascribed to the solvent effect, as solutions of the same compound in different solvents might have different light absorbance spectra.

In section 2.1, we provided a method for solvent effect evaluation.

"The solvent effect is not uncommon when measuring aerosol extract absorbance in difference solvents (Chen and Bond, 2010; Mo et al., 2017; Moschos et al., 2021), but is rarely accounted for in previous studies. To evaluate the influence of solvent effects on light absorption of different solvent extracts of the same sample, solutions of 4-nitrophenol at 1.90 mg $L^{-1}$, 4-nitrocatechol at 1.84 mg $L^{-1}$, and 25-PAH mixtures (Table S2) at 0.0080 mg $L^{-1}$ and 0.024 mg $L^{-1}$ (each species) in the five solvents and solvent mixtures were made up for five times and analyzed for UV/Vis spectra. The absorbance of PAH mixtures in water was not provided due to their low solubility." (Lines 227–234)

Figure S6 shows that PAH solutions have very similar absorbance spectra across the five solvents, indicating that the solvent effect does not impact the light absorption of organic compounds with a PAH structure. According to the results shown in Tables 1 and 2, DMF extracts of ambient aerosols contain more low-volatility OC (OC3 and OC4) and have higher light absorption than other solvent extracts. Considering that low-volatility OC is less water soluble and has a high degree of conjugation probably featured by a PAH structure, the large difference in light absorption between DMF and other solvent extracts is likely caused by the fact that DMF can dissolve more low-volatility OC.

Therefore, Table S5 and Figure S6 are used to demonstrate that the solvent effect has little influence on the light absorption of PAHs in different solvents. We did not identify the low-volatility PAHs only soluble in DMF in this work.

**5.** What are the 25 PAHs in the mixture solution and can you give some example structures that DMF have higher solubility than MeOH.

*Reply:*

The species information of the 25-PAH mixture is provided in Table S2 of the supplementary information. As we replied to the reviewer's 4th comment, the PAH mixture was used to evaluate the solvent impact on light absorption, and all the 25 species were dissolved.

Since we did not perform organic speciation for DMF and MEOH extracts, the structure that DMF has higher solubility than MeOH was not identified.

In the revised manuscript, we added

"However, we cannot rule out the impact of solvent effects on the comparison of light absorption spectra between MeOH and DMF extracts (Figure S4), and more work is warranted in identifying the structures more soluble in DMF than in MeOH." (Lines 378–381)

**6.** Line 283-284. As the author put it, the lower capability of MeOH in dissolving low-volatility OC fractions (OC3 and OC4) would lead to an underestimation of BrC absorption. Can you give an estimation of the underestimation so that the readers have intuitive knowledge?

*Reply:*

Based on the light absorption measurements of collocated samples from 09/2018–09/2019 in suburban Nanjing, the average $Abs_{365,d}$ was 30.7% higher than $Abs_{365,m}$ after $Q_b$ corrections. But the underestimation might vary with the time and location due to the changes in BrC sources.

The difference in $Abs_{365}$ between DMF and MeOH extracts were provided in the original manuscript.

"As shown in Table 3, average $Abs_{365,d}$ and $MAE_{365,d}$ values were 30.7% ($p < 0.01$) and 17.3% ($p < 0.05$) larger than average $Abs_{365,m}$ and $MAE_{365,m}$." (Lines 334–336)

In the revised manuscript, we added some text in the abstract and conclusions to show the difference and limits.

"The average light absorption coefficient at 365 nm of DMF extracts was 30.7% higher ($p < 0.01$) than that of MeOH extracts." (Lines 44–46)

"The difference between MeOH and DMF extract absorption might change with the time and location due to the variations in BrC sources." (Lines 500–502)

**7.** Line 132. There should be a space before and after multiple sign.

*Reply:*

We have added a space before and after the multiplication sign in Eqs. 1–2.

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