

Xu et al. examined the influence of solvent selection on brown carbon (BrC) absorption measurements and source analysis for ambient aerosols. Water, methanol, methanol-DCM mixtures, THF, and DMF were tested. Measurement results showed that DMF exhibited the highest extraction efficiency of ambient organic carbon (OC), particularly for low-volatile OC, and DMF extracts also had significant higher light absorption than other solvent extracts. Moreover, the comparison of sources between DMF and methanol extract absorption is very interesting and indicates that the methanol-extraction method will underestimate BrC contributions from non-combustion sources. The authors suggested that DMF can extract more BrC than commonly used solvents. DMF might be an important solvent for investigating low-volatile OC in the near future. This manuscript provides very useful information for further studies on radiative forcing and sources of organic aerosols, and I recommend the publication of this manuscript in ACP, though I'd like the authors to address some minor specific comments below.

1. In this work, several solvent extracts of ambient OC were measured for light absorption, would the authors consider changing the title to “The dependence of brown carbon absorption on solvent selection and its impacts on source analysis”, or something similar to highlight the differences in different solvent extraction methods?

Reply:

In the current work, we examined the difference in the extraction efficiency and light absorption of solvent-extractable OC across five solvents and solvent mixtures. Only the solvent with the highest extraction efficiency (N, N-dimethylformamide, DMF) was applied to extract a matrix of ambient PM_{2.5} samples for light absorption measurement. In comparison to methanol (MeOH)-extractable OC, DMF extracts showed significant ($p < 0.01$) higher light absorption, and the light absorption of methanol-insoluble OC is mainly linked with unburned fossil fuel and polymerization processes of aerosol organics. Other solvents or solvent mixtures (water, MeOH/DCM, and THF) were not examined for source apportionment of BrC absorption.

Reviewer 3 suggests adding “potential” to the original title of the manuscript, as methanol can extract biomass burning BrC efficiently ($> 90\%$). The ambient OC is a complex mixture coming from both primary and secondary sources. In this work, only ambient OC was extracted using different solvents. The methanol extraction method had a lower extraction efficiency than the DMF extraction method, and underestimated ambient BrC absorption. 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. Line 31. “However, undissolved OC fractions will lead to underestimated BrC absorption.” What is the magnitude of this underestimation? Also, what about the mass? If the undissolved fraction has low light absorption, the underestimation might not be large, right?

Reply:

Here, we only mentioned a potential problem associated with the methanol extraction method. As we stated in the introduction (lines 101–103, 108–113)

“The light absorption of biomass burning OM is majorly contributed by large molecules (MW > 500~1000 Da; Di Lorenzo and Young, 2016; Di Lorenzo et al., 2017) and depends on burn conditions (Saleh et al., 2014).”

“Methanol can extract > 90% OM from biomass burning (Chen and Bond, 2010; Xie et al., 2017b), while the extraction efficiency (η , %) decreases to ~80% for ambient organic aerosols (Xie et al., 2019b; Xie et al., 2022) possibly due to other sources emitting large hydrophobic molecules and oligomerizations of small molecules during the aging process (Cheng et al., 2021; Li et al., 2021). The light-absorbing properties and structures of methanol-insoluble OC (MIOC) are still unknown.”

In this work, we demonstrated that DMF can extract more low-volatility OC from ambient OC than MeOH, and the MeOH-insoluble OC contained strong light-absorbing chromophores. These results have already been included in the abstract.

“Among the five solvents and solvent mixtures, DMF dissolved the highest fractions of ambient OC (up to ~95%), followed by MeOH and MeOH/DCM mixtures (< 90%), and the DMF extracts had significant ($p < 0.05$) higher light absorption than other solvent extracts. This is because the OC fractions evaporating at higher temperatures (> 280°C) are less soluble in MeOH (~80%) than in DMF (~90%) and contain stronger light-absorbing chromophores.” (Lines 35–40)

3. Lines 41-42, “the light absorption of DMF and MeOH extracts of collocated aerosol samples in Nanjing showed distinct time series. Specifically, what is the difference, and do they have any common temporal patterns?

Reply:

In the revised manuscript, we specified the difference by changing the original expression to

“Moreover, the light absorption of DMF and MeOH extracts of collocated aerosol samples in Nanjing showed consistent temporal variations in winter when biomass burning dominated BrC absorption. While the average light absorption of DMF extracts was more than two times greater than the MeOH extracts in late spring and summer.” (Lines 40–44)

4. Lines 58-60, “The radiative forcing (RF) of the light-absorbing organic carbon, also termed “brown carbon” (BrC), is not well quantified due to the lack of its emission data and large uncertainties in *in situ* BrC measurements” The secondary formation will also add complexity on RF estimation of BrC. Please mention it.

Reply:

Thanks, the original expression has been changed to

“The radiative forcing (RF) of the light-absorbing organic carbon, also termed “brown carbon” (BrC), is not well quantified due to the lack of its emission data,

complex secondary formations, and large uncertainties in *in situ* BrC measurements (Wang et al., 2014; Wang et al., 2018; Saleh, 2020).” (Lines 83–86)

5. Lines 261–262, “THF based on the two methods for rOC measurements (*section 2.2*) are compared in Figures S1 and S2.” Would the authors consider putting these two figures in the main text? They provide very useful information.

Reply:

In this study, filters extracted using MeOH, MeOH/DCM (1:1), MeOH/DCM (1:2), and THF were air-dried in a fume hood and analyzed for residual OC (rOC, $\mu\text{g m}^{-3}$). Filters extracted in water and DMF cannot be air-dried in the short term due to the low volatility of solvents, and their rOC was measured after baking at 100 °C for 2 h. To examine if the baking process would influence rOC measurements, the rOC of filters extracted in MeOH, MeOH/DCM mixtures, and THF were also measured after the baking process and compared with those determined after air drying (*Section 2.3*).

The results shown in Figures S1 and S2 indicate that baking extracted filters to dryness would have little influence on SEOc measurements (Lines 299–308).

“Concentrations of extracted OC fractions in MeOH, MeOH/DCM mixtures, and THF based on the two methods for rOC measurements (*section 2.2*) are compared in Figures S1 and S2. The total SEOc concentrations derived from the two methods are compared in Figure S3. All the scatter data of SEOc fell along the 1:1 line with significant correlations ($r > 0.85$, $p < 0.01$). Because the measurement uncertainty of dominant species is lower than minor ones (Hyslop and White, 2008; Yang et al., 2021), the slightly greater relative difference between the two methods for extractable OC1 was likely attributed to its low concentrations ($< 1 \mu\text{g m}^{-3}$; Tables 1 and S1). Thus, baking extracted filters to dryness was expected to have little influence on SEOc measurements, particularly for low-volatility OC fractions (OC2–OC4).”

These two figures were only used to validate rOC measurements for filters extracted in water and DMF, and were not cited elsewhere or directly linked with the main topic of the manuscript. Therefore, we kept these two figures in the supplementary information.

6. Section 3.1.2. Is the difference across solvent extraction methods related to the physicochemical properties of OC? If it is true, please state which factors have a substantial influence.

Reply:

According to the results provided in Tables 1 and 2, DMF and MeOH (or MeOH/DCM mixtures) had comparable extraction efficiencies for more volatile OC (OC1 and OC2). However, DMF exhibited significant ($p < 0.05$) higher efficiency in extracting low-volatility OC (OC3 and OC4) than other solvents, and the low-volatility OC accounted for more than 60% of OC concentrations. This is expected to be the main reason for the fact that the light absorption of DMF extracts was significantly ($p < 0.05$)

higher than other solvent extracts, as low-volatility OC contains stronger light-absorbing chromophores (Saleh et al., 2014).

The difference in the light absorption across solvent extraction methods might depend on the fraction of low-volatility OC. In another word, the difference will increase as the fraction of low-volatility OC increases.

In the revised manuscript, the original expression (lines 294–296)

“Given that the relative difference in extraction efficiency of total OC between MeOH and DMF was less than 10%, low-volatile OC should contain stronger light-absorbing chromophores (Saleh et al., 2014).” was changed to

“Given that the relative difference in extraction efficiency of total OC between MeOH and DMF was less than 10% and DMF dissolved more OC3 and OC4 than other solvents (Table 1), low-volatility OC should contain stronger light-absorbing chromophores (Saleh et al., 2014) and its mass fraction might determine the difference in BrC absorption across solvent extraction methods.” (Lines 333–337)

7. Page 13, lines 298–299. “This is because the light absorption of DMF extracts depends less on wavelengths than other solvent extracts ($\text{\AA} \sim 4.5$, Table 2).”

Page 14, lines 339–341. “In comparison to \AA_m (6.81 ± 1.64 ; Table 3), the lower average \AA_d ($5.25 \pm 0.64, p < 0.01$) supports that more-absorbing BrC had less spectral dependence than less-absorbing BrC.”

In Tables 2 and 3, there seems to be a negative relationship between the MAE and \AA values. To illustrate that strong BrC chromophores had less spectral dependence than weak ones, I would suggest showing the relationship visually by plotting MAE vs. \AA .

Reply:

The linear relationships between average \AA and $\text{MAE}_{365/550}$ of individual solvent extracts in Table 2 are provided in Figure S5, and those for $\text{MAE}_{365,d}$ versus \AA_d and $\text{MAE}_{365,m}$ versus \AA_m are shown in Figure S7.

In the manuscript, the original expression

“This is because the light absorption of DMF extracts depends less on wavelengths than other solvent extracts ($\text{\AA} \sim 4.5$, Table 2).” (lines 298–299) was changed to

“This is because the light absorption of DMF extracts that contain stronger BrC chromophores depends less on wavelengths than other solvent extracts ($\text{\AA} \sim 4.5$, Table 2). As shown in Figure S5, average \AA and $\text{MAE}_{365/550}$ values of individual solvent extracts in Table 2 are negatively correlated.” (Lines 339–342)

And the original expression

“In comparison to \AA_m (6.81 ± 1.64 ; Table 3), the lower average \AA_d ($5.25 \pm 0.64, p < 0.01$) supports that more-absorbing BrC had less spectral dependence than less-absorbing BrC.” (lines 339–341) was changed to

“Both $\text{MAE}_{365,d}$ and $\text{MAE}_{365,m}$ were negatively correlated ($p < 0.01$) with their corresponding \AA values (Figure S7), and the lower average \AA_d ($5.25 \pm 0.64, p < 0.01$)

compared to \AA_m (6.81 ± 1.64 ; Table 3) supports that more-absorbing BrC had less spectral dependence than less-absorbing BrC.” (Lines 400–403)

8. Figures 2 and 3. I would suggest the authors to put Abs365, MAE365, and \AA on the y-axis.

Reply:

Figures 2 and 3 have been revised as suggested.

References

Saleh, R., Robinson, E. S., Tkacik, D. S., Ahern, A. T., Liu, S., Aiken, A. C., Sullivan, R. C., Presto, A. A., Dubey, M. K., Yokelson, R. J., Donahue, N. M., and Robinson, A. L.: Brownness of organics in aerosols from biomass burning linked to their black carbon content, *Nat. Geosci.*, 7, 647-650, <https://doi.org/10.1038/ngeo2220>, 2014.