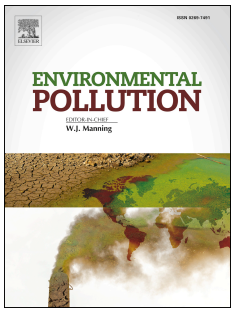
A new method for extraction of methanol-soluble brown carbon: Implications for investigation of its light absorption ability

Yan Fangping, Kang Shichang, Sillanpää Mika, Hu Zhaofu, Gao Shaopeng, Chen Pengfei, Gautam Sangita, Reinikainen Satu-Pia, Li Chaoliu

DOI: 10.1016/j.envpol.2020.114300

Journal Pre-proof



A new method for extraction of methanol-soluble brown carbon: Implications for investigation of its light absorption ability

Fangping Yan, Shichang Kang, Mika Sillanpää, Zhaofu Hu, Shaopeng Gao, Pengfei Chen, Sangita Gautam, Satu-Pia Reinikainen, Chaoliu Li

PII: S0269-7491(19)36036-1

DOI: https://doi.org/10.1016/j.envpol.2020.114300

Reference: ENPO 114300

To appear in: *Environmental Pollution*

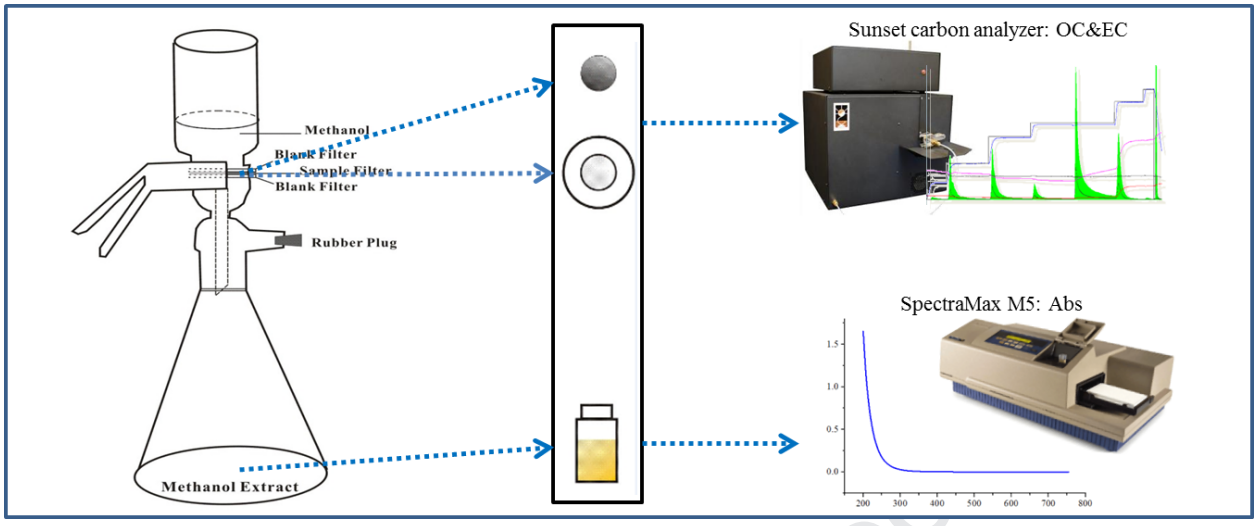
Received Date: 15 October 2019

Revised Date: 28 February 2020

Accepted Date: 28 February 2020

Please cite this article as: Yan, F., Kang, S., Sillanpää, M., Hu, Z., Gao, S., Chen, P., Gautam, S., Reinikainen, S.-P., Li, C., A new method for extraction of methanol-soluble brown carbon: Implications for investigation of its light absorption ability, *Environmental Pollution* (2020), doi: https://doi.org/10.1016/j.envpol.2020.114300.

Fangping Yan: Methodology, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing. **Shichang Kang:** Validation, Writing - Review & Editing, Supervision, Project administration, Funding acquisition. **Mika Sillanpää:** Writing - Review & Editing. **Shaopeng Gao:** Resources, Writing - Review & Editing. **Zhaofu Hu:** Investigation, Writing - Review & Editing. **Pengfei Chen:** Resources, Writing - Review & Editing. **Sangita Gautam:** Investigation. **Satu-Pia Reinikainen:** Writing - Review & Editing. **Chaoliu Li:** Conceptualization, Validation, Writing - Review & Editing, Supervision, Funding acquisition.



A new method for extraction of methanol-soluble brown carbon: Implications for investigation of its light absorption ability

Fangping Yan[a,b,c], Shichang Kang[c,d,e], Mika Sillanpää[f], Zhaofu Hu[c,e], Shaopeng Gao[a], Pengfei Chen[c], Sangita Gautam[a,e], Satu-Pia Reinikainen[b], Chaoliu Li[a,d*]

[a]Key Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing 100101, China

[b] LUT School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, 53851, Lappeenranta, Finland

[c]State Key Laboratory of Cryospheric Sciences, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou, 730000, China

[d]CAS Center for Excellence in Tibetan Plateau Earth Sciences, Chinese Academy of Sciences, Beijing 100085, P.R. China

[e]University of Chinese Academy of Sciences, Beijing 100049, China

[f]Department of Civil and Environmental Engneering, Floride International University, Miami, FI, USA.

Corresponding author:

*E-mail: lichaoliu@itpcas.ac.cn;

Address: Building 3, Yard 16, Lincui road, Chaoyang district, Beijing, China, 100101

ABSTRACT

As an important component of organic carbon (OC), brown carbon (BrC) plays a significant role in radiative forcing in the atmosphere. Water-insoluble OC (WIOC) generally has higher light absorption ability than water-soluble OC (WSOC). The mass absorption cross-section (MAC) of WIOC is normally investigated by dissolving OC in methanol. However, all the current methods have shortcomings due to neglecting the methanol insoluble particulate carbon that is detached from the filter and suspended in methanol extracts, which results in MAC uncertainties of the methanol-soluble BrC and its climate warming estimation. In this study, by investigating typical biomass combustion sourced aerosols from the Tibetan Plateau and ambient aerosols from rural and urban areas in China, we evaluated the extractable fraction of OC for the existing methods. Moreover, a new method was developed to overcome the methanol insoluble particulate carbon detachment problem to achieve more reliable MAC values. We found that OC can be dissolved in methanol in a short time (e.g., one hour) and ultrasonic treatment and long-term soaking do not significantly increase the extractable OC fraction. Additionally, we proved that methanol insoluble particulate carbon detachment in methanol does exist in previous methods, causing overestimation of the BrC mass extracted by methanol and thus the underestimation of MAC values. We therefore recommend the newly developed extraction method in this study to be utilized in future related studies to quantitatively obtain the light absorption property of methanol-soluble BrC.

Keywords: methanol-soluble brown carbon; MAC; biomass aerosol; ambient aerosol

Capsule

A new method is developed to overcome the particulate carbon detachment problem during the extraction of methanol-soluble BrC, and thus the reliable MAC is obtained.

1. Introduction

Aerosol particles are among the largest sources of uncertainties in estimating radiative climate forcing (Anderson et al., 2003). As an important part of aerosol particles, organic carbon (OC) plays an important role in solar radiation absorbing in addition to its solar radiation scattering, especially in the ultraviolet (UV) wavelength range (Laskin et al., 2015; Yan et al., 2018). Recently, increasing attention has been focused on those carbon fractions that absorb solar radiation, i.e., brown carbon (BrC), in both models and in situ observation studies (Andreae and Gelencsér, 2006; Kirillova et al., 2014; Lin et al., 2014; Saleh et al., 2013; Shamjad et al., 2015; Xie et al., 2019). For instance, it is estimated that BrC accounts for approximately 24% of the combined black carbon (BC) and BrC warming effects at the tropopause (Zhang et al., 2017). BrC is generally divided into water-soluble brown carbon (WS-BrC) and water-insoluble brown carbon. Light absorption of the latter carbon fraction is generally evaluated by treating the sample with methanol (Chen and Bond, 2010). Therefore, this BrC fraction is called methanol-soluble brown carbon (MeS-BrC). To date, the method for investigating the light absorption of WS-BrC in aerosol samples has been well established, and little uncertainty exists regarding the value of the mass absorption cross-section of WS-BrC ($MAC_{WS\text{-}BrC}$) because OC dissolved in water can be easily and accurately measured by a TOC analyzer after filtering the extracts (Li et

al., 2016b). However, OC dissolved in methanol (i.e., MeS-BrC) cannot be directly measured by this method due to the interference of organic solvent, so that indirect calculations have to be adopted (Chen and Bond, 2010; Cheng et al., 2017; Huang et al., 2018). Moreover, the treatment of samples with methanol is still a complicated issue, and no consensus has been reached. To date, aerosol samples are treated with methanol using multiple methods (e.g., different treatment times, with or without sonication) (method details and comparison are provided in Table 1). However, all existing methods have shortcomings. For example, the methanol insoluble particulate carbon detaching from the filter and entering into the methanol cannot be quantitatively measured, thus the indirect calculation of MeS-BrC in previous studies was conducted by assuming either OC of original filter samples could be completely extracted by methanol or the methanol insoluble particulate carbon detachment is ignorable (Table 1), which caused the overestimation of MeS-BrC and accordingly the underestimation of the mass absorption cross-section of MeS-BrC ($MAC_{MeS\text{-}BrC}$) (Chen and Bond, 2010; Cheng et al., 2016). In addition, sonication treatment generally increases the extractable fraction of carbon compared to other methods without sonication treatment (Polidori et al., 2008); thus, both $MAC_{MeS\text{-}BrC}$ and $MAC_{WS\text{-}BrC}$ values of the samples treated by sonication should be higher than those without sonication. Currently, a comparison of methanol extractable OC fraction by the three existing methods presented in Table 1 is still lacking. Because mass absorption cross-section of BrC (MAC_{BrC}) data are the basic input of radiative models of aerosol particles, the aforementioned limitations and uncertainties will ultimately

be propagated to climate forcing estimation. Therefore, it is urgent to establish a reliable method for MAC_{BrC} to better evaluate the radiative forcing of carbonaceous particles.

Normally, the BrC derived from biomass combustion sourced aerosols is more easily dissolved in water and methanol than that derived from fossil-sourced and ambient aerosols (Chen and Bond, 2010). In this study, $PM_{2.5}$ samples (particulate matter with a diameter smaller than 2.5 μm) originated from yak dung combustion, from a typical urban city on the Tibetan Plateau and from rural areas in East China (which is seriously polluted) were collected (Table S1). The collected samples were treated with methanol by the previous three methods to investigate the difference in the methanol extractable OC fractions among these methods. On this basis, a new method is developed to provide more reliable $MAC_{MeS\text{-}BrC}$ values for aerosol samples.

97 Table 1 Information and comparison of three previous extraction methods and the one in this study.

Method	Extraction process	Calculation of MeS-BrC	Potential problems	Reference
Method 1	Filter samples were immersed in methanol for 1 h without shaking or sonication	MeS-BrC=OC of original filter−OC remaining on methanol extracted-filter	The methanol insoluble particulate carbon detachment was ignored	(Cheng et al., 2017)
Method 2	Filter samples were sonicated for 1 h in methanol	MeS-BrC=OC of original filter	The OC of original filter samples was assumed to be completely extracted by methanol	(Huang et al., 2018)
Method 3	Filter samples were sonicated in methanol for 1 h, the solution was kept at room temperature for 20 h, then it was again sonicated for another 1 h	MeS-BrC=OC of original filter−OC remaining on methanol extracted-filter	The methanol insoluble particulate carbon detachment was ignored	(Chen and Bond, 2010)
New method	Filter samples were placed in the middle of a sandwich filtration assembly as presented in Figure 1, and extracted with methanol by three times. The total residence time of methanol on filters is 1 h	MeS-BrC=OC of original filter−OC remaining on middle and bottom methanol extracted filters in sandwich filtration assembly, i.e., equation (2)		This study

98

2. Methodology

2.1. Field sites

$PM_{2.5}$ filter samples were collected at four sites in China, namely, Nam Co, Lhasa, Zhangbo and Yangdian (Table S1). Nam Co is a typical remote area on the Tibetan Plateau where local residents burn yak dung for heating and cooking. The aerosol particles emitted from these combustion activities have an important contribution to glacier retreat on the Tibetan Plateau (Li et al., 2016a). Several studies have been conducted on the OC and element carbon (EC) ratios and $MAC_{WS\text{-}BrC}$ values at this site (Chen et al., 2015; Hu et al., 2017). Lhasa is the largest city on the south-central Tibetan Plateau; the aerosols in this city are greatly influenced by fossil combustion (Li et al., 2016a). Zhangbo and Yangdian are two typical rural areas in Guanzhong and Huabei Plain, respectively, with serious air pollution in East China.

The $PM_{2.5}$ samples collected at Nam Co were directly emitted from the yak dung combustion plumes (Chen et al., 2015), which were classified as biomass aerosols. The $PM_{2.5}$ samples collected in the ambient environment at other three sampling sites were classified as ambient aerosols. Due to different sources, the light absorption characteristics of aerosol in two categories are different.

2.2. Extract assembly

A total of 33 aerosol samples were collected for the experiments (Table S1). The filter samples from the urban and rural sites were acidified by fumigation with 37% HCl for 24 h to remove carbonate carbon which interferes the measurement of EC and OC by the carbon analyzer before the experiments followed the practical protocols

provided in previous studies (Bosch et al., 2014; Chen et al., 2013; Li et al., 2016a; Pio et al., 2007). The carbonate carbon removed by HCl fumigation accounted for approximately 5.5±2.6% of the total OC of the study aerosols. The analytical procedure in this study is presented in Figure S1. First, a subsample (punch #1) of the original filter was cut out for the measurement of initial OC mass. Second, a 3.8 cm^2 subsample (punch #2) was cut out and treated with 38 mL methanol using a sandwich filter assembly to prevent the loss of particles from the filter (Figure 1). In summary, the subsample was punched and placed in a pre-combusted quartz filter (pore size: 0.45 μm, Pall TissuquartzTM) with an opening of the same area. The reassembled filter samples were then placed between two pre-combusted quartz filters with the bottom of the subsample facing upward. The thusly formed three-filter sandwich was placed on the glass sand core funnel of a vacuum filtration assembly as presented in Figure 1. After blocking the funnel, 38 mL methanol was added to the filter in three times to keep the long residence time, and the total residence time of the methanol lasted for approximately 1 h to ensure a high OC fraction extracted by methanol. The remaining methanol was then pumped through the filter. Thereafter, the filters were dried in glass petri dishes at 60 °C for two hours. Punches of 0.526 cm^2 were obtained from the center of the original filter samples, the methanol-treated filter subsamples and the bottom filters of the sandwich filtration assembly. OC and EC of the punched samples were measured using a thermal-optical transmittance (TOT) carbon analyzer (Sunset Laboratory, Tigard, OR, USA) following the IMPROVE-A protocol. The sum of the OC masses of the two punches from the sandwich filtration assembly was

regarded as the methanol-insoluble OC fraction. The difference between the OC mass of the original sample and the methanol-insoluble OC is the mass of the OC dissolved in methanol, which was used in the calculation of $MAC_{MeS\text{-}BrC}$. Third, a subsample (punch #3) was sonicated in ultrapure water to obtain the $MAC_{WS\text{-}BrC}$ value. The detailed method has been described in our previous article (Li et al., 2016c).

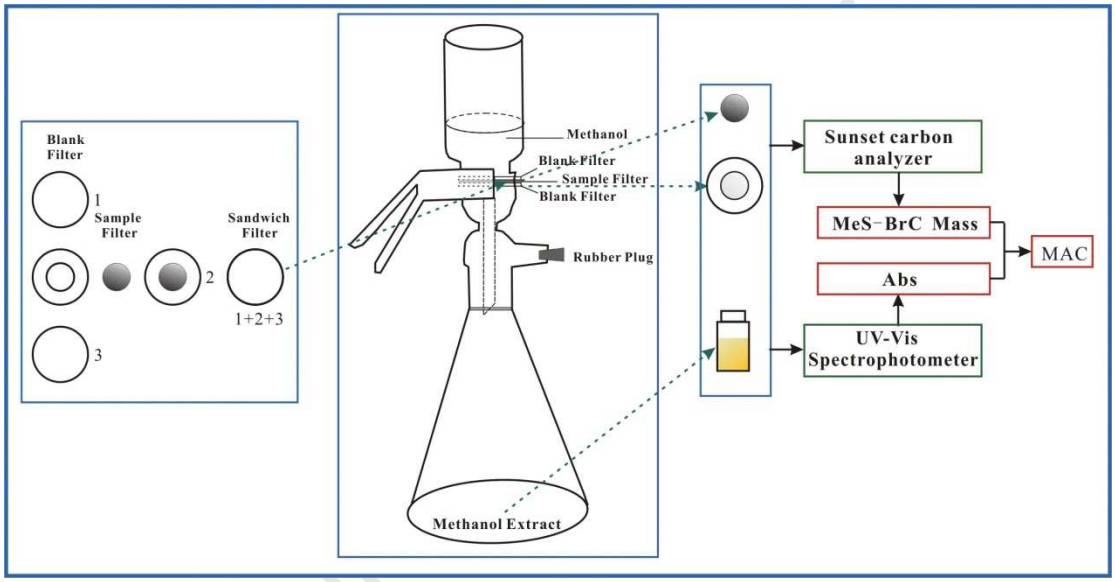


Figure 1. Filtration unit developed in this study to extract MeS-BrC.

2.3. Light absorption measurement and calculation

The light absorption spectra of WS-BrC and MeS-BrC were measured using an ultraviolet-visible (UV-Vis) absorption spectrophotometer (SpectraMax M5, USA), by scanning from 200-700 nm with a step size of 5 nm. The MAC value was calculated based on the Beer-Lambert law (Bosch et al., 2014; Kirillova et al., 2014):

$$MAC = \frac{Abs}{C.L} \times \ln(10) \quad (1)$$

where Abs is the light absorbance measured directly by the spectrophotometer, L is the absorbing path length (1 cm); C is the mass of OC dissolved in methanol

159 (MeS-BrC) or ultrapure water (WS-BrC).

160 The mass of WS-BrC was directly measured by the TOC analyzer, while the
161 mass of MeS-BrC was obtained by indirect calculation due to the interference of
162 methanol as follow:

163 $$MeS\text{-}BrC=OC_{original}\text{-}OC_{2,sandwich}\text{-}OC_{3,sandwich} \quad (2)$$

164 where $OC_{original}$ is the total OC mass of original filter; $OC_{2,sandwich}$ and $OC_{3,sandwich}$ are
165 the OC mass of middle and bottom filters extracted by methanol in the sandwich
166 filtration assembly present in Figure 1.

167 Under the assumption that the OC soluble in water can also be dissolved in
168 methanol, MAC of the water-insoluble OC (MAC_{WIOC}) can be calculated as the
169 following ratio:

170 $$MAC_{WIOC} = \frac{[Abs_{365,methanol} - Abs_{365,water}]}{([MeS-BrC]-[WS-BrC]).L} \times \ln 10 \quad (3)$$

171 where $Abs_{365,\ methanol}$ and $Abs_{365,\ water}$ are the light absorbance measured at 365 nm of
172 filtered methanol and water extracts; [MeS-BrC] and [WS-BrC] are the mass of
173 MeS-BrC and WS-BrC.

174 **3. Results and discussion**

175 **3.1. The loss of methanol insoluble particulate carbon in three previous methods**

176 The loss of methanol insoluble particulate carbon from the filter during the
177 methanol extraction was considered insignificant and negligible in a previous study
178 (Cheng et al., 2017), although it has been reported that this phenomenon will cause
179 $MAC_{MeS\text{-}BrC}$ underestimation (Chen and Bond, 2010; Kirillova et al., 2016). Herein, to
180 evaluate the loss of methanol insoluble particulate carbon into methanol from the

filter, light absorption of the methanol extracts using the third method in Table 1 was measured before and after filtration. If the light absorbance at wavelength of 365 nm (Abs_{365}) of the methanol extract after filtration was lower than that before filtration, the loss of methanol insoluble particulate carbon from the filter must occur. Although this approach provides an indirect estimate, the particle loss can thus be evaluated effectively. For instance, due to the detachment of methanol insoluble particulate carbon, Abs_{365} for the unfiltered extracts of ambient and biomass aerosols increases approximately 101% and 45%, respectively compared to those of filtered extracts (Figure 2a), suggesting that the loss of the methanol insoluble particulate carbon does exit in previous methods. Moreover, by collecting these detached OC and those remaining OC on methanol-extracted filters together and measuring by TOT carbon analyzer, the mass of MeS-BrC could be overestimated by 10% and 43% for the biomass and ambient extracts, respectively (Figure 2c) if we assume methanol completely extracts OC of the filter samples (as presented by Huang et al., 2018, i.e., method 2 in Table 1). In contrast, the new extraction method developed in this study is reliable for obtaining accurate MeS-BrC mass and thus reliable $MAC_{MeS\text{-}BrC}$ values by preventing the detachment of the methanol insoluble particulate carbon, which is also verified by the similar average Abs_{365} values compared with the previous filtration methods (Figure 2b). Additionally, the larger Abs increase of the ambient aerosol extracts due to the detachment of methanol insoluble particulate carbon might be explained by the lower fraction of MeS-BrC (i.e., a low ratio of methanol-soluble OC to total OC of the original filter sample) and the existence of large mineral particles

with an easy detachment inclination which can be the coating of carbonaceous matter in ambient aerosols (Figure S2); meanwhile, the finer biomass combustion carbon particles adhere to the filter paper more easily compared to the ambient particles. Thus, failing to consider the particle loss would cause large uncertainties in MAC estimation, especially for the ambient aerosols.

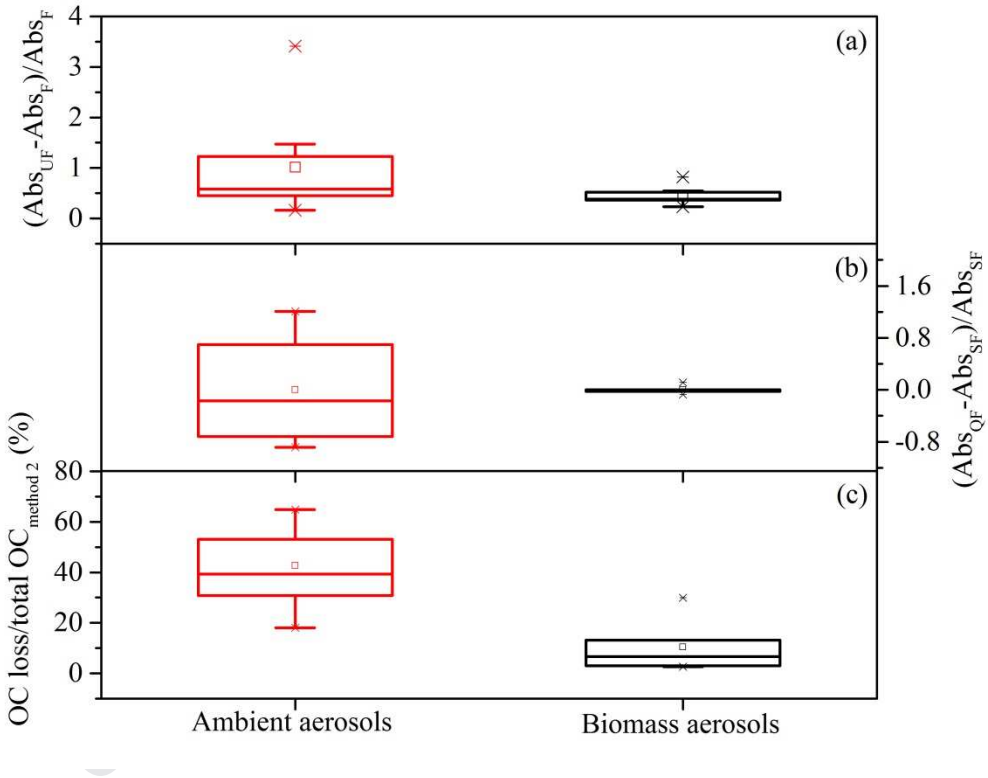


Figure 2. The increase ratios of Abs_{365} of the unfiltered (Abs_{UF}) methanol extracts compared to those of Abs_{365} of the filtered extracts (Abs_F) (a), the increase ratios of Abs_{365} of the extracts filtered by a quartz filter (Abs_{QF}) compared to those of Abs_{365} of the extracts filtered a by syringe filter (Abs_{SF}) (b), and the ratio of OC loss to total OC of original filter samples using method 2 in Table 1.

3.2. Abs values of MeS-BrC by four different methods

The MeS-BrC in the ambient and biomass aerosols was extracted using the existing three methods (Table 1 and Text S1) and the method we developed in this study. The Abs_{365} values were measured and compared. The results indicated that the

Abs_{365} values of MeS-BrC using the new method were between those obtained using the first two methods but slightly lower than those obtained using the third method (Figure 3). Moreover, the differences in Abs_{365} among the methanol extracts from these four methods were statistically insignificant for both ambient and biomass aerosols ($p>0.05$, N=33) (Table S2). Therefore, we propose that the complex treatments of sonication and a longer residence time do not significantly contribute to a larger amount of carbon extracted. Additionally, it is demonstrated that the syringe filter in the previous three methods and the quartz filter paper in this new method do not cause significant differences in the Abs_{365} values (Figure S3). Consequently, it is reasonable to adopt the new method developed in this study to investigate the light absorption of MeS-BrC quantitatively and accurately. However, it should also be pointed out that the theoretical mass absorption cross-section at 365 nm (MAC_{365}) of the methanol extracts based on the Abs_{365} values obtained using the third method should be the highest among these four methods due to the elevated Abs_{365} values as a result of the sonication treatment, although the increase is statistically insignificant ($p>0.05$, N=33). In addition, the theoretical MAC_{365} divergence of the ambient aerosols between the third method and the new method would be larger than that of the biomass aerosols, which may also indicate that the OC in biomass aerosols is more easily extracted by methanol even without sonication treatment, but sonication treatment has a relatively large effect on OC faction extracted by methanol in ambient aerosols.

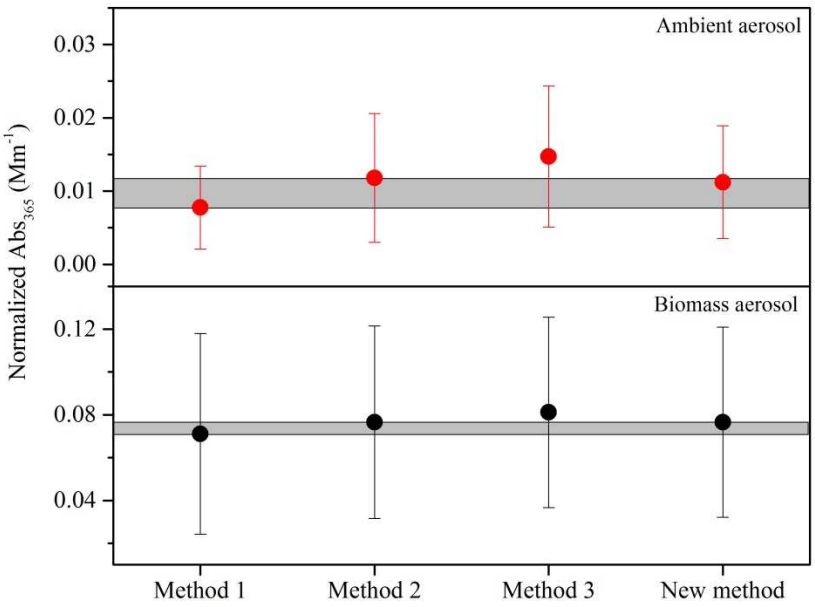


Figure 3. Normalized light absorbance of MeS-BrC at 365 nm by the four different extraction methods. Note: the large standard deviation (SD) for mean values was attributed to the large variation in the particulate carbon mass in each collected sample.

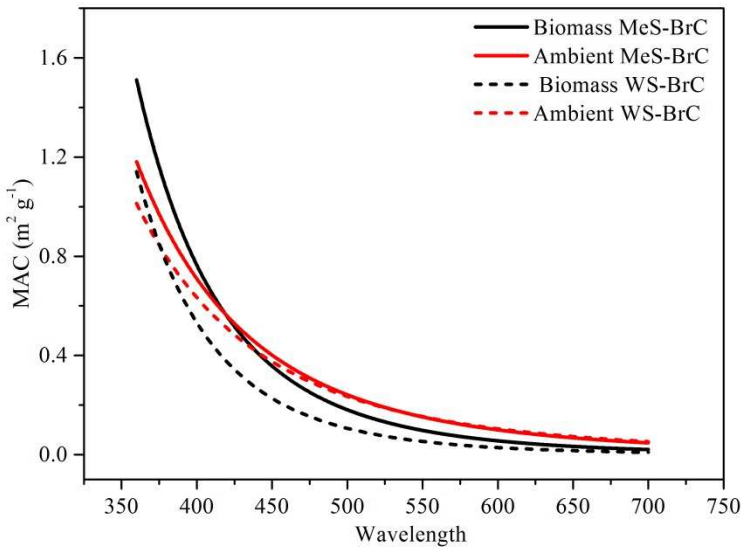
3.3. WS-BrC versus MeS-BrC and the light absorption properties

Approximately 93.0±3.8% (87-96%) of the biomass combustion sourced OC could be extracted within 1 h by methanol in this study, which is likely the lower bound of the previously reported values of 92%-98% for wood burning aerosols (Chen and Bond, 2010). Meanwhile, the average methanol extractable OC fraction of the ambient aerosols was approximately 79.3±10.0% (55%-93%) (Figure S2), which was lower than the average value of 89% for the ambient aerosols in Beijing (Cheng et al., 2017). This phenomenon was possibly because, on the one hand, the aerosol sources were different between this study and the previous ones, and on the other hand, the previous two studies failed to consider the methanol insoluble particulate carbon detachment from the filter during analysis. Correspondingly, the extractable

254 OC fractions by ultrapure water were small (63.3±13.3% and 55.2±29.1% for the
255 biomass and ambient aerosols, respectively), close to the previously reported values
256 (Cong et al., 2015; Graham et al., 2002; Srinivas and Sarin, 2013). All these results
257 disprove the assumption in several previous studies that methanol extracts almost all
258 the OC from filters (Huang et al., 2018; Kirillova et al., 2016; Zhu et al., 2018), thus
259 causing $MAC_{MeS\text{-}BrC}$ underestimation, especially for the ambient aerosols.

260 By using the new method, the MAC_{365} values of the methanol-extracted biomass
261 OC and ambient OC were 1.55±0.43 $m^2\ g^{-1}$ (1.07-2.44 $m^2\ g^{-1}$) and 1.14±0.50 $m^2\ g^{-1}$
262 (0.55-1.51 $m^2\ g^{-1}$), respectively, in this study. The MeS-BrC fraction has higher MAC
263 values than the WS-BrC fraction across the near-UV wavelength range (Figure 4),
264 consistent with previous results (Chen and Bond, 2010; Kirchstetter et al., 2004; Sun
265 et al., 2007; Zhang et al., 2013). It is clear that the MAC_{365} value of OC from biomass
266 combustion sourced aerosols were higher than that of OC from ambient aerosols;
267 moreover, the MAC_{365} values in Lhasa were lower than those at the other two sites
268 (Table S3) because the fossil fuel contribution to the aerosols in Lhasa was larger than
269 those of the other two sites (Li et al., 2016b). Furthermore, the OC/EC ratios in Lhasa,
270 Zhangbo and Yangdian were 3.4, 7.1 and 7.3, respectively, reflecting the larger fossil
271 fuel contribution of the Lhasa aerosol as reported in previous studies (Hu et al., 2017;
272 Li et al., 2016b). Therefore, it is crucial to obtain the reliable light absorption of OC in
273 the atmosphere not only in the heavily polluted regions but also in the background
274 remote regions of the Tibetan Plateau because there contains the largest number of
275 glaciers outside the polar regions which has been experiencing dramatic retreat due to

276 the climate change and the deposition of light-absorbing impurities (Kang et al., 2019).
277 Thus, quantitative investigation of the light-absorbing OC and its effect on glaciers
278 should be taken seriously.



279

280 **Figure 4**. Average MAC spectra of WS-BrC and MeS-BrC in the ambient and
281 biomass aerosols.

282 The OC compounds that were only extractable by methanol (i.e., WIOC) were
283 more light-absorbing than the WS-BrC compounds (Figure 5 and Table S3). The
284 estimated average MAC_{WIOC} values at 365 nm for the biomass and ambient aerosols
285 were 2.34±0.78 m^2 g^{-1} and 1.59±0.76 m^2 g^{-1}, approximately 2.3 and 1.6 times of the
286 estimated $MAC_{WS\text{-}BrC}$ values, respectively. Previous studies have suggested that this
287 strong light-absorbing WIOC are likely polycyclic aromatic hydrocarbons with a large
288 molecule weight or certain large molecules containing conjugated aromatic rings
289 (Apicella et al., 2004; Chen and Bond, 2010; Zhang et al., 2013), which could be
290 produced during fossil fuel and biomass combustion in both flaming and smoldering
291 combustion states (Evans and Milne, 1987; Schauer et al., 2001). Correspondingly,

the less light-absorbing WS-BrC compounds were identified as humic-like substance and protein-like substances (Sun et al., 2007; Wu et al., 2019).

As a BrC proxy, Abs_{365} of WIOC also exhibited a strong correlation with WIOC mass in both the ambient and biomass aerosols besides the significant correlation between WS-BrC and its Abs value (Figure S4), which suggested that a significant fraction of WIOC is consisted of BrC chromophores. Therefore, the study of MeS-BrC in aerosols can facilitate a better understanding of its role in climate forcing. In addition, the new method in this study provides a reliable and quantitative measurement for this kind of MeS-BrC.

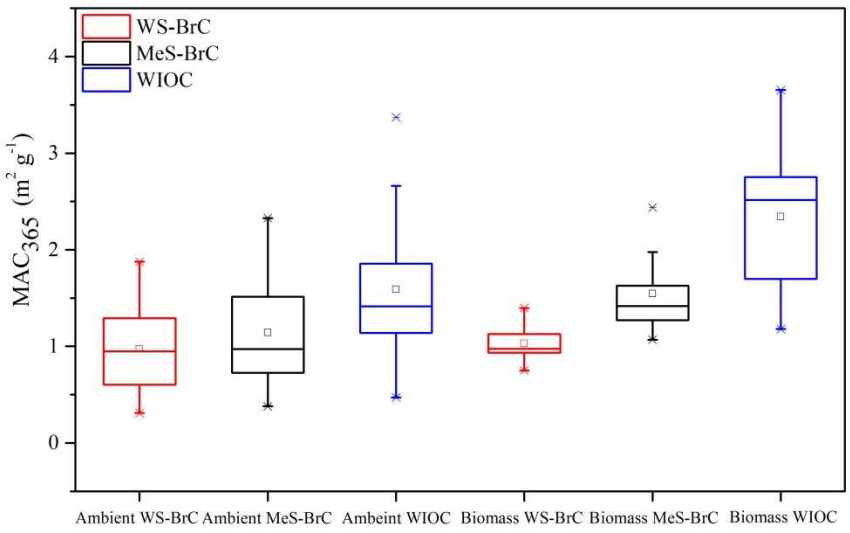


Figure 5. Average MAC_{365} of the water and methanol extracts of ambient and the biomass aerosols.

4. Conclusion

By comparing the sandwich filtration assembly developed in this study with the three previous methods, we proved that the three existing methods do experience the

detachment of methanol insoluble particulate carbon from the filter during extraction, which causes large overestimation in the calculation of the MeS-BrC mass and eventually leads to the underestimation of $MAC_{MeS\text{-}BrC}$. Correspondingly, the sandwich filtration method provides not only comparable light absorption data of the methanol extracts with the existing methods using traditional sonication process but also the reliable amount of the methanol-extractable OC. Thus, the sandwich filtration method can be utilized to measure the light absorption ability of the methanol-soluble OC in atmospheric aerosols more accurately by overcoming the particulate carbon loss problem.

Note

The authors declare no competing financial interest.

Acknowledgements

This study was supported by the second Tibetan Plateau Scientific Expedition and Research Program (STEP) (2019QZKK0605), the NSFC (41971096, 41675130 and 41630754), the Strategic Priority Research Programme of the Chinese Academy of Sciences, Pan-Third Pole Environment Study for a Green Silk Road (Pan-TPE) (XDA20040501), and the State Key Laboratory of Cryospheric Science (SKLCS-ZZ-2017). This study is part of a framework across the HTP: Atmospheric Pollution and Cryospheric Change (APCC).

References

Anderson, T.L., Charlson, R.J., Schwartz, S.E., Knutti, R., Boucher, O., Rodhe, H., Heintzenberg, J., 2003. Climate forcing by aerosols--a hazy picture. Science 300, 1103-1104.

Andreae, M.O., Gelencsér, A., 2006. Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. Atmospheric Chemistry and Physics 6, 3131-3148.

Apicella, B., Alfè, M., Barbella, R., Tregrossi, A., Ciajolo, A., 2004. Aromatic structures of carbonaceous materials and soot inferred by spectroscopic analysis. Carbon 42, 1583-1589.

Bosch, C., Andersson, A., Kirillova, E.N., Budhavant, K., Tiwari, S., Praveen, P., Russell, L.M., Beres, N.D., Ramanathan, V., Gustafsson, Ö., 2014. Source‐diagnostic dual‐isotope composition and optical properties of water‐soluble organic carbon and elemental carbon in the South Asian outflow intercepted over the Indian Ocean. Journal of Geophysical Research: Atmospheres 119, 11,743-711,759.

Chen, B., Andersson, A., Lee, M., Kirillova, E.N., Xiao, Q., Kruså, M., Shi, M., Hu, K., Lu, Z., Streets, D.G., 2013. Source forensics of black carbon aerosols from China. Environ Sci Technol 47, 9102-9108.

Chen, P., Kang, S., Bai, J., Sillanpää, M., Li, C., 2015. Yak dung combustion aerosols in the Tibetan Plateau: Chemical characteristics and influence on the local atmospheric environment. Atmospheric Research 156, 58-66.

Chen, Y., Bond, T.C., 2010. Light absorption by organic carbon from wood combustion. Atmospheric Chemistry and Physics 10, 1773-1787.

Cheng, Y., He, K., Du, Z., Engling, G., Liu, J., Ma, Y., Zheng, M., Weber, R., 2016. The characteristics of brown carbon aerosol during winter in Beijing. Atmospheric Environment 127, 355-364.

Cheng, Y., He, K., Engling, G., Weber, R., Liu, J.M., Du, Z.Y., Dong, S.P., 2017. Brown and black carbon in Beijing aerosol: Implications for the effects of brown coating on light absorption by black carbon. Sci Total Environ 599-600, 1047-1055.

Cong, Z., Kang, S., Kawamura, K., Liu, B., Wan, X., Wang, Z., Gao, S., Fu, P., 2015. Carbonaceous aerosols on the south edge of the Tibetan Plateau: concentrations, seasonality and sources. Atmospheric Chemistry and Physics 15, 1573-1584.

Evans, R.J., Milne, T.A., 1987. Molecular characterization of the pyrolysis of biomass. Energy & Fuels 1, 123-137.

Graham, B., Mayol‐Bracero, O.L., Guyon, P., Roberts, G.C., Decesari, S., Facchini, M.C., Artaxo, P., Maenhaut, W., Köll, P., Andreae, M.O., 2002. Water‐soluble organic compounds in biomass burning aerosols over Amazonia 1. Characterization by NMR and GC‐MS. Journal of Geophysical Research: Atmospheres 107, LBA 14-11-LBA 14-16.

Hu, Z., Kang, S., Li, C., Yan, F., Chen, P., Gao, S., Wang, Z., Zhang, Y., Sillanpää, M., 2017. Light absorption of biomass burning and vehicle emission-sourced carbonaceous aerosols of the Tibetan Plateau. Environ Sci Pollut Res Int 24, 15369-15378.

Huang, R.J., Yang, L., Cao, J., Chen, Y., Chen, Q., Li, Y., Duan, J., Zhu, C., Dai, W., Wang, K., Lin, C., Ni, H., Corbin, J.C., Wu, Y., Zhang, R., Tie, X., Hoffmann, T., O'Dowd, C., Dusek, U., 2018. Brown Carbon Aerosol in Urban Xi'an, Northwest China: The Composition and Light Absorption Properties. Environ Sci Technol 52, 6825-6833.

Kang, S., Zhang, Q., Qian, Y., Ji, Z., Li, C., Cong, Z., Zhang, Y., Guo, J., Du, W., Huang, J., You, Q., Panday, A.K., Rupakheti, M., Chen, D., Gustafsson, Ö., Thiemens, M.H., Qin, D., 2019. Linking atmospheric pollution to cryospheric change in the Third Pole region: current progress and future

prospects. National Science Review 6, 796-809.

Kirchstetter, T.W., Novakov, T., Hobbs, P.V., 2004. Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon. Journal of Geophysical Research: Atmospheres 109, D21208, doi:10.1029/2004JD004999.

Kirillova, E.N., Andersson, A., Han, J., Lee, M., Gustafsson, Ö., 2014. Sources and light absorption of water-soluble organic carbon aerosols in the outflow from northern China. Atmospheric Chemistry and Physics 14, 1413-1422.

Kirillova, E.N., Marinoni, A., Bonasoni, P., Vuillermoz, E., Facchini, M.C., Fuzzi, S., Decesari, S., 2016. Light absorption properties of brown carbon in the high Himalayas. Journal of Geophysical Research: Atmospheres 121, 9621-9639.

Laskin, A., Laskin, J., Nizkorodov, S.A., 2015. Chemistry of atmospheric brown carbon. Chemical reviews 115, 4335-4382.

Li, C., Bosch, C., Kang, S., Andersson, A., Chen, P., Zhang, Q., Cong, Z., Chen, B., Qin, D., Gustafsson, O., 2016a. Sources of black carbon to the Himalayan-Tibetan Plateau glaciers. Nat Commun 7, 12574.

Li, C., Chen, P., Kang, S., Yan, F., Hu, Z., Qu, B., Sillanpää, M., 2016b. Concentrations and light absorption characteristics of carbonaceous aerosol in $PM_{2.5}$ and PM_{10} of Lhasa city, the Tibetan Plateau. Atmospheric Environment 127, 340-346.

Li, C., Yan, F., Kang, S., Chen, P., Hu, Z., Gao, S., Qu, B., Sillanpää, M., 2016c. Light absorption characteristics of carbonaceous aerosols in two remote stations of the southern fringe of the Tibetan Plateau, China. Atmospheric Environment 143, 79-85.

Lin, G., Penner, J.E., Flanner, M.G., Sillman, S., Xu, L., Zhou, C., 2014. Radiative forcing of organic aerosol in the atmosphere and on snow: Effects of SOA and brown carbon. Journal of Geophysical Research: Atmospheres 119, 7453-7476.

Pio, C.A., Legrand, M., Oliveira, T., Afonso, J., Santos, C., Caseiro, A., Fialho, P., Barata, F., Puxbaum, H., Sanchez‐Ochoa, A., 2007. Climatology of aerosol composition (organic versus inorganic) at nonurban sites on a west‐east transect across Europe. Journal of Geophysical Research: Atmospheres 112, D23S02, doi:10.1029/2006JD008038.

Polidori, A., Turpin, B.J., Davidson, C.I., Rodenburg, L.A., Maimone, F., 2008. Organic $PM_{2.5}$: fractionation by polarity, FTIR spectroscopy, and OM/OC ratio for the Pittsburgh aerosol. Aerosol Science and Technology 42, 233-246.

Saleh, R., Hennigan, C., McMeeking, G., Chuang, W., Robinson, E., Coe, H., Donahue, N., Robinson, A., 2013. Absorptivity of brown carbon in fresh and photo-chemically aged biomass-burning emissions. Atmospheric Chemistry and Physics 13, 7683-7693.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R., 2001. Measurement of emissions from air pollution sources. 3. C1−C29 organic compounds from fireplace combustion of wood. Environ Sci Technol 35, 1716-1728.

Shamjad, P., Tripathi, S., Pathak, R., Hallquist, M., Arola, A., Bergin, M., 2015. Contribution of brown carbon to direct radiative forcing over the Indo-Gangetic Plain. Environ Sci Technol 49, 10474-10481.

Srinivas, B., Sarin, M., 2013. Light absorbing organic aerosols (brown carbon) over the tropical Indian Ocean: impact of biomass burning emissions. Environmental research letters 8, 044042.

Sun, H., Biedermann, L., Bond, T.C., 2007. Color of brown carbon: A model for ultraviolet and visible light absorption by organic carbon aerosol. Geophysical Research Letters 34, L17813,

414 doi:10.1029/2007GL029797.
415 Wu, G., Ram, K., Fu, P., Wang, W., Zhang, Y., Liu, X., Stone, E.A., Pradhan, B.B., Dangol, P.M.,
416 Panday, A.K., Wan, X., Bai, Z., Kang, S., Zhang, Q., Cong, Z., 2019. Water-Soluble Brown
417 Carbon in Atmospheric Aerosols from Godavari (Nepal), a Regional Representative of South Asia.
418 Environ Sci Technol 53, 3471-3479.
419 Xie, M., Chen, X., Holder, A.L., Hays, M.D., Lewandowski, M., Offenberg, J.H., Kleindienst, T.E.,
420 Jaoui, M., Hannigan, M.P., 2019. Light absorption of organic carbon and its sources at a
421 southeastern US location in summer. Environmental Pollution 244, 38-46.
422 Yan, J., Wang, X., Gong, P., Wang, C., Cong, Z., 2018. Review of brown carbon aerosols: Recent
423 progress and perspectives. Science of The Total Environment 634, 1475-1485.
424 Zhang, X., Lin, Y.H., Surratt, J.D., Weber, R.J., 2013. Sources, composition and absorption Angstrom
425 exponent of light-absorbing organic components in aerosol extracts from the Los Angeles Basin.
426 Environ Sci Technol 47, 3685-3693.
427 Zhang, Y., Forrister, H., Liu, J., Dibb, J., Anderson, B., Schwarz, J.P., Perring, A.E., Jimenez, J.L.,
428 Campuzano-Jost, P., Wang, Y., 2017. Top-of-atmosphere radiative forcing affected by brown
429 carbon in the upper troposphere. Nature Geoscience 10, 486.
430 Zhu, C.S., Cao, J.J., Huang, R.J., Shen, Z.X., Wang, Q.Y., Zhang, N.N., 2018. Light absorption
431 properties of brown carbon over the southeastern Tibetan Plateau. Sci Total Environ 625, 246-251.

Highlights

- Light absorption of water-insoluble BrC is studied by extracting OC with methanol
- Uncertainties of previous methods to extract methanol-soluble BrC are discussed
- A new extraction method is developed to obtain reliable MAC of methanol-soluble BrC

This is an original work, not published or under consideration for publication elsewhere. There is no conflict of interests.