In this manuscript, the authors investigate the light absorption characteristics of solvent-extractable brown carbon aerosol in ambient samples affected by multiple sources. The manuscript raises the topic of the effect of the selected solvent, or solvent mixture, on the extraction efficiency of organics and subsequently on the absorbance measured by UV-visible spectroscopy and associated light absorption properties (mass-normalized absorbance and its wavelength dependence). They find that N, N-dimethylformamide dissolves BrC associated with unburned fossil fuel and polymerization processes of aerosol organics more efficiently than methanol. The study results and potential implications are of interest to readers of *Atmospheric Chemistry and Physics*. Nevertheless, I would only recommend publication of this manuscript upon careful consideration by the authors of the specific comments below and subsequent clarifications and fine-tuning of some discussions in the revised manuscript.

**Specific comments**
**1.** Line 1: the message of the title may not be universal and could be considered misleading. If the authors prefer the current title to largely remain (although Reviewer 1 has already provided an alternative that may better reflect the paper content), I strongly recommend they change it to: "Potential underestimation…". The main reason is that methanol still efficiently extracted biomass burning-related BrC, which has been more widely studied in the literature.

*Reply:*

Thanks for the reviewer's suggestion. In this work, only ambient OC was extracted using different solvents. The results showed that the MeOH extraction method had a lower extraction efficiency than the DMF extraction method, and underestimated ambient BrC absorption. But methanol can still extract biomass burning BrC efficiently (> 90%).
In the revised manuscript, we changed the title to
"*Potential* underestimation of *ambient* brown carbon absorption based on the methanol extraction method and its impacts on source analysis"

**2.** Lines 44-45: for completeness, please clarify the following details in the abstract: (1) BrC aerosols associated with biomass burning, and coal (?), combustion sources were still highly soluble in MeOH; (2) the different MeOH solubility of BrC from different (seasonal) sources was likely the main reason for the aforementioned distinct time series. Therefore, (3) a more accurate alternative to the sentence: "These results highlight the necessity of replacing MeOH with DMF for further investigations on structures…" could be: "These results highlight the importance of testing different solvents to investigate the structures and light absorption of BrC, particularly of the low-volatility fraction potentially associated with certain non-traditional sources.". Please also rephrase related statements in Lines 103-104, 105-107, 227-228 ("potential underestimation"), 415, 418 ("may sometimes"), 423-424 ("…may potentially underestimate the contribution of solvent-extractable…"), and elsewhere if applicable.

*Reply:*

The original expression in lines 42–46 was changed to
"Source apportionment results indicated that the MeOH solubility of BrC associated with biomass burning, lubricating oil combustion, and coal combustion is

similar to their DMF solubility. The BrC linked with unburned fossil fuels and polymerization processes of aerosol organics was less soluble in MeOH than in DMF, which was likely the main reason for the large difference in time series between MeOH and DMF extract absorption. These results highlight the importance of testing different solvents to investigate the structures and light absorption of BrC, particularly for the low-volatility fraction potentially originating from non-combustion sources." (Lines 46–54)

The original expressions in lines 103–107 and 227-228 were changed to
"By comparing with the study results in Xie et al. (2022), this study evaluated potential underestimation of BrC absorption in methanol and its impacts on BrC source attributions. These results suggest that different solvents should be used in future investigations on the absorption, composition, sources, and formation pathways of low-volatility BrC." (Lines 132–136)

"To examine the influence of potential BrC underestimation based on the methanol extraction method on source apportionment, ………" (Lines 261–262)

and the original expressions in lines 415, 418, and 423–424 were changed to
"Comparisons of extraction efficiencies and light absorption of ambient aerosol extracts across selected solvents and solvent mixtures indicate that MeOH may sometimes be replaced with DMF for measuring BrC absorption, as low-volatility OC fractions containing strong chromophores are less soluble in MeOH than in DMF." (Lines 490–493)

"……, and had a potential to underestimate the contribution of BrC to total aerosol absorption." (Lines 497–498)

**3.** Line 93: the sentence is more informative with the following (or similar) addition referring to the extractable aerosol fraction: "…directly if the latter is not converted to particulate absorption with Mie calculations, solvent-matrix, and pH effects are not accounted for, and solvent solubility is not high.".

*Reply:*

Thanks for the reviewer's suggestion, and the original expression was changed to
"Given that the solvent extract absorption is not converted to particulate absorption with Mie calculations, solvent and pH effects are not accounted for, and BrC is not completely dissolved in typical solvents (e.g., water and methanol), BrC absorption in particles and solution can hardly be compared directly." (Lines 118–122)

**4.** Line 120: that is likely true for DMF; THF has been tested for biomass burning-influenced ambient BrC (Moschos et al., 2021); do the two observations agree? The authors state "rarely" in this sentence: do any other studies exist that have tested any of these two solvents for extracting BrC aerosol?

*Reply:*

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Moschos et al. (2021) selected methanol to extract ambient aerosols based on the comparison of the absorbance with five other solvents: water, acetonitrile, acetone, tetrahydrofuran (THF), and dichloromethane. Only a winter and summer filters were extracted using different solvents, and the light absorption of THF extracts was much lower than that of MeOH extracts, which was consistent with the results in this study.

To the best of our knowledge, no other study has ever tested THF and DMF for extracting BrC.

The original expression was changed to

"Except for water and MeOH, DCM and THF were rarely used to extract OC for light absorption measurements (Cheng et al., 2021; Moschos et al. 2021), and DMF has not ever been tested for extracting BrC in literature." (Lines 149–151)

**5.** Line 195: when measuring the absorbance of solvent extracts, solvent-matrix effects (Reichardt, 2003) are not uncommon (yet rarely accounted for in the BrC research). Chen and Bond (2010; cited in the preprint), Mo et al. (2017), and Moschos et al. (2021) observed higher absorbance of water-extracted BrC aerosol that was further diluted/re-dissolved in methanol (for the same total extract volume). Could the authors discuss, in the revised manuscript, similar effects for their selected solvents/mixtures, as well as the implications for the results presented here when not correcting for such (i.e., currently, the solvent-matrix vs. solubility effects are not decoupled)? Can the authors rule out a solvent-matrix effect that would affect the wavelength-dependent comparison between MeOH and DMF, for example, in Fig. S4?

*Reply:*

As we replied to reviewer 2's 4th comment, the difference in light absorption of aerosol extracts across solvents might be partly ascribed to the solvent effect, as the same compound in different solvents might have different light absorbance spectra. To evaluate the influence of solvent effects on aerosol extract absorption, the light absorbance of typical BrC chromophores (4-nitrophenol, 4-nitrocatechol, and PAHs) in different solvents were compared (Lines 227–234; Table S5 and Figure S6).

Although the difference in light absorption between MeOH and DMF extracts is likely attributed to the fact that the low-volatility OC in ambient aerosols is more soluble in DMF, we cannot confirm that the solvent effect has no influence.

In the revised manuscript, we added more discussions on the potential influences of solvent effects on aerosol extract absorption.

"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

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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. Furthermore, the absorbance of 4-nitrophenol and 4-nitrocatechol in DMF at 365 nm ($A_{365}$) was lower than that in MeOH, and PAH solutions showed very similar absorbance spectra across the five solvents (Figure S6g–l and Table S5). Considering that low-volatility OC fractions (e.g., OC3 and OC4) in the ambient are less water soluble (Table 1) and have a high degree of conjugation (Chen and Bond, 2010; Lin et al., 2014), their structures are probably featured by a PAH skeleton. Therefore, the large difference in $Abs_{365}$ between DMF and MeOH extracts (Table 2) was primarily ascribed to the fact that DMF can dissolve more OC3 and OC4 than methanol (Table 1). 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 353–381)

Two statements were added to the method and conclusion sections.

"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." (Lines 227–229)

"However, the influence of the solvent effect was not accounted for in this work when comparing the light absorption of different solvent extracts." (Lines 499–500)

**6.** Line 312: here, the authors have the opportunity to discuss also potential pH effects, e.g., the absorbance red-shift for the water-extract of 4-nitro-catechol in Fig. S5 and the isosbestic point ~365 nm, which seem to be consistent with the observation of Lin et al. (2017) for water vs. organic-solvent BrC aerosol extracts.

*Reply:*

Here we added the following discussions in 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)." (Lines 353–357)

**7.** Line 426: please clarify: "…in cold periods, when coal/biomass burning sources dominated the aerosol emissions..." if that is the case.

*Reply:*

Yes, that's true. The original expression was changed to

"Although light-absorbing properties of DMF and MeOH extracts had good agreement in cold periods, when biomass and coal burning sources dominated BrC emissions, their distinct time series in spring and summer implies that the contributions of certain BrC sources were underestimated or missed when the MeOH extraction method was used." (Lines 506–510)

**8.** Conclusions and implications section: It is important here to provide a broader view that will allow future studies to confirm these observations, while other approaches may still be helpful: for example, the authors could state that a combination of solvents with a broad polarity index (e.g., Lin et al., 2018) may still be good choice to cover different conditions, e.g., a mixture of non-polar (e.g., hexane), polar protic (e.g., MeOH) and polar aprotic solvents (e.g., DMF) for a range of BrC-containing samples influenced by different sources. Based on this and other comments above, there is no "universal evidence" from this study that DMF is the unique-best solvent for BrC under all conditions. At the same time, a more balanced discussion in the revised manuscript would encourage future studies to test DMF and potentially verify or revise the authors' observations.

*Reply:*

Thanks for the reviewer's suggestion. The first paragraph of the conclusions and implications section was changed to

"Comparisons of extraction efficiencies and light absorption of ambient aerosol extracts across selected solvents and solvent mixtures indicate that MeOH may sometimes be replaced with DMF for measuring BrC absorption, as low-volatility OC fractions containing strong chromophores are less soluble in MeOH than in DMF. Existing modeling studies on the radiative forcing of BrC (Feng et al., 2013; Wang et al., 2014; Zhang et al., 2020) often retrieved or estimated its optical properties from laboratory or ambient measurements based on water/methanol extraction methods (Chen and Bond, 2010; Hecobian et al., 2010; Liu et al., 2013; Zhang et al., 2013), and had a potential to underestimate the contribution of BrC to total aerosol absorption. However, the influence of the solvent effect was not accounted for in this work when comparing the light absorption of different solvent extracts. The difference between MeOH and DMF extract absorption might change with the time and location due to the variations in BrC sources. The results of this work also imply the necessity of applying different solvents or combinations of solvents with broad polarity and dissolving capability to study BrC composition and absorption, particularly for low-volatility fractions." (Lines 490–505)

**9.** Line 434: does that refer to the isoprene oxidation factor in Fig. 3? That is an important finding; the figure can be cited once more in this section together with this statement.

*Reply:*

This refers to the factors influenced by the polymerization processes of organic components. For example, the dust resuspension and isoprene oxidation factors.
Here we cited Fig. 3 again in the statement.

"……, but the structures and light-absorbing properties of potential polymerization products in ambient aerosols (Figure 3e, g) are less understood and warrant further study." (Lines 515–517)

**10.** Figure 3: please mention (possibly in the caption) that the biogenic emission factor *Abs* is below the detection limit (if that is the case).
Further, I agree with Reviewer 2 that it is critical to provide evidence for the robustness of the PMF solution for a reader to assess the quality of the results and the validity of the associated conclusions.
Could the authors also discuss the yearly evolution of the *Abs* relative difference between the two solvents for each PMF factor in Fig. 3? The relative difference seems low for coal and biomass burning throughout the year; what are the time-series trend and day-to-day variability for the other factors (those where both solvents seem to dissolve a non-negligible fraction of their chemical constituents)?
Finally, based on the statement in Lines 297-299, could the authors reproduce Fig. 3 for *Abs* at a longer wavelength and compare the two PMF results?

*Reply:*

The contributions of individual factors to $Abs_{365,d}$ and $Abs_{365,m}$ were output from PMF modeling, not measurements. Thus, the factor contributions cannot be compared with the detection limit.

As we replied to reviewer 2's second comment, we added a section (Text S2) describing the preparation of input data set and the determination of the final factor number, including robustness analysis and $Q/Q_{exp}$ changes (Table S4). The robust analysis results showed that the final PMF solution was valid and interpretable.

"*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 ($\eta$) 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 $Q/Q_{exp}$ with varying factor numbers is also a typical indicator of factor number selection (Liu et al., 2017; Wang et al., 2017, 2018). Specifically, $Q/Q_{exp}$ 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, $Q/Q_{exp}$ 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 S8). 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."

The relative difference in contributions of each factor to $Abs_{365,d}$ and $Abs_{365,m}$ is the same throughout the year due to the PMF calculation method. Thus, the time series of the absolute difference is shown instead in Figure S9. The ARPD and COD values between factor contributions to $Abs_{365,d}$ and $Abs_{365,m}$ are also added to each plot in Figure S9.

More discussions on the difference in factor contributions to $Abs_{365,d}$ and $Abs_{365,m}$ were added in the revised manuscript.

"Figure 3 compares the time series of factor contributions to $Abs_{365,d}$ and $Abs_{365,m}$. ARPD and COD values between factor contributions to $Abs_{365,d}$ and $Abs_{365,m}$ and the absolute difference are exhibited in Figure S9. $Abs_{365,d}$ and $Abs_{365,m}$ had comparable contributions from biomass burning, lubricating oil combustion, and coal combustion (Figure 3a, c, d). The small COD values of these three factors (0.0041–0.17) indicated no significant divergence. The biogenic emission and isoprene oxidation factors exhibited complete difference (ARPD = 200%, COD = 1; Figure S9f, g) as they had no contribution to $Abs_{365,m}$. Among the eight factors, the non-combustion fossil, dust resuspension, and isoprene oxidation factors had the largest median difference in factor contributions to $Abs_{365,d}$ and $Abs_{365,m}$ (0.63–0.67 $Mm^{-1}$) with substantial heterogeneity (COD > 0.20), followed by the secondary inorganics factor (0.20 $Mm^{-1}$, COD = 0.41). The temporal variations of the absolute difference shown in Figure S9 are identical to the contributions of individual factors to $Abs_{365,d}$ or $Abs_{365,m}$ (Figure 3)." (Lines 444–457)

"This might explain the elevated difference between $Abs_{365,d}$ and $Abs_{365,m}$ contributions of the isoprene oxidation factor in summer (Figure S9g)." (Lines 472–

473)

The light absorption of methanol extracts becomes very weak at $\lambda > 400$ nm (e.g., Figure S4), and more than 20% of methanol extract samples have no light absorption at $\lambda = 450$, 500, and 550 nm. Due to the limit in observation number ($N = 102$), we performed PMF source apportionment for $Abs_{\lambda,d}$ and $Abs_{\lambda,m}$ at $\lambda = 400$ nm using the same speciation data, and reproduced Figure 3 at $\lambda = 400$ nm.

Table 1. Comparisons of light-absorbing coefficients of ambient $PM_{2.5}$ extracts in DMF and MeOH at 365 nm and 400 nm.

| | DMF | | | MeOH[a] | | |
|---|---|---|---|---|---|---|
| | Median | Mean ± std | Range | Median | Mean ± std | Range |
| $Abs_{365}$, Mm-1 | 6.99 | 8.42 ± 5.40 | 1.14–30.8 | 5.59 | 6.43 ± 4.66 | 0.38–29.6 |
| $Abs_{400}$, Mm-1 | 4.39 | 5.44 ± 3.55 | 0.76–19.9 | 3.18 | 3.88 ± 2.96 | 0.21–10.7 |

[a] Data for MeOH extracts were obtained from Xie et al. (2022).

As shown in the figure below, the biomass burning, lubricating oil combustion, and coal combustion have comparable contributions to $Abs_{400,d}$ and $Abs_{400,m}$; the non-combustion fossil, dust resuspension, and isoprene oxidation factors lead the difference between $Abs_{400,d}$ and $Abs_{400,m}$ contributions. These results still indicate that large BrC molecules from unburned fossil fuels and potential polymerization processes are less soluble in MeOH than in DMF. Our discussions and conclusions remain the same even if the wavelength is shifted to 400 nm. Therefore, we did not compare the two PMF results in the revised manuscript.
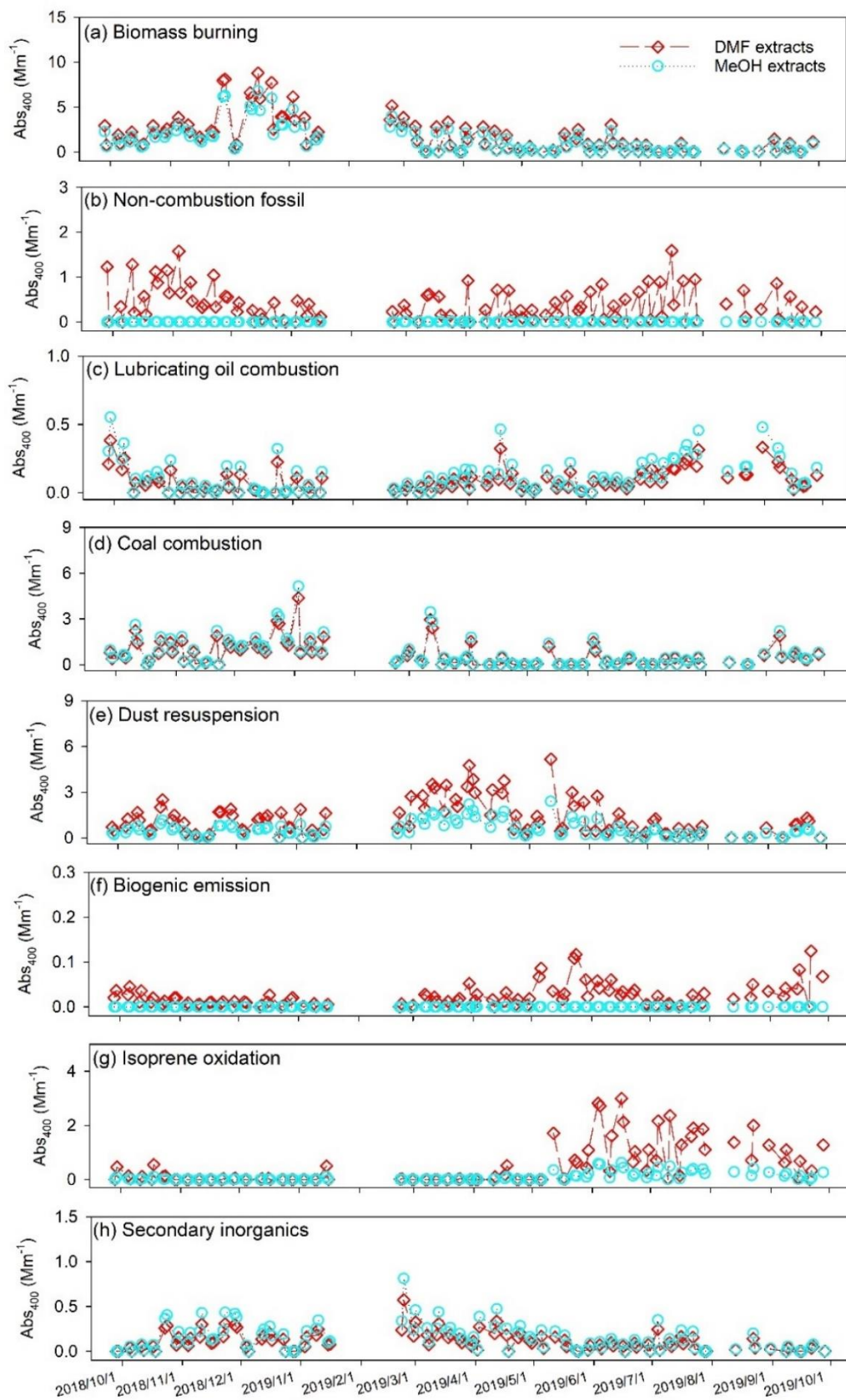
Figure 1. Time series of factor contributions to Abs$_{400}$ of DMF and MeOH extracts of ambient PM$_{2.5}$ samples.

**Technical corrections**
**1.** Lines 281, 295, 315 & 416: "low-volatility".

*Reply:*

The "low-volatile" was changed to "low-volatility" throughout the manuscript.

**2.** Table 3: correct the superscript to "Mm-1".

*Reply:*

Thanks. It has been corrected as suggested.

**3.** Table S3: please provide the units of the tabulated data other than *Abs*365.

*Reply:*

Units were added for other data in Table S3.

**References**

Moschos, V., Gysel-Beer, M., Modini, R. L., Corbin, J. C., Massabò, D., Costa, C., Danelli, S. G., Vlachou, A., Daellenbach, K. R., Szidat, S., Prati, P., Prévôt, A. S. H., Baltensperger, U., and El Haddad, I.: Source-specific light absorption by carbonaceous components in the complex aerosol matrix from yearly filter-based measurements, Atmos. Chem. Phys., 21, 12809-12833, 10.5194/acp-21-12809-2021, 2021.