The authors thank the referees to review our manuscript and particularly for the valuable comments and suggestions that have significantly improved the manuscript. We provide below point-by-point responses (in blue) to the referees' comments and have made changes accordingly in the revised manuscript.

Referee #1

Brown carbon (BrC) is a fraction of organic aerosols with effective light absorption, which has significant effects on radiative forcing and climate. In the present study, the light absorbing properties, chromophores composition, and sources of BrC were investigated for aerosols collected in Xi'an, Northwest China. The results showed that AAE and MAE365 both present distinct seasonal differences and were due to the differences in sources and chemical composition of BrC chromophores. Some organic compounds including 12 PAHs, 10 NACs and 3 MOPs were quantified, which contributions to the light absorption of methanol-soluble BrC light absorption at 365 nm ranged from 1.1% to 3.3%, and thereby indicates that the light absorption of BrC is likely determined by an amount of chromophores with strong light absorption ability. Four major sources of methanol-soluble BrC were identified by PMF, which including secondary formation, vehicle emission, coal combustion and biomass burning and a large variation of BrC sources was observed in different seasons. Overall the manuscript is written well, and with some further explanation of collected data and further elaboration on the results it will be ready for publication. Below are specific revision comments for the authors to consider in their next revision:

Specific comments

1) Line 113: Please provide the unit of Absλ.

Response: The unit of Abs_{λ} ($M\ m^{-1}$) have been provided.

2) Line 122: Please provide the unit of MAE365.

Response: The unit of MAE_{365} ($m^2 gC^{-1}$) have been provided.

3) Line 126: "MOSC" should be "MSOC".

Response: Change made.

4) Lines 139-140: "The concentrations of NACs were analyzed following the method by Al-Naiema and Stone (2017). Briefly……". The details of experiment have some differences to that of reference (Al-Naiema and Stone, 2017). For example, the silylation was conducted by heating at 70 °C for 3h in this study, however it was conducted by heating at 100 °C for 90 min in the reference (Al-Naiema and Stone, 2017). In addition, according to the reference (Al-Naiema and Stone, 2017), the derivatization method used in the current study is only used for levoglucosan and phthalic acid isomers. Please check this section.

Response: Thanks for your careful reading. The silylation reaction with BSTFA at 70 °C for 3 h is a routine derivatization method for polar organic species before GC-MS analysis (e.g., Wang et al., 2006; Al-Naiema and Stone, 2017). In Al-Naiema and Stone (2017), the derivatization was conducted by heating to 70 °C for 3 h for levoglucosan and phthalic acid isomers, but modified slightly by heating to 100 °C for 90 min for nitromonoaromatics to get more symmetrical peak shapes and higher intensities than the derivatization method used for levoglucosan and phthalic acid isomers. In our study, however, with the routine method of "70 °C for 3 h" we also got symmetrical peak shapes and high intensities for NACs (see Figure below), and both NACs and other organic compounds can be simultaneously analyzed.

In line 144-162, we have changed "The concentrations of NACs were analyzed…following methods described by Wang et al. (2006)" to "Prior to the GC-MS analysis, the silylation derivatization was conducted using a routine method (e.g., Wang et al., 2006; Al-Naiema and Stone, 2017). Briefly, a quarter of…and a GC inlet of 280 °C. The GC oven temperature was held at 50 °C for 2 min, ramped to 120 °C at a rate of 15 °C min^{-1}, and finally reached 300 °C at a rate of 5 °C min^{-1} (held for 16 min). Note that the derivatization for NACs was conducted at 70 °C for 3 h which is slightly different from the protocol used in Al-Naiema and Stone (2017), because symmetrical peak shapes and high intensities for NACs can also be obtained under this condition in our study (see Fig. S1).

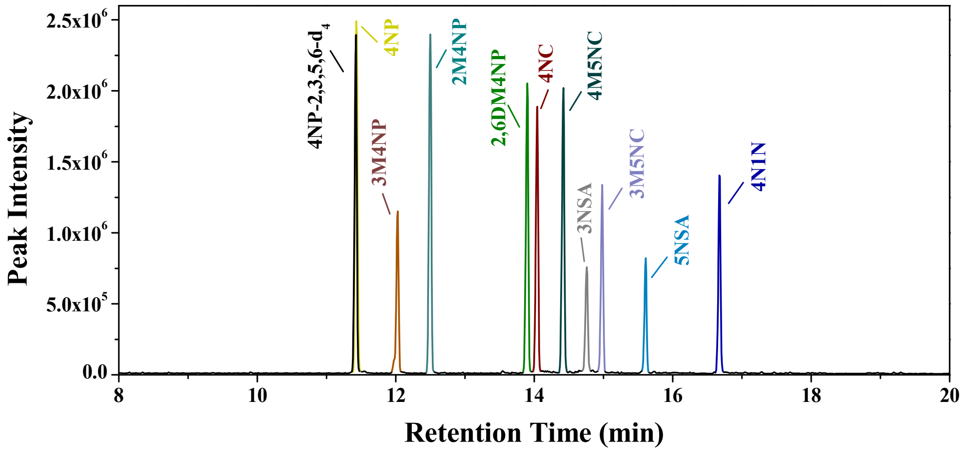

Figure S1. Selected ion monitoring chromatograms (GC-MS) for nitrated aromatic compound (NAC) standards (2 ug mL^{-1}) measured in our study.

5) How about the uncertainty of organic compounds and PMF analysis?

Response: We re-checked the uncertainties (RSDs) and have now added these values in the revised manuscript.

In line 167, it now reads "…the uncertainties (RSDs) are < 10% for measured organic compounds..

In line 335-336, it now reads "The uncertainties for PMF analysis are < 10% for secondary formation and biomass burning, < 15% for vehicle emission and coal burning."

6) Lines 179-183: As shown in the paper "The higher WSOC fraction in OC during summer may be related to biomass burning emissions…? Why biomass burning have a large emissions in summer? The seasonal variation of biomass burning should be

small.

"The lower WSOC fractions in OC during winter could be attributed to enhanced emissions from coal combustion and motor vehicles": I think the seasonal variation of motor vehicles emissions should be very small.

This explanation of seasonal variations of WSOC/OC should be revised based the experimental results and the supporting references.

Response: Daellenbach et al. (2016) reported that ~65% of biomass burning OA mass is water soluble, higher than cooking OA (~54%) and much higher than traffic OA (~11%). Therefore, we considered that biomass burning emissions, together with SOA, may contribute to higher WSOC fraction in summer, consistent with those reported in Ram et al. (2012) and Yan et al. (2015). The emissions of biomass burning indeed show large seasonal variation in northwest China (e.g., Xi'an). For example, Huang et al., (2018) reported the concentration of levoglucosan in Xi'an was about 11 times higher in winter than in summer because of large biomass burning for residential heating in winter. In summer, it is mainly from open burning of agricultural residues, e.g., wheats that were planted in previous winter and harvested in June/July.

To clarify this point, in 196-198, we changed "The higher WSOC…Yan et al., 2015)" to "The higher WSOC fraction in OC during summer is largely contributed by SOA and to some extent by biomass burning emissions because both SOA and biomass burning OA consist of high fraction of WSOC (Ram et al., 2012; Yan et al., 2015, Daellenbach et al., 2016)."

In winter, more water-insoluble organics are emitted by enhanced coal combustion for residential heating. We have changed "could be attributed to enhanced emissions from coal combustion and motor vehicles" to "could be attributed to enhanced emissions from coal combustion".

7) Lines 212-215: the average MAE365 value (1.18) in fall is more similar to that in spring and summer.

Response: Thanks for pointing this out. We have revised it to "…with highest values in winter (1.85 and 1.50 m^2 gC^{-1}, respectively), followed by fall (1.18 and 1.52 m^2 gC^{-1}), spring (1.01 and 0.79 m^2 gC^{-1}), and summer (0.91 and 1.21 m^2 gC^{-1})."

8) Lines 218-220: How about the contribution of the large amount of coal combustion and biomass burning activities in rural region around Xi`an?

Response: The rural and remote sites in Fig. 2 refer to regions with less anthropogenic activities. We have clarified this point in the revised manuscript. In line 239-240, it now reads "…are obviously higher in urban sites than in rural and remotes sites that are less influenced by anthropogenic activities."

9) Line 212-216: The unit of MAE365 is m2 gC-1, however the unit of MAE365 is m2 g-1 in Fig 2 and S2, Table 1. Please correct the errors. This is also important for the calculation of light absorption contribution of various organic compounds.

Response: In Fig. 2 and S2, Table 1, we have changed the unit to m^2 gC^{-1}.

10) Lines 77-78: Other important references about BrC materials directly emitted from coal combustion should added, such as "Sun et al., ACP, 2017, 17, 4769", "Li et al., EST 2019, 53, 595", "Song et al., EST 2019, 53, 13607", etc.

Response: Thanks. We have now cited those references in the revised manuscript. In line 78-79, it now reads "…are also important primary sources of BrC (Sun et al., 2017; Yan et al., 2017; Xie et al., 2017; Li et al., 2019; Song et al., 2019)."

11) Line 247: The "autumn" should be revised to "fall".

Response: Change made.

12) The PAHs, NACs and MOPs are important strong light-absorbing organic compounds, however the total contributions of PAHs, NACs and MOPs to the light absorption of methanol soluble BrC at 365 nm are small, only 1.05%- 3.26%. What is the major contribution to the light absorbing BrC?

Response: This is indeed a very good question. As discussed in Laskin et al. (2015), our understanding of the BrC molecular composition and chemistry as well as the link with optical properties is still in its early stages. The light-absorbing contribution (at 365 nm) of the 25 chromophores measured in our study is small but comparable to those in previous studies (Mohr et al., 2013; Zhang et al., 2013; Teich et al., 2017; Huang et al., 2018). Also, the light absorption contribution is ~5 times higher than the carbon mass contribution to OC, indicating that these three groups of chromophores (PAHs, NACs and MOPs) are important components of BrC with high potential to absorb light on a same carbon mass basis.

Indeed, a large fraction of BrC chromophores are still not identified so far, and more studies are therefore necessary. Based on laboratory and ambient studies, more organics should be considered in future studies, including imidazoles (Kampf et al., 2012; Teich et al., 2016), quinones (Lee et al., 2014; Pillar et al., 2017), nitrogenous PAHs (Lin et al., 2016; Lin et al., 2018), polyphenols (Lin et al., 2016; Pillar et al., 2017) and oligomers with higher conjugation (Lin et al., 2014; Lavi et al., 2017).

We have added the following discussion. In line 308-314, it now reads "…with strong light absorption ability (Kampf et al., 2012; Teich et al., 2017). Of note, a large fraction of BrC chromophores are still not identified so far, and more studies are therefore necessary to better understand the BrC chemistry. Based on laboratory and ambient studies, imidazoles (Kampf et al., 2012; Teich et al., 2016), quinones (Lee et al., 2014; Pillar et al., 2017), nitrogenous PAHs (Lin et al., 2016; Lin et al., 2018), polyphenols (Lin et al., 2016; Pillar et al., 2017) and oligomers with higher conjugation (Lin et al., 2014; Lavi et al., 2017) could be included in future studies."

13) Section 3.3: the sources of BrC were quantified with a PMF model. However I have several concerns: 1) Why the contribution of biomass burning was not identified in spring? In general, the biomass burning activities should happen in every seasons. 2) the contribution of SOA is lowest in Fall. Why? Could you give some explaination? 3) the contribution of vehicle emissions are more than 1/3 in spring and fall. Could you give some discussion to interpret the reason for this seasonal variations of source compostions.

Response: We thank reviewer for raising these concerns, as we agree that further clarification will improve the manuscript. Here we provide responses to each of the question raised.

1) The biomass burning activities in Xi'an and surrounding areas were mainly in winter heating period and two harvest seasons (wheat in June and maize in Oct, respectively). Therefore, we believe that the biomass burning contribution in spring (April-May in our study) might be too small to be identified.

2) For the contribution of secondary formation to total $Abs_{365,MSOC}$, we ought to look at contributions from both relative and absolute terms. As shown in Table R1, the calculated absolute contributions of secondary formation to $Abs_{365,MSOC}$ were 1.75, 2.55, 1.70, 6.20 M m^{-1} in spring, summer, fall, and winter, respectively. While the high contribution in winter can be attributed to abundant precursors (volatile organic compounds) co-emitting with the other primary sources (especially coal combustion and biomass burning), the high contribution in summer might be due to strong photochemical activity. For spring and fall, the absolute contributions from secondary formation were very similar, indicating moderate precursor emission and moderate photochemical activity. The low relative contribution of secondary formation to $Abs_{365,MSOC}$ in fall was due in part to the large contributions from primary emissions, e.g., coal burning (29% or 4.47 M m^{-1}) and biomass burning (22% or 3.39 M m^{-1}) that made up a total $Abs_{365,MSOC}$ in fall.

To avoid confusion, we replace Figure 5 with pie charts representing absolute contributions by the surface area of the sums of pies.

3) As shown in Table. R2, the seasonal differences of hopane concentrations (~10 times) was much smaller than those of PAHs (~30 times) and levoglucosan (~160 times), indicating that the differences of vehicle emission strength were relatively small among seasons. In summer, secondary formation contributed to over 60% of $Abs_{365,MSOC}$, although the total value of $Abs_{365,MSOC}$ was the smallest (4.05 M m^{-1}) among the four seasons. In winter, on the contrary, primary emissions from coal burning and biomass burning, other than vehicle emission, made up 80% of the total $Abs_{365,MSOC}$, which by itself was the highest (34.42 M m^{-1}) in the four seasons. Without as efficient secondary formation as in summer and as abundant other primary emissions as in winter, vehicle emission in spring and fall stood out as the significant contributor to $Abs_{365,MSOC}$. Note that the absolute contributions of vehicle emission to $Abs_{365,MSOC}$ were still higher in spring and fall than those in summer and winter (Table R1, or Table S4), yet these differences by a factor of 2–9 are still less pronounced than the differences (spring/fall vs winter) for other primary emissions (>40 times for coal burning and >25 times for biomass burning). Nevertheless, we agree with the reviewer that relative (and absolute) contribution of vehicle emission in fall was relatively higher, which might be affected by higher relative humidity in fall (on average 83% in fall vs. 61-69% in other seasons) resulting in higher vehicular $PM_{2.5}$ emissions (Chio et al., EPA, 2010). We have now added the following discussion in lines 349-363 the revised manuscript:

"…(wood and crop residues) and coal combustion for heating. In terms of absolute contributions to absorption of MSOC at 365 nm (see Table S4), secondary formation contributed 1.75, 2.55, 1.70, 6.20 M m^{-1} in spring, summer, fall, and winter, respectively. The high contribution in winter can be attributed to abundant precursors (volatile organic compounds) co-emitted with other primary sources (especially coal burning and biomass burning), while the high contribution in summer might be due to strong photochemical activity. For spring and fall, the absolute contributions from secondary formation were very similar, indicating moderate precursor emission and moderate photochemical activity. Also it should be noted that the absolute contributions of vehicle emission to absorption of MSOC at 365 nm were still higher in spring and fall than those in summer and winter, yet these differences by a factor of 2-9 are still less pronounced than the differences (spring/fall vs. winter) for other primary emissions (> 40 times for coal burning and > 25 times for biomass burning). In particular, the high vehicle contribution in fall might be affected by high relative humidity in fall (83% in fall vs. 61-69% in other seasons, on average) resulting in high vehicular $PM_{2.5}$ emissions (Chio et al., 2010). Such large seasonal difference…"

Table R1. Seasonal light absorption of methanol-soluble BrC at wavelength of 365 nm and the sources contributions.

	Spring	Summer	Fall	Winter
$Abs_{365,MSOC}$ (M m^{-1})	4.73	4.05	15.41	34.42
Sources contribution to $Abs_{365,MSOC}$ (%)				
Secondary formation	37	63	11	18
Vehicle emission	34	16	38	2
Coal burning	29	9	29	44
Biomass burning	0	12	22	36
Sources contribution to $Abs_{365,MSOC}$ (M m^{-1})				
Secondary formation	1.75	2.55	1.70	6.20
Vehicle emission	1.61	0.65	5.86	0.69
Coal burning	1.37	0.36	4.47	15.41
Biomass burning	0	0.49	3.39	12.39

Table R2. Seasonal mean (± standard deviation) of the measured compounds.

Compounds	Spring	Summer	Fall	Winter
o-ph	3.92±2.29	6.50±3.57	8.70±5.04	11.19±7.56
HP1	0.22±0.08	0.10±0.05	0.69±0.48	1.47±0.54
HP2	0.23±0.11	0.11±0.06	0.66±0.44	1.15±0.41
HP3	0.09±0.04	0.07±0.02	0.31±0.22	0.48±0.18
HP4	0.09±0.03	0.07±0.02	0.27 ±0.19	0.55±0.27
PI	0.17±0.10	-	0.70±0.37	0.97±0.51
FLU	0.52±0.21	0.19±0.10	1.96±0.98	11.88±5.42
PYR	0.46±0.21	0.18±0.09	1.73±0.86	10.06±4.41
CHR	0.68±0.29	0.23±0.13	2.47±1.21	10.13±5.47
BaA	0.33±0.16	0.12±0.07	1.73±0.93	8.15±3.78
BaP	0.88±0.53	0.43±0.30	4.42±2.70	9.35±7.84
BbF	1.59±0.82	0.74±0.56	6.22±3.55	15.32±13.14
BkF	0.43±0.20	0.25±0.13	1.60±0.81	3.85±3.11
IcdP	2.02±1.19	0.84±0.43	9.22±4.89	13.46±12.37
BghiP	0.20±0.06	0.72±0.59	7.03±3.55	8.12±3.68
9,10AQ	2.23±1.75	0.20±0.11	1.16±0.66	8.56±4.20
BEN	0.26±0.12	0.28±0.15	2.29±2.10	6.82±3.25
BbF11O	0.19±0.08	0.17±0.11	1.18±1.03	5.16±2.61
LEV	1.21±0.36	9.79±4.49	85.43±47.56	193.21±68.57
VaA	0.23±0.14	0.06±0.02	0.44±0.3	3.03±1.43
VAN	0.32±0.18	0.07±0.03	0.48±0.37	2.60±0.10
SyA	2.24±1.74	0.43±0.22	3.75±2.95	15.88±7.62

References

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Referee #2

In this work, the authors investigated the optical properties, chemical composition and sources of brown carbon (BrC) in Xi'an from 2015-2016. They identified three groups of BrC chromophores including PAHs and their derivatives, nitrophenols and methoxyphenols, of which some were not identified as BrC chromophores in previous studies (e.g., methoxyphenols). The authors then quantified the contribution of these identified chromophores to the total light absorption of BrC at the wavelength from 300-500 nm, which is important dataset because the link between BrC absorption and chemical composition is a key for estimating the effect of BrC on radiative forcing but such data are still very limited particularly for ambient measurements. Finally, the authors quantified the sources of BrC by PMF using these identified chromophores and found the seasonal difference in the contributing sources. In general, the results are provided in a concise format and the discuss is well stated and directly related to the important aspects of BrC, i.e., the links between optical properties, chromophore composition, and sources of BrC. Also, the paper is well written and organized. I recommend publication in ACP after minor revision.

Specific comments

1. The peak values of the light absorption contribution of the measured chromophores are not always at 365 nm. Therefore, it could be better to include the average light absorption contribution of these chromophores to BrC at the wavelength of 300-500 nm.

Response: Thanks for pointing it out. We have now added description of the average light absorption contribution of these chromophores to BrC at the wavelength of 300-500 nm.

In line 282-284, it now reads "The total contributions of PAHs, NACs and MOPs to the light absorption of methanol-soluble BrC ranged from 0.47% (summer) to 1.56% (winter) at the wavelength of 300-500 nm and ranged from 1.05% (summer) to 3.26% (winter) at the wavelength of 365 nm."

2. Previous studies often discussed the light-absorption contribution of chromophores to

water-soluble BrC. The authors discussed only the contribution to methanol-soluble BrC in this study. Should they also discuss the contribution to water-soluble BrC from the identified chromophores?

Response: Indeed, previous studies often discussed the light-absorption contribution of water-soluble chromophores (e.g., NACs) to water-soluble BrC (Zhang et al., 2013; Teich et al., 2017). However, in our study, we also quantified water-insoluble but methanol-soluble chromophores, e.g., PAHs. We believe that the methanol-soluble chromophores are under-represented, despite of a great deal of efforts spent on water-soluble chromophores. Therefore, we tend to focus on the contributions of these methanol-soluble chromophores to BrC.

3. Page 6, line 162. Change "9,10-anthracenequinone (9,10-AQ)" to "9,10-anthracenequinone (9,10 AQ)".

Response: Change made.

4. Page 6, line 163-166. Not all species are non-light absorbing. For example, picene contains five benzene ring and should be light-absorbing species. It could be better to change "non-light absorbing markers" to "commonly used markers".

Response: We have changed "non-light absorbing markers" to "commonly used markers" in the revised manuscript.

5. Page 11, line 300-301. 9,10 AQ, BEN and BbF11O are not only from combustion emission but also from secondary formation. Please clarify it.

Response: We have changed it. In line 328-331, it now reads "The inputs include vanillic acid, vanillin, and syringyl acetone for BrC from biomass burning, FLU, PYR, CHR, BaA, BaP, BbF, BkF, IcdP and BghiP, for BrC from incomplete combustion and other light absorbing chromophores 9,10AQ, BEN, and BbF11O."

6. Page 26. Figure 2. Change m2 g-1 to m2 gC-1.

Response: Chang made.

Referee #3

This manuscript describes how different organic compounds contribute to the absorption properties of ambient aerosols in Xi'an (Northwest China). PM2.5 samples were collected during all four seasons and analyzed for optical properties (spectrophotometer measurements), total organic carbon (TOC), 12 polycyclic aromatic hydrocarbons (PAHs), 10 nitrated aromatic compounds (NAC), 3 methoxyphenols, and 4 hopanes. Prior to the analyses, the filters were extracted with water and methanol. The aim of this study was to estimate the contribution of BrC species to the optical properties of ambient PM2.5. This study is scientifically important. The manuscript is well organized and well written. However, there are four major comments.

In summary, I recommend this manuscript for publication after the author addresses the major questions.

Major comments:

1. The author extracted and analyzed many non-polar organic compounds (PAHs, hopanes, etc.). However, for the extraction, solvents with high polarity indexes were used (water and methanol). By using these solvents, the author would not be able to extract non-polar compounds and estimate their contribution to the non-polar BrC fraction of the collected PM2.5. Sengupta et al. (2018) highlighted the importance of the non-polar fraction of BrC aerosols. Plus, the reference to this study is missing.

Response: The organic compounds quantified in our study were extracted by a mixture of dichloromethane/methanol (2:1, v/v) which can extract both polar and non-polar organic compounds (e.g., PAHs, hopanes, levoglucosan). However, the light absorption was measured by extracting BrC into methanol because methanol can extract ~90% of OC for ambient aerosol (e.g., Chen and Bond, 2010; Cheng et al., 2016; Xie et al., 2019) and has been widely used for BrC extraction (e.g., Cheng et al., 2016; Huang et al., 2018; Zhu et al., 2018). Meanwhile, these 25 organic compounds including the PAHs can all be dissolved in methanol, as we did for their standards.

We agree that non-polar fraction of BrC is important and the reference has been added.

In line 204-206, it now reads"…the optical properties of BrC could be largely underestimated when using water as the extracting solvent as non-polar fraction of BrC is also important to light absorption of BrC (Sengupta et al., 2018)."

2. Many organic species from different glasses and with different volatility levels were measured. However, only one deuterated internal standard (4-nitrophenol-d4) was used to account for potential losses of analytes during the extraction and preconcentration procedures. How were losses of other organic species (besides 4-nitrophenol) taken into account?

Response: In our study, 4-nitrophenol-2,3,5,6-d4 was used as an internal standard to correct for potential loss for NACs quantification (Chow et al., 2015). For the quantification of other organic compounds, an external standard method was used through daily calibration with working standard solutions. Also, for every 10 samples, a procedural blank and a spiked sample (i.e., ambient sample spiked with known amounts of standards) were measured to check the interferences and recoveries. The measured recoveries are 80-102% for measured organic compounds.…We have added this description in the revised manuscript.

3. It was highlighted that different sources make different contributions to the chemical composition of PM2.5 collected in Xi'an. At the same time, the discussion (description) of these sources (how far they are from the sampling site, meteorological conditions, transport, types of biomass-burning fuels, etc.) is missing. Therefore, it is very hard to evaluate what composition of PM2.5 should be expected.

Response: The focus of this study was the seasonal differences in BrC optical properties (e.g., Abs, MAE), chromophore composition, and the sources. In particular, the BrC sources were resolved using these measured chromophores instead of commonly used non-light absorbing organic markers as model inputs, which can greatly minimize the bias in quantifying the BrC sources using non-light absorbing markers. A comprehensive characterization of the $PM_{2.5}$ composition was not the objective of this study. Certainly, it will be interesting to understand how the BrC is affected by e.g., meteorological conditions, types of biomass fuels, and the formation and transformation of optical properties and chemical composition during transport. However, each of these aspects require intensive studies in the future.

4. Lines 304–310. References and data are missing on four used factors of the source apportionment.

Response: The profiles for the four factors, which were resolved in our ME-2 model, are shown in Figure S3. These profiles (data) are not from literature. To make it clear, in the section "Source apportionment of BrC" we have added the following "…(see Table S2). This source apportionment protocol is very similar to our previous study (Huang et al., 2014)."

Some minor comments:

Line 55. References are needed on adverse health effects of PAHs.

Response: We have added references. In line 55-56, it now reads "…on human health (Bandowe et al., 2014; Shen et al., 2018)".

Lines 99, 108, 112, 139. Company name (+city, state, country) of material and instruments is missing.

Response: Company name (+city, state, country) of material and instruments have been added.

Line 101. "…quartz-fiber filters (20.3 × 25.4 cm, Whatman, QM-A, Clifton, NJ, USA)…"

Line 111-112. "…methanol (HPLC grade, J. T. Baker, Phillipsburg, NJ, USA)…"

Line 115-116. "…liquid waveguide capillary cell (LWCC-3100, World Precision Instrument, Sarasota, FL, USA)…"

Line 142-143. "…gas chromatograph-mass spectrometer (GC-MS, Agilent Technologies, Santa Clara, CA, USA)…"

Line 149. What is the company (+city, country, etc.) of the GC column?

Response: The company of the GC column has been added.

Line 155. "…DB-5MS column (Agilent Technologies, Santa Clara, CA, USA)…"

Line 204. References on absorption properties (above 300 nm) of PAHs are needed.

Response: A reference have been added, i.e., Samburova et al., 2016.

Line 215. It should be specified that "such large seasonal differences indicate seasonal difference in BrC sources" for the Xi'an area (Northwest China). Again, a good description of these sources is needed in the manuscript.

Response: We have added the following discussion in this paragraph. It now reads "…indicate seasonal difference in BrC sources. For example, contributions from coal combustion and biomass burning were much larger in winter than in other seasons due to large residential heating activities (also see Section 3.3 for more details)."

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Characterization of the light absorbing properties, chromophores composition and sources of brown carbon aerosol in Xi'an, Northwest China

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Abstract

The impact of brown carbon aerosol (BrC) on the Earth's radiative forcing balance has been widely recognized but remains uncertain, mainly because the relationships among BrC sources, chromophores, and optical properties of aerosol are poorly understood. In this work, the light absorption properties and chromophore composition of BrC were investigated for samples collected in Xi'an, Northwest China from 2015 to 2016. Both absorption Ångström exponent and mass absorption efficiency show distinct seasonal differences, which could be attributed to the differences in sources and chromophore composition of BrC. Three groups of light-absorbing organics were found to be important BrC chromophores, including those show multiple absorption peaks at wavelength > 350 nm (12 polycyclic aromatic hydrocarbons and their derivatives) and those show single absorption peak at wavelength < 350 nm (10 nitrophenols and nitrosalicylic acids and 3 methoxyphenols). These measured BrC chromophores show distinct seasonal differences and contribute on average about 1.1% and 3.3% of light absorption of methanol-soluble BrC at 365 nm in summer and winter, respectively, about 7 and 5 times higher than the corresponding carbon mass fractions in total organic carbon. The sources of BrC were resolved by positive matrix factorization (PMF) using these chromophores instead of commonly used non-light absorbing organic markers as model inputs. Our results show that in spring vehicular emissions and secondary formation are major sources of BrC (~70%), in fall coal combustion and vehicular emissions are major sources (~70%), in winter biomass burning and coal combustion become major sources (~80%), while in summer secondary BrC dominates (~60%).

1 Introduction

Brown carbon (BrC) is an important component of atmospheric aerosol particles and has significant effects on radiative forcing and climate (Feng et al., 2013; Laskin et al., 2015; Zhang et al., 2017a). BrC can efficiently absorb solar radiation and reduce the photolysis rates of atmospheric radicals (Jacobsan, 1999; Li et al., 2011; Mok et al., 2016), which ultimately influences the atmospheric photochemistry process, the formation of secondary organic aerosol (SOA), and therefore the regional air quality (Mohr et al., 2013; Laskin et al., 2015; Moise et al., 2015). In addition, some components in BrC, such as nitrated aromatic compounds (NACs) (Teich et al., 2017; Wang et al., 2018) and polycyclic aromatic hydrocarbons (PAHs) (Samburova et al., 2016; Huang et al., 2018), have adverse effects on human health (Bandowe et al., 2014; Shen et al., 2018). The significant effects of BrC on environment, climate, air quality and living things call for more studies to understand its chemical characteristics, sources and the links with optical properties.

Investigating the chemical composition of BrC at molecular level is necessary, because even small amounts of compounds can have a significant effect on the light absorption properties of BrC and profound atmospheric implication (Mohr et al., 2013; Zhang et al., 2013; Teich et al., 2017; Huang et al., 2018). A number of studies have investigated the BrC composition at molecular level (Mohr et al., 2013; Zhang et al., 2013; Chow et al., 2015; Samburova et al., 2016; Lin et al., 2016, 2017, 2018; Teich et al., 2017; Huang et al., 2018; Lu et al., 2019). For example, Zhang et al. (2013) measured 8 NACs in Los Angeles and found that they contributed about 4% of water-soluble BrC absorption at 365 nm. Huang et al. (2018) measured 18 PAHs and their derivatives in Xi'an and found that they accounted for on average ~1.7% of the overall absorption of methanol-soluble BrC. A state-of-the-art high performance liquid chromatography-photodiode array-high resolution mass spectrometry (HPLC-PDA-HRMS) was applied to investigate the elemental composition of BrC chromophores in biomass burning aerosol (Lin et al., 2016, 2017, 2018). Despite these efforts, the molecular composition of atmospheric BrC still remains largely unknown due to its complexity in emission sources and formation processes.

Field observations and laboratory studies show that BrC has various sources, including primary emissions such as combustion and secondary formation from various atmospheric processes (Laskin et al., 2015). Biomass burning, including forest fires and burning of crop residues, is considered as the main source of BrC (Teich et al., 2017; Lin et al., 2017). Coal burning and vehicle emissions are also important primary sources of BrC (Yan et al., 2017; Xie et al., 2017; Sun et al., 2017; Li et al., 2019; Song et al., 2019). Secondary BrC is produced through multiple-phase reactions occurring in or between gas phase, particle phase, and cloud droplets. For example, nitrification of aromatic compounds (Harrison et al., 2005; Lu et al., 2011), oligomers of acid-catalyzed condensation of hydroxyl aldehyde (De Haan et al., 2009; Shapiro et al., 2009), and reaction of ammonia (NH_3) or amino acids with carbonyls (De Haan et al., 2011; Nguyen et al., 2013; Flores et al., 2014) can all produce BrC. Condensed phase reactions and aqueous-phase reactions have also been found to be important formation pathways for secondary BrC in ambient air (Gilardoni et al., 2016). In addition, atmospheric aging processes can lead to either enhancement or bleaching of the BrC absorption (Lambe et al., 2013; Lee et al., 2014; Zhong and Jang, 2014), further challenging the characterization of BrC.

As the starting point of the Silk Road, Xi'an is an important inland city in northwestern China experiencing severe particulate air pollution, especially during heating period with enhanced coal combustion and biomass burning activities (Wang et al., 2016; Ni et al., 2018). In this study, we performed spectroscopic measurement and chemical analysis of $PM_{2.5}$ filter samples in Xi'an to investigate: 1) seasonal variations in the light absorption properties and chromophore composition of BrC, and their relationships; 2) sources of BrC in different seasons based on positive matrix factorization (PMF) model with light-absorbing organic markers as input species.

2 Experimental

2.1 Aerosol sampling

A total of 112 daily ambient $PM_{2.5}$ filter samples were collected on pre-baked (780 °C, 3 h) quartz-fiber filters (20.3 × 25.4 cm, Whatman, QM-A, Clifton, NJ, USA) in November-December 2015, April-May, July, October-November 2016, representing winter, spring, summer and fall, respectively. Filter samples were collected using a Hi-Vol $PM_{2.5}$ air sampler (Tisch, Cleveland, OH) at a flow rate of 1.05 m^3 min^{-1} on the roof (~10 m above ground level, 34.22°N, 109.01°E) of the Institute of Earth Environment, Chinese Academy of Sciences, which was surrounded by residential areas without large industrial activities. After collection, the filter samples were wrapped in baked aluminum foils and stored in a freezer (-20 °C) until further analysis.

2.2 Light absorption measurement

One punch of loaded filter (0.526 cm^2) was taken from each sample and sonicated for 30 minutes in 10 mL of ultrapure water (> 18.2 MΩ · cm) or methanol (~~J. T. Baker, ~~HPLC grade, J. T. Baker, Phillipsburg, NJ, USA). The extracts were then filtered with a 0.45 μm PTFE pore syringe filter to remove insoluble materials. The light absorption spectra of water-soluble and methanol-soluble BrC were measured with an UV-Vis spectrophotometer (300-700 nm) equipped with a liquid waveguide capillary cell (LWCC-3100, World Precision Instrument, Sarasota, FL, USA) following the method by Hecobian et al. (2010). The measured absorption data can be converted to the absorption coefficient Abs_λ ($M\ m^{-1}$) by equation (1):

$$Abs_\lambda = (A_\lambda - A_{700})\frac{V_l}{V_a \times L} \times \ln(10) \qquad (1)$$

where A_{700} is the absorption at 700 nm, serving as a reference to account for baseline drift, V_l is the volume of water or methanol that the filter was extracted into, V_a is the volume of sampled air, L is the optical path length (0.94 m). A factor of ln(10) is used to convert the log base-10 (recorded by UV-Vis spectrophotometer) to natural logarithm to provide base-e absorption coefficient. The absorption coefficient of water-soluble or methanol-soluble organics at 365 nm (Abs_{365}) is used to represent water-soluble or methanol-soluble BrC absorption, respectively.

The mass absorption efficiency (MAE: $m^2\ gC^{-1}$) of BrC in the extracts can be calculated as:

$$MAE_\lambda = \frac{Abs_\lambda}{M} \qquad (2)$$

where M ($\mu gC\ m^{-3}$) is the concentration of water-soluble organic carbon (WSOC) for water extracts or methanol-soluble organic carbon (MSOC) for methanol extracts. Note that organic carbon (OC) is often used to replace MSOC because direct measurement of MSOC~~MOSC~~ is technically difficult and many studies have shown that most of OC (~ 90%) can be extracted by methanol (Chen and Bond, 2010; Cheng et al., 2016; Xie et al., 2019).

The wavelength-dependent light absorption of chromophores in solution, termed as absorption Ångström exponent (AAE), can be described as:

$$Abs_\lambda = K \cdot \lambda^{-AAE} \qquad (3)$$

where K is a constant related to the concentration of chromophores and AAE is calculated by linear regression of log Abs_λ versus log λ in the wavelength range of 300-410 nm.

2.3 Chemical analysis

OC was measured with a thermal/optical carbon analyzer (DRI, model 2001) following the IMPROVE-A protocol (Chow et al., 2011). WSOC was measured with a TOC/TN analyzer

(TOC−L, Shimadzu, Japan) (Ho et al., 2015).

Organic compounds listed in Table S1 were analyzed with a gas chromatograph-mass spectrometer (GC-MS, Agilent Technologies, Santa Clara, CA, USA). ~~The concentrations of NACs were analyzed following the method by Al-Naiema and Stone (2017).~~ Prior to the GC-MS analysis, the silylation derivatization was conducted using a routine method (e.g., Wang et al., 2016; Al-Naiema and stone, 2017). Briefly, a quarter of 47 mm filter sample was ultrasonically extracted with 2 mL of methanol for 15 minutes and repeated three times. ~~4-Nitrophenol-2,3,5,6-d_4 was added as an internal standard before extraction to correct for potential loss of analytes during the extraction process.~~ The extracts were filtered with a 0.45 µm PTFE syringe filter and then evaporated with a rotary evaporator to ~1 mL and dried with a gentle stream of nitrogen. Then, 50 µL of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA-TMCS; Fluka Analytical 99%) and 10 µL of pyridine were added. The mixture was heated for 3 h at 70 °C for silylation. After reaction, 140 µL of n-hexane were added to dilute the derivatives. Finally, 2 µL aliquot of the derivatized extracts were introduced into the GC-MS, which was equipped with a DB-5MS column (Agilent Technologies, Santa Clara, CA, USA), electron impact (EI) ionization source (70 eV), and a GC inlet of 280 °C. The GC oven temperature was held at 50 °C for 2 min, ramped to 120 °C at a rate of 15 °C min^{-1}, and finally reached 300 °C at a rate of 5 °C min^{-1} (held for 16 min). Note that the derivatization for NACs was conducted at 70 °C for 3 h which is slightly different from the protocol used in Al-Naiema and stone (2017), because symmetrical peak shapes and high intensities for NACs can also be obtained under this condition in our study (see Fig. S1). In our study, 4-nitrophenol-2,3,5,6-d4 was used as an internal standard to correct for potential loss for NACs quantification (Chow et al., 2015). For the quantification of other organic compounds, an external standard method was used through daily calibration with working standard solutions. Also, for every 10 samples, a procedural blank and a spiked sample (i.e., ambient sample spiked with known amounts of standards) were measured to check the interferences and recoveries. The measured recoveries are 80-102% and the uncertainties (RSDs) are < 10% for measured organic compounds. ~~The concentrations of PAHs and its oxygenated derivatives, methoxyphenols (MOPs), levoglucosan, hopanes and phthalic acid were analyzed following methods described by Wang et al. (2006).~~

2.4 Source apportionment of BrC

Source apportionment of methanol-soluble BrC was performed using positive matrix factorization (PMF) as implemented by the multilinear engine (ME-2; Paatero, 1997) via the Source Finder (SoFi) interface written in Igor Wavemetrics (Canonaco et al., 2013). $Abs_{365,MSOC}$ and those light-absorbing species including fluoranthene (FLU), pyrene (PYR), chrysene (CHR), benzo(a)anthracene (BaA), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), indeno[1,2,3-cd]pyrene (IcdP), benzo(ghi)perylene (BghiP), 9,10-anthracenequinone (9,10-AQ), benzanthrone (BEN), benzo[b]fluoren-11-one (BbF11O), vanillic acid, vanillin and syringyl acetone were used as model inputs, together with some commonly used~~non-light absorbing~~ markers, i.e., phthalic acid, hopanes (17α(H),21β(H)-30-norhopane, 17α(H),21β(H)-hopane, 17α(H),21β(H)-(22S)-homohopane, 17α(H),21β(H)-(22R)-homohopane, referred to as HP1-HP4, respectively), picene, and levoglucosan. The input data include species concentrations and uncertainties. The method detection limits (MDLs), calculated as three times of the standard deviation of the blank filters, were used to estimate species-specific uncertainties, following Liu et al. (2017). Furthermore, for a clear separation of sources profiles, the contribution of corresponding markers was set to 0 in the sources unrelated to the markers (see Table S2). This source apportionment protocol is very similar to our previous study (Huang et al., 2014).

3 Results and discussion

3.1 Light absorption properties of water- and methanol-soluble BrC

Fig. 1 shows the temporal profiles of Abs_{365} of water- and methanol-soluble BrC, together with the concentrations of WSOC and OC (representing MSOC). They all show similar seasonal variations with the highest average in winter, followed by fall, spring and summer (see Table S3). WSOC contributed annually 54.4 ± 16.2% of the OC mass, with the highest contribution in summer (66.1 ± 15.5%) and the lowest contribution in winter (45.1 ± 10.2%). The higher WSOC fraction in OC during summer is largely contributed by SOA and to some extent by biomass burning emissions because both SOA and biomass burning OA consist of high fraction of WSOC~~may be related to biomass burning emissions and SOA formation which~~

produce more WSOC (Ram et al., 2012; Yan et al., 2015; Daellenbach et al., 2016). The lower WSOC fractions in OC during winter could be attributed to enhanced emissions from coal combustion and motor vehicles which produce a large fraction of water-insoluble organics (Dai et al., 2015; Daellenbach et al., 2016; Yan et al., 2017). $Abs_{365,MSOC}$ is approximately 2 times (range 1.7-2.3) higher than $Abs_{365,WSOC}$, which is similar to the results measured in Beijing (Cheng et al., 2016), southeastern Tibetan Plateau (Zhu et al., 2018), Gwangju, Korea (Park et al., 2018) and the Research Triangle Park, USA (Xie et al., 2019), indicating that the optical properties of BrC could be largely underestimated when using water as the extracting solvent as non-polar fraction of BrC is also important to light absorption of BrC (Sengupta et al., 2018). In Fig. S21 we summarized those previously reported $Abs_{365,WSOC}$ (as $Abs_{365,MSOC}$ was not commonly measured in many previous studies) values at different sites in Asian urban and remote areas and the US. $Abs_{365,WSOC}$ is significantly higher in most Asian urban regions than in the Asian remote sites and the US, and show clear seasonal variations. The high light absorption of BrC in Asian urban regions, especially during winter, may have important effects on regional climate and radiation forcing (Park et al., 2010; Laskin et al., 2015). As discussed in Feng et al. (2013), the average global climate forcing of BrC was estimated to be 0.04-0.11 W m^{-2} and above 0.25 W m^{-2} in urban sites of south and east Asia regions, which is about 25% of the radiative forcing of black carbon (BC, 1.07 W m^{-2}). Thus, to further understand the influence of BrC on regional radiation forcing, it is essential to identify and quantify the sources of BrC in Asia.

The seasonal averages of AAE of water-soluble BrC were between 5.32 and 6.15 without clear seasonal trend (see Table S3). The seasonal averages of AAE of methanol-soluble BrC were relatively lower than those of water-soluble BrC, ranging from 4.45 to 5.18 which is similar to the results in Los Angeles Basin (Zhang et al., 2013) and Gwangju, Korea (Park et al., 2018). This is because methanol can extract more compounds with high conjugation degree and strong light-absorbing capability (e.g., PAHs) at longer wavelength (> 350 nm) (Samburova et al., 2016). The AAE values of water-soluble BrC (as AAE of methanol-soluble BrC was not commonly measured in many previous studies) in urban, rural and remote regions show a large difference (see Fig. 2a), typically with much lower AAE values in urban regions than those in rural and remote regions, indicating the difference in sources and chemical composition of chromophores. The urban regions are mainly affected by anthropogenic emissions. Therefore, urban BrC may contain a large amount of aromatic chromophores with high conjugation degree, which absorb light at a longer wavelength and have lower AAE values (Lambe et al., 2013; Wang et al., 2018).

The average MAE_{365} values of water- and methanol-soluble BrC show large seasonal variations, with highest~~r~~ values in winter (1.85 and 1.50 $m^2\ gC^{-1}$, respectively), followed by ~~and~~ fall (1.18 and 1.52 $m^2\ gC^{-1}$), ~~and lower values in~~ spring (1.01 and 0.79 $m^2\ gC^{-1}$), and summer (0.91 and 1.21 $m^2\ gC^{-1}$). Such large seasonal differences indicate seasonal difference in BrC sources. For example, contributions from coal burning and biomass burning were much larger in winter than in other seasons due to large residential heating activities (also see Section 3.3 for more details).~~, as discussed below.~~ Compared to previous studies (Fig. 2b), the average values of $MAE_{365,WSOC}$ are obviously higher in urban sites than in rural and remote sites that are less influenced by anthropogenic activities. The higher $MAE_{365,WSOC}$ values in urban regions is likely associated with enhanced anthropogenic emissions from e.g., coal combustion and biomass burning, and the lower $MAE_{365,WSOC}$ values in rural and remote regions could be attributed to biogenic sources or aged secondary BrC (Lei et al., 2018; Xie et al., 2019).

3.2 Chemical characterization of the BrC chromophores

Given the complexity in emission sources and formation processes, the molecular composition of atmospheric BrC remains largely unknown. PAHs, NACs and MOPs have recently been found as major chromophores in biomass burning-derived BrC (Lin et al., 2016, 2017, 2018). However, these compounds can also be directly emitted by coal combustion and motor vehicle or formed by secondary reactions (Harrison et al., 2005; Iinuma et al., 2010; Liu et al., 2017; Wang et al., 2018; Lu et al., 2019), making source attribution of atmospheric BrC more challenging. To obtain the exact molecular composition of BrC chromophores and understand the influence of a specific chromophore on BrC optical property, we measured the light absorption characteristics of available chromophore standards including 12 PAHs, 10 NACs and 3 MOPs, and quantified their concentrations in $PM_{2.5}$ samples with GC-MS. The light absorption contribution of individual chromophores to that of methanol-soluble BrC in the wavelength range of 300-500 nm was estimated according to its concentration and mass absorption efficiency (see Supplementary). Fig. 3 shows the contribution of carbon content in identified BrC chromophores to the total OC mass. They all show obvious seasonal variations with the highest values in winter and lowest in summer. The seasonal difference can be up to a factor of 5-6. The contribution of PAHs ranged from 0.12% in summer to 0.47% in winter, NACs from 0.02% in summer to 0.13% in winter, and MOPs from 0.01% in summer to 0.06% in winter. It should be noted that NACs are dominated by 4-nitrophenol and 4-nitrocatechol in spring, fall and winter, but by 4-nitrophenol and 5-nitrosalicylic acid in summer. The difference is likely due to enhanced summertime formation of 5-nitrosalicylic acid, which is more oxidized than other nitrated phenols measured in this study (Wang et al., 2018).

The seasonally averaged contributions of PAHs, NACs, MOPs and total measured chromophores to light absorption of methanol-soluble BrC between 300 to 500 nm are shown in Fig. 4. They show large seasonal variations and wavelength dependence. Specifically, PAHs made the largest contribution to BrC light absorption in fall ~~autumn~~, followed by winter, spring and summer, and show two large absorption peaks at about 365 nm and 380 nm, which are mainly associated with the absorption of BaP, BghiP, IcdP, FLU, BkF and BaA (see Fig. S3~~2~~). Compared to PAHs, NACs show the largest contribution in winter, followed by fall, spring and summer, and exhibit only one absorption peak at about 320 nm in spring and summer and at about 330 nm in fall and winter. The red shift in the absorption peak could be attributed to the increase of contributions from 4-nitrocatechol, 4-methyl-5nitrocatechol and 3-methyl-5-nitrocatechol which have absorption peak at about 330-350 nm (see Fig. S3~~2~~). Different from PAHs and NACs, MOPs contribute the most in winter, followed by spring, fall and summer, and only show one absorption peak at about 310 nm. The difference in light absorption contributions of different chromophores in different seasons reflects the difference in sources, emission strength and atmospheric formation processes.

The total contributions of PAHs, NACs and MOPs to the light absorption of methanol-soluble BrC ranged from 0.47% (summer) to 1.56% (winter) at the wavelength of 300-500 nm and ranged from 1.05% (summer) to 3.26% (winter) at the wavelength of 365 nm ~~ranged from 1.05% (summer) to 3.26% (winter)~~ (see Table 1). The average contribution of PAHs to the BrC light absorption at 365 nm was 0.97% in summer (the lowest) and 2.69% in fall (the highest), the contribution of NACs was 0.09% in summer and 0.82% in winter, and the contribution of MOPs was 0.006% in summer and 0.024% in winter. The low contributions of these measured chromophores to the light absorption of methanol-soluble BrC are consistent with previous studies. For example, Huang et al. (2018) measured 18 PAHs and their derivatives, which on average contributed ~1.7% of the overall absorption of methanol-soluble BrC in Xi'an. Mohr et al. (2013) estimated the contribution of five NACs to particulate BrC light absorption at 370 nm to be ~4% in Detling, UK. Zhang et al. (2013) measured eight NACs, which accounted for ~4% of water-soluble BrC absorption at 365 nm in Los Angeles. Teich et al. (2017) determined eight NACs during six campaigns at five locations in summer and winter, and founded that the mean contribution of NACs to water-soluble BrC absorption at 370 nm ranged from 0.10% to 1.25% under acidic conditions and from 0.13% to 3.71% under alkaline conditions. Slightly different from these previous studies, we investigated the contributions of three groups of chromophores with different light-absorbing properties to the light absorption of BrC, and provided further understanding in the relationships between optical properties and chemical composition of BrC in the atmosphere. For example, vanillin, which has negligible contribution to BrC light absorption at 365 nm, can produce secondary BrC through oxidation and thus enhance the light absorption by a factor of 5-7 (Li et al., 2014; Smith et al., 2016). The contribution of PAHs to the light absorption of methanol-soluble BrC at 365 nm was 5-13 times that of their mass fraction of carbon in OC, 6-9 times for NACs, and 0.4-0.7 times for MOPs (4-8 times at 310 nm for MOPs). These results further demonstrate that even a small amount of chromophores can have a disproportionately high impact on the light absorption properties of BrC, and that the light absorption of BrC is likely determined by a number of chromophores with strong light absorption ability (Kampf et al., 2012; Teich et al., 2017). Of note, a large fraction of BrC chromophores are still not identified so far, and more studies are therefore necessary to better understand the BrC chemistry. Based on laboratory and ambient studies, imidazoles (Kampf et al., 2012; Teich et al., 2016), quinones (Lee et al., 2014; Pillar et al., 2017), nitrogenous PAHs (Lin et al., 2016; Lin et al., 2018), polyphenols (Lin et al., 2016; Pillar et al., 2017) and oligomers with higher conjugation (Lin et al., 2014; Lavi et al., 2017) could be included in future studies.

3.3 Sources of BrC

Two approaches have been used to quantify the sources of BrC, including multiple linear regression and receptor models such as PMF. For example, Washenfelder et al. (2015) utilized multiple linear regression to determine the contribution of individual OA factors resolved by PMF to OA light absorption in the southeastern America. Moschos et al. (2018) combined the time series of PMF-resolved OA factors with the time series of light absorption of water-soluble OA extract as model inputs to quantify the sources of BrC in Magadino and Zurich, Switzerland. Xie et al. (2019) quantified the sources of BrC in southeastern America using Abs_{365}, elemental carbon (EC), OC, WSOC, isoprene sulfate ester, monoterpene sulfate ester, levoglucosan and isoprene SOA tracers as PMF model inputs. However, it should be noted that previous studies mainly rely on the correlation between measured light absorption and organic tracers that do not contain a BrC chromophore, and therefore may lead to bias in BrC source apportionment. To better constrain the sources of BrC (i.e., contribution to $Abs_{365,MSOC}$), we used BrC chromophores as PMF model inputs. The inputs include vanillic acid, vanillin, and syringyl acetone for BrC from biomass burning, and FLU, PYR, CHR, BaA, BaP, BbF, BkF, IcdP, BghiP, ~~9,10AQ, BEN, and BbF11O~~ for BrC from incomplete combustion and other light absorbing chromophores 9,10AQ, BEN, and BbF11O. In addition, we included commonly used markers~~non-light absorbing~~ levoglucosan for biomass burning, phthalic acid for secondary BrC, hopanes for vehicle emission and picene for coal burning in the model inputs.

Four factors were resolved, including vehicle emission, coal burning, biomass burning and secondary formation. The uncertainties for PMF analysis are < 10% for secondary formation and biomass burning, < 15% for vehicle emission and coal burning. The profile of each factor is shown in Fig. S4~~3~~. The first factor is characterized by a high contribution of phthalic acid, a tracer of secondary formation of OA. The second factor is dominated by hopanes, mainly from vehicular emissions. The third factor is characterized by high contributions of PI, BaP, BbF, BkF, IcdP, BghiP, mainly from coal combustion emissions, while the fourth factor has high contributions of levoglucosan, vanillic acid, vanillin, syringyl acetone from biomass burning emissions. The seasonal difference in relative contribution of each factor to BrC light absorption is shown in Fig. 5. In spring, vehicular emissions (34%) and secondary formation (37%) were the main contributors to BrC and coal combustion also had a relatively large contribution (29%). In summer, secondary formation constituted the largest fraction (~60%), mainly due to enhanced photochemical formation of secondary BrC. In fall, vehicular emissions (38%), coal combustion (29%) and biomass burning (22%) all had significant contributions to BrC. In winter, coal combustion (44%) and biomass burning (36%) were the main contributors, due to emissions from residential biomass burning (wood and crop residues) and coal combustion for heating. In terms of absolute contributions to absorption of MSOC at 365 nm (see Table S4), secondary formation contributed 1.75, 2.55, 1.70, 6.20 M m^{-1} in spring, summer, fall and winter, respectively. The high contribution in winter can be attributed to abundant precursors (volatile organic compounds) co-emitted with other primary sources (especially coal burning and biomass burning), while the high contribution in summer might be due to strong photochemical activity. For spring and fall, the absolute contributions from secondary formation were very similar, indicating moderate precursor emission and moderate photochemical activity. Also it should be noted that the absolute contributions of vehicle emission to absorption of MSOC at 365 nm were still higher in spring and fall than those in summer and winter, yet these differences by a factor of 2-9 are still less pronounced than the differences (spring/fall vs. winter) for other primary emissions (> 40 times for coal burning and > 25 times for biomass burning). In particular, the high vehicle contribution in fall might be affected by high relative humidity in fall (83% in fall vs. 61-69% in other seasons, on average) resulting in high vehicular $PM_{2.5}$ emissions (Chio et al., 2010). Such large seasonal difference in emission sources and atmospheric processes of BrC indicates that more studies are required to better understand the relationship between chemical composition, formation processes, and light absorption properties of BrC.

4 Conclusion

The light absorption properties of water- and methanol-soluble BrC in different seasons were investigated in Xi'an. The light absorption coefficient of methanol-soluble BrC was approximately 2 times higher than that of water-soluble BrC at 365 nm, and had an average MAE_{365} value of 1.27 ± 0.46 m^2 gC^{-1}. The average MAE_{365} value of water-soluble BrC was 1.19

± 0.51 m^2 gC^{-1}, which is comparable to those in previous studies at urban sites but higher than those in rural and remote areas. The seasonally averaged AAE values of water-soluble BrC ranged from 5.32 to 6.15, which are higher than those of methanol-soluble BrC (between 4.45 and 5.18). In combination with previous studies, we found that AAE values of water-soluble BrC were much lower in urban regions than those in rural and remote regions. The difference of optical properties of BrC in different regions could be attributed to the difference in sources and chemical composition of BrC chromophores. The contributions of 12 PAHs, 10 NACs and 3 MOPs to the light absorption of methanol-soluble BrC were determined and showed large seasonal variations. Specifically, the total contribution to methanol-soluble BrC light absorption at 365 nm ranged from 1.1% to 3.3%, which is 5-7 times higher than their carbon mass fractions in total OC. This result indicates that the light absorption of BrC is likely determined by an amount of chromophores with strong light absorption ability. Four major sources of methanol-soluble BrC were identified, including secondary formation, vehicle emission, coal combustion and biomass burning. On average, secondary formation and vehicular emission were the main contributors of BrC in spring (~70%). Vehicular emission (38%), coal burning (29%) and biomass burning (22%) all contributed significantly to BrC in fall. Coal combustion and biomass burning were the major contributors in winter (~80%), and secondary formation was the predominant source in summer (~60%). The large variations of BrC sources in different seasons suggest that more studies are needed to understand the seasonal difference in chemical composition, formation processes, and light absorption properties of BrC, as well as their relationships.

5 Abbreviations of organics

PAHs (Polycyclic Aromatic Hydrocarbons)

BaA	Benzo(a)anthracene
BaP	Benzo(a)pyrene
BbF	Benzo(b)fluoranthene
BbF11O	Benzo[b]fluoren-11-One
BEN	Benzanthrone

BghiP	Benzo(ghi)perylene
BkF	Benzo(k)fluoranthene
CHR	Chrysene
FLU	Fluoranthene
IcdP	Indeno[1,2,3-cd]pyrene
PYR	Pyrene
9,10AQ	9,10-Anthracenequinone
NACs (Nitrated Aromatic Compounds)	
2M4NP	2-Methyl-4-Nitrophenol
2,6DM4NP	2,6-Dimethyl-4-Nitropheol
3M4NP	3-Methyl-4-Nitrophenol
3M5NC	3-Methyl-5-Nitrocatechol
3NSA	3-Nitrosalicylic Acid
4M5NC	4-Methyl-5-Nitrocatechol
4NC	4-Nitrocatechol
4NP	4-Nitrophenol
4N1N	4-Nitro-1-Naphthol
5NSA	5-Nitrosalicylic Acid
MOP (Methoxyphenols)	
SyA	Syringyl Acetone
VaA	Vanillic Acid
VAN	Vanillin
Hopanes	
HP1	17α(H),21β(H)-30-Norhopane
HP2	17α(H),21β(H)-Hopane
HP3	17α(H),21β(H)-(22S)-Homohopane
HP4	17α(H),21β(H)-(22R)-Homohopane

Data availability. Raw data used in this study are archived at the Institute of Earth Environment, Chinese Academy of Sciences, and are available on request by contacting the corresponding author.

Supplement. The Supplement related to this article is available online at

Author contributions. RJH designed the study. Data analysis was done by WY, LY, and RJH. WY, LY and RJH interpreted data, prepared the display items and wrote the manuscript. All authors commented on and discussed the manuscript.

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Table 1. Annual and seasonal mean contributions of measured PAHs, NACs and MOPs to methanol-soluble BrC light absorption at 365 nm. Hyphens denote the measured value of more than one third of the samples is below the detection limit.

Compounds	MAE_{365}	Contribution to BrC light absorption at 365 nm (%)				
	(m^2 gC^{-1})	Annual	Spring	Summer	Fall	Winter
Fluoranthene (FLU)	4.25	0.11	0.05	0.02	0.05	0.15
Pyrene (PYR)	0.46	0.01	0.00	0.00	0.01	0.01
Chrysene (CHR)	0.00	0.00	0.00	0.00	0.00	0.00
Benzo(a)anthracene (BaA)	2.06	0.04	0.01	0.01	0.02	0.05
Benzo(a)pyrene (BaP)	9.31	1.04	0.76	0.39	1.16	1.10
Benzo(b)fluoranthene (BbF)	4.10	0.17	0.14	0.07	0.17	0.18
Benzo(k)fluoranthene (BkF)	3.47	0.04	0.03	0.02	0.04	0.04
Indeno[1,2,3-cd]pyrene (IcdP)	4.68	0.51	0.50	0.24	0.71	0.46
Benzo(ghi)perylene (BghiP)	8.95	0.29	0.28	0.16	0.41	0.26
9,10-Anthracenequinone (9,10AQ)	0.28	0.01	0.00	0.00	0.00	0.01
Benzanthrone (BEN)	6.13	0.11	0.08	0.05	0.11	0.12
Benzo[b]fluoren-11-one (BbF11O)	1.89	0.02	0.02	0.01	0.02	0.03
4-Nitrophenol (4NP)	2.17	0.08	0.06	0.02	0.05	0.10
4-Nitro-1-naphthol (4N1N)	9.71	-	-	-	-	0.03
2-Methyl-4-nitrophenol (2M4NP)	2.81	0.03	0.01	0.01	0.01	0.04
3-Methyl-4-nitrophenol (3M4NP)	2.65	0.02	0.01	0.00	0.01	0.03
2,6-Dimethyl-4-nitrophenol (2,6DM4NP)	3.27	-	-	-	-	0.01
4-Nitrocatechol (4NC)	7.91	0.27	0.05	0.03	0.20	0.35
3-Methyl-5-nitrocatechol (3M5NC)	5.77	-	-	-	0.05	0.11
4-Methyl-5-nitrocatechol (4M5NC)	7.29	-	-	-	0.06	0.13
3-Nitrosalicylicacid (3NSA)	3.86	-	-	-	-	0.01
5-Nitrosalicylicacid (5NSA)	3.36	0.03	0.01	0.02	0.04	0.02
Syringyl acetone (SyA)	0.25	0.01	0.01	0.00	0.01	0.01
Vanillin (VAN)	8.17	0.01	0.00	0.00	0.00	0.01
Vanillic acid (VaA)	0.66	0.00	0.00	0.00	0.00	0.00
Total	103.46	2.80	2.02	1.05	3.13	3.26

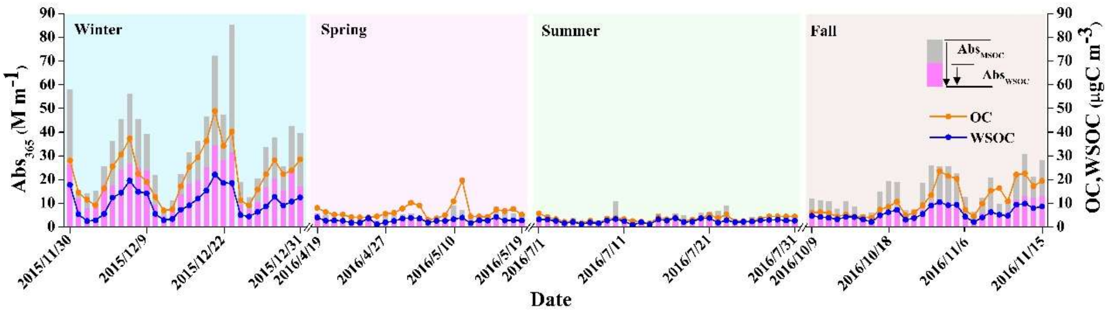


Figure 1. Time series of the light absorption coefficient of water-soluble and methanol-soluble BrC at 365 nm ($Abs_{365,WSOC}$ and $Abs_{365,\ MSOC}$, respectively), as well as OC and WSOC concentrations.

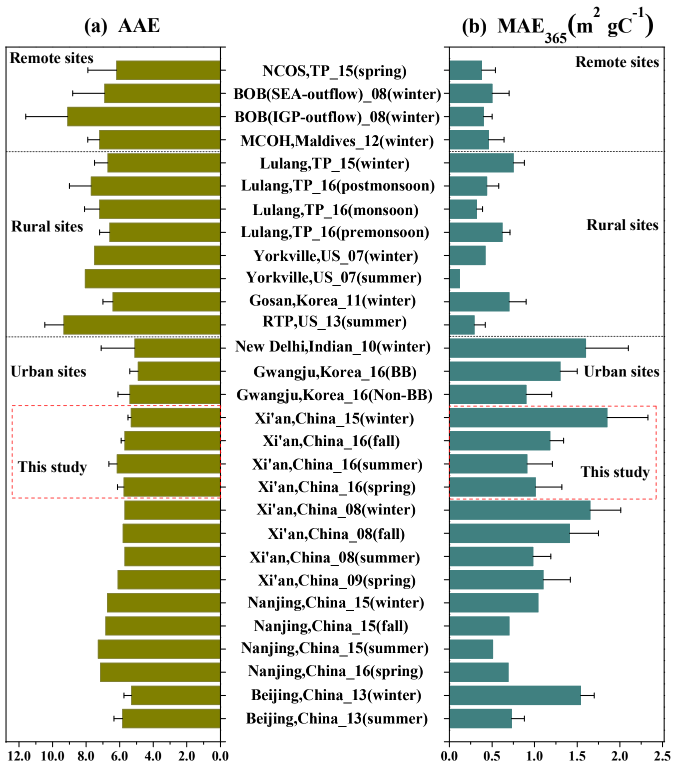


Figure 2. Comparison of AAE (left column) and MAE365 (right column) values of water-soluble BrC at remote sites (Srinivas and Sarin, 2013; Bosch et al., 2014; Zhang et al., 2017b), rural sites (Hocobian et al., 2010; Kirillova et al., 2014a; Zhu et al., 2018; Xie et al., 2019) and urban sites (Kirillova et al., 2014b; Yan et al., 2015; Chen et al., 2018; Huang et al., 2018; Park et al., 2018).

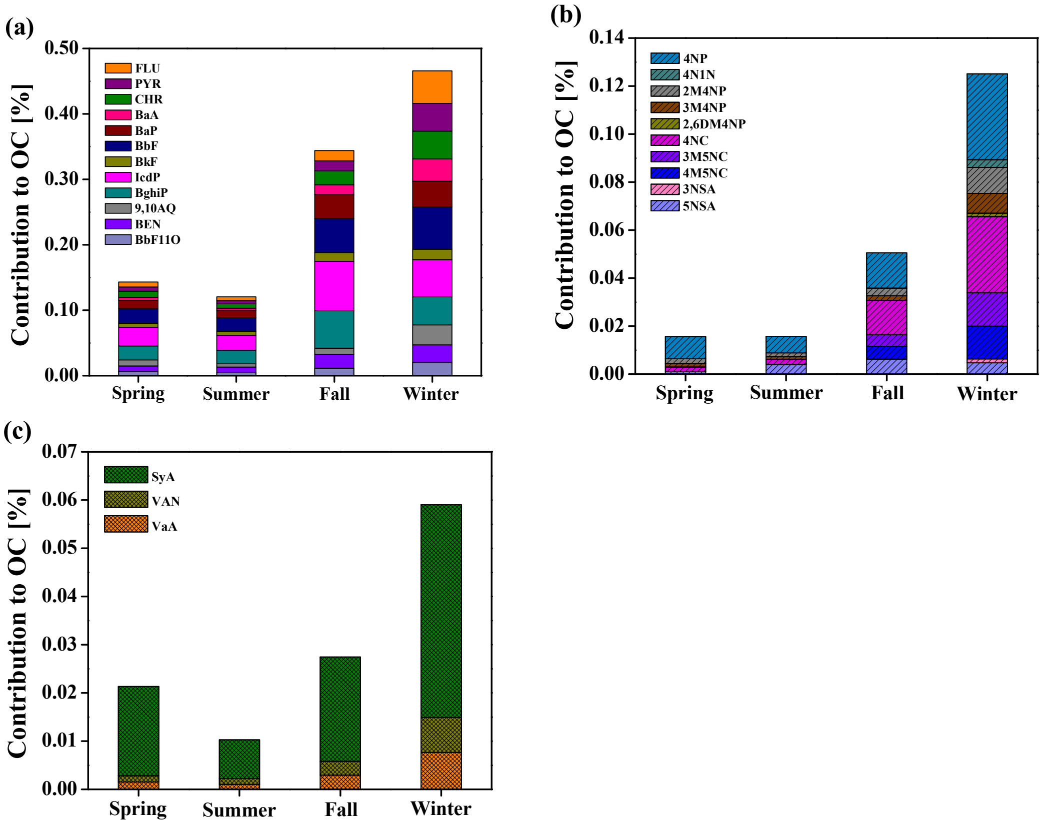
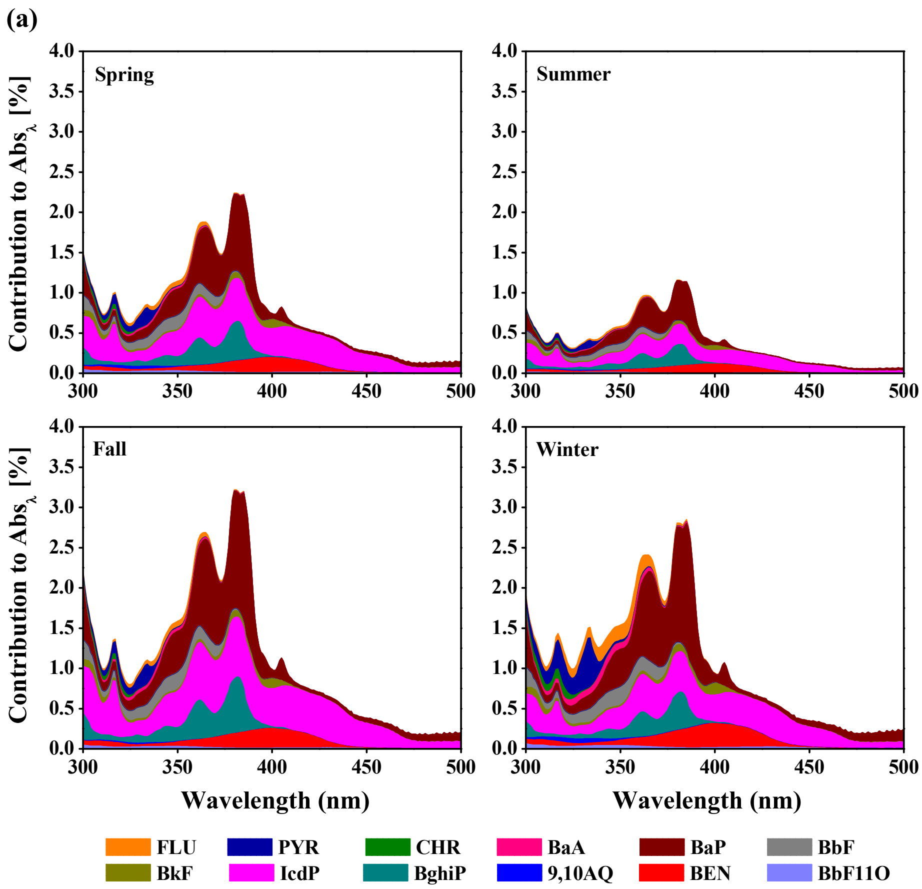
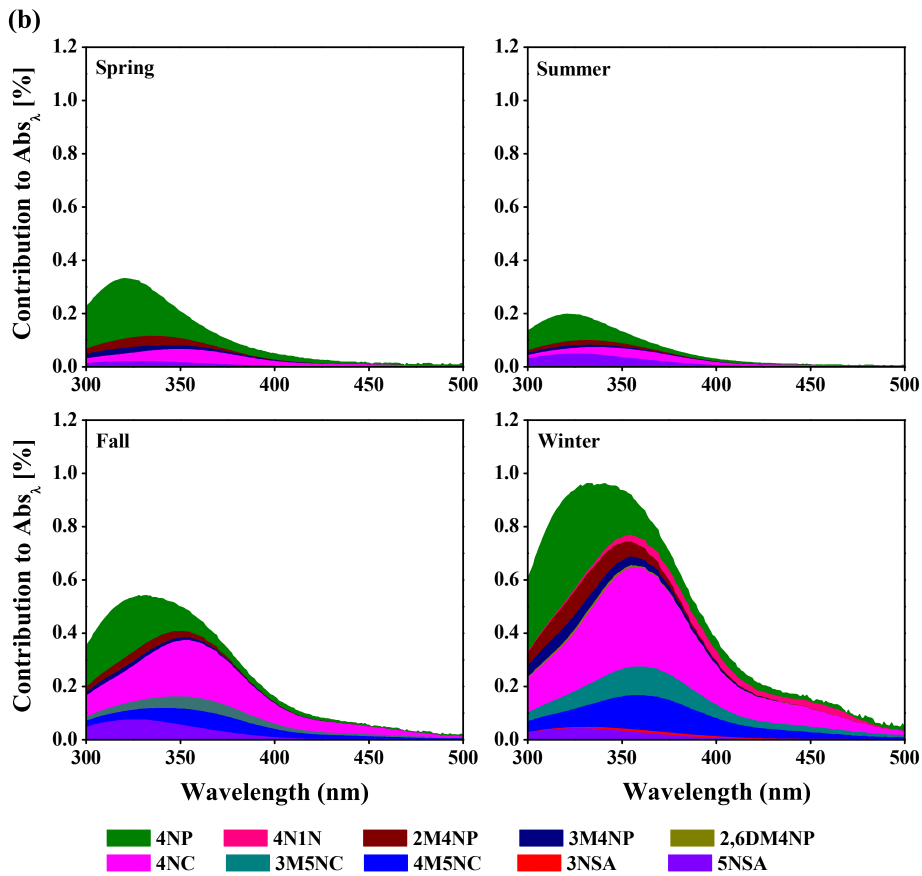


Figure 3. Contributions of (a) PAHs, (b) NACs, and (c) MOPs carbon mass concentrations to the total OC concentrations.


(a)
Spring
Summer
Fall
Winter
Contribution to Abs$_\lambda$ [%]
Wavelength (nm)
FLU
PYR
CHR
BaA
BaP
BbF
BkF
IcdP
BghiP
9,10AQ
BEN
BbF11O


(b)
Spring
Summer
Fall
Winter
Contribution to Abs$_\lambda$ [%]
Wavelength (nm)
4NP
4N1N
2M4NP
3M4NP
2,6DM4NP
4NC
3M5NC
4M5NC
3NSA
5NSA

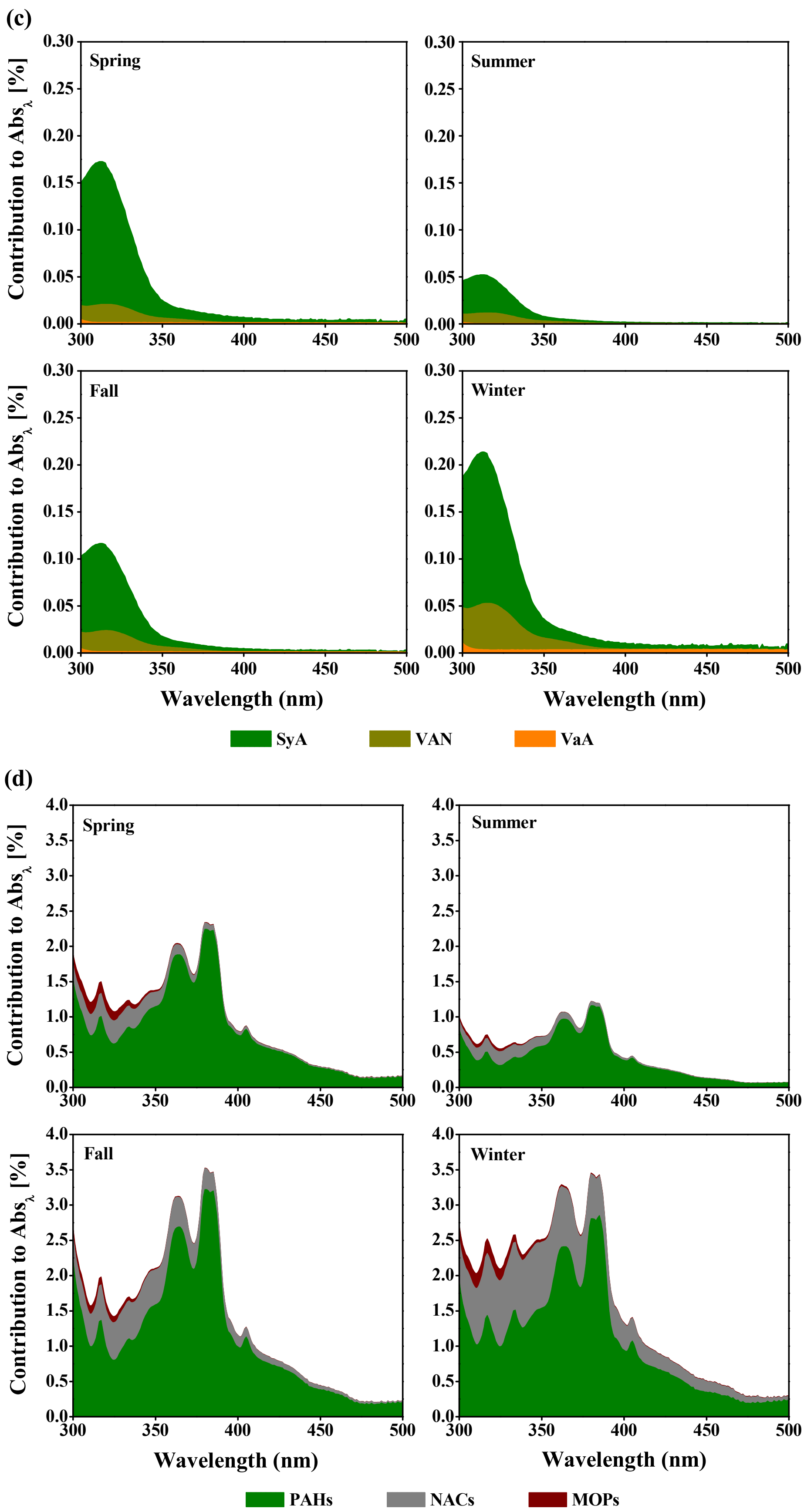


Figure 4. Light absorption contributions of (a) PAHs, (b) NACs, (c) MOPs and (d) total

measured chromophores to Abs_{MSOC} over the wavelength range of 300 to 500 nm in spring, summer, fall and winter.

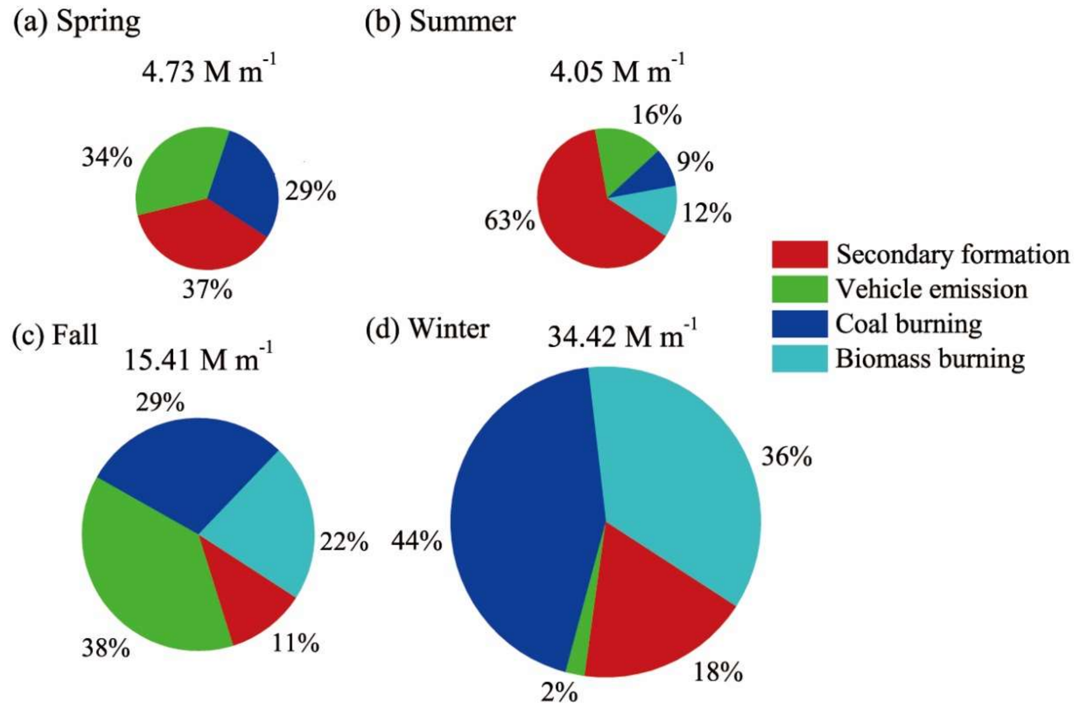


Figure 5. Contributions of the major sources to $Abs_{365,MSOC}$ in Xi'an during spring, summer, fall and winter.