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Title: Optical properties and molecular compositions of water-soluble and water-insoluble brown carbon (BrC) aerosols in Northwest China
Author(s): Jianjun Li et al.
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Dear Editor,

After reading the comments from the two referees, we have carefully revised our manuscript. Our response to the comments and related revisions are attached with this letter.

Anything about our paper, please feel free to contact me at dkwzhang@ucdavis.edu.

Best regards,

Sincerely yours

Qi Zhang

Mar. 18, 2020

Anonymous Referee #2

This paper presents measurements of water soluble and insoluble brown carbon (BrC) in different seasons in Guangzhong Basin in China. The possible sources and radiative effects of BrC are also discusses. The paper is well written and within the scope of ACP. I would recommend the publication of this manuscript in ACP if the comments below are well addressed.

Response: We thank the referee's comments, which are very helpful for us to improve our work. Detailed revision and response to the comments are list below.

Specific comments:

L148: delete "and"

Response: Suggestion taken. Please see Line 150.

L171: Can the author give an estimate of the bias of MAC_{ λ _,WI-BrC} in your measurement. It would be also good to provide measurement uncertainties of other derived parameters.

Response: We thank the referee's suggestion. We added the uncertainties of $Abs_{\lambda,WI\text{-}BrC}$ and $MAC_{\lambda,WI\text{-}BrC}$ in the revised manuscript. (Please see Line 173-174)

L192: Can the author give some details of why 1.3 was used?

Response: We thank the referee's suggestion. More details were provided in Line 196-205.

L203: how do these numbers compare with the measurement in other polluted regions (e.g. NCP, PRD and YRD) in China?

Response: We thank the referee's comment. We added a comparison of AAE value measured in this study with those in typical cities in NCP, PRD and YRD, please see Line 222-224.

L219: Since there is a tip at 360 and definitely influences 365, maybe it is better to use another wavelength for reporting abs?

Response: We do agree with the referee's comment. So we added an table (Table S1) to compare the Abs and MAC in wavelength of 340-380 nm. We found that the influence of the tip seems insignificant on the average Abs_{365} or MAC_{365}. Thus, in order to be consistence with previous studies, we still use 365 nm for reporting Abs and MAC, and gave a detailed explanation at Line 251-254.

L221: I would not call it "significant higher"

Response: Suggestion taken. We revised to "much higher" in Line 266.

L236: Since your site represents reginal background conditions (is it?), how these

numbers compare with other reginal background measurements?
Response: We thank the referee's comment. We added a comparison with some data reported in other regional or background sites in China, please see Line 260-262 and Table 2.

L311-315: Why is levoglucosan concentration much higher in daytime than in nighttime in summer? Abs_{365,WI-BrC} shows higher R2 with levoglucosan concentration. Does it mean POA from biomass burning is also an important contributor to BrC in daytime in summer? I think based only on the correlations, it is difficult to judge if primary emission or photochemical formation is more important.
Response: We thank the referee's comment. Yes, the concentration of levoglucosan is also higher in daytime than in nighttime in summer due to enhanced emission from BB for domestic cooking. As described in Line 303-305, "$Abs_{365,WI\text{-}BrC}$ in both summer and winter correlate well with levoglusocan (r^2=0.74 and 0.62, respectively), demonstrating an important contribution of biomass burning to WI-BrC…". However, we cannot quantitively judge if primary emission or photochemical formation is more important for WI-BrC in summer. Thus in "Conclusion", we concluded that "These results demonstrated that photochemical formation of BrC and enhanced BB emissions (e.g., from cooking) contributed to the higher daytime MACs in summer" (Line 495-497). Moreover, to avoid the confusion, we also revised the sentence "This difference was mainly attributed to enhanced photochemical formation of WI-BrC species, such as oxygenated polycyclic aromatic hydrocarbons (OPAHs)" in the Abstract to " This difference was partly attributed to enhanced photochemical formation of WI-BrC species, such as oxygenated polycyclic aromatic hydrocarbons (OPAHs)" (Line 42-43).

L398: Correlations with RH, sulfate and NO_2 do not necessarily mean that aqueous oxidation has played a role in the formation of WS-BrC. We can see WI-BrC shows the same trend during the period. During haze event, the stagnant meteorological condition with low wind speed promotes the accumulation of BrC no matter how it is produced.
Response: We thank the referee's comment. Indeed, the correlations of $Abs_{365,WS\text{-}BrC}$ with RH, sulfate and NO_2 are not necessarily to prove the aqueous formation of WS-BrC. However, we have more evidence for this. Firstly, the temporal variation of $Abs_{365,WI\text{-}BrC}$ and $Abs_{365,WS\text{-}BrC}$ is actually different. $Abs_{365,WS\text{-}BrC}$ increases continuously during the haze period, whereas $Abs_{365,WI\text{-}BrC}$ presents obvious diurnal variation (Figure 1). Secondly, the relationship of RH, sulfate and NO_2 with $Abs_{365,WS\text{-}BrC}$ are much stronger than those with $Abs_{365,WI\text{-}BrC}$, but levoglucosan and PAHs have stronger correlation with $Abs_{365,WI\text{-}BrC}$. These results suggested that $Abs_{365,WI\text{-}BrC}$ were more related with primary emissions, but aqueous oxidation was an important source for WS-BrC. In addition, in our previous study in Xi'an (~40 km away from the sampling site in this study), we further analyzed the stable carbon isotope composition and also found a secondary formation of BrC in winter (Wu et al., 2020). Thus, we confirmed that aqueous oxidation has played a role in the

formation of WS-BrC. More detailed description also added in the manuscript, please see Line 423-430.

Figure 2e and f not mentioned in the text.
Response: We thank the referee's reminder. Figure 2e and f were deleted in the revised manuscript.

Reference

Wu, C., Wang, G., Li, J., Li, J., Cao, C., Ge, S., Xie, Y., Chen, J., Li, X., Xue, G., Wang, X., Zhao, Z., and Cao, F.: The characteristics of atmospheric brown carbon in Xi'an, inland China: sources, size distributions and optical properties, Atmos. Chem. Phys., 20, 2017-2030, 10.5194/acp-20-2017-2020, 2020.

Anonymous Referee #3

In this work, the authors examined the absorption properties and molecular compositions of water-soluble and –insoluble PM2.5 brown carbon from a rural site in China. Seasonal variation, day time vs night time, as well as water-soluble vs water-insoluble of absorbance and MAC values of particles were discussed. Their results showed the contribution of photochemical formation of brown carbon and biomass burning emissions to higher daytime MACs in summer in the region. They also suggest the important role of aqueous-phase reactions and nitrated aromatic compounds in the formation of secondary brown carbon. Overall, the authors have done a great job in analyzing and discussing their data. The work is also well presented. I recommend acceptance.

Response: We thank the referee's comments.

Specific comments:

1) Line 120 should it be "_8am to 8pm"?
Response: Suggestion taken. Please see Line 121.

2) Section 2.4 please indicate where to subtract the signal from blanks in your calculations.
Response: We thank the referee's comment. We added the information at Line 163-164.

3) Line 170 what is M in Eq. 3?
Response: We thank the referee's comment. We added an explanation about M in Eq. 3, please see 172.

4) Line 222 "Abs_{365} of WS-BrC is significantly higher than WI-BrC in summer, but values are comparable in winter". However, Figure 2 shows Abs_{365} of WI-BrC is higher than WS-BrC in winter. Please explain.
Response: We thank the referee's comment. The averaged value of Abs_{365} of WI-BrC and WS-BrC in winter were 19.6±8.3 Mm^{-1} and 21.9±13.5 Mm^{-1}, respectively. So we revised the sentence as "On average, $Abs_{365,WS-BrC}$ is significantly higher than $Abs_{365,WI-BrC}$ in summer (5.00±1.28 Mm^{-1} vs. 2.95±1.94 Mm^{-1}), but the values vary slightly in winter (19.6±8.3 Mm^{-1} vs. 21.9±13.5 Mm^{-1})" (Line 240-242).

5) Line 405 an increase of MAC_{365} during New Year's Eve was observed but an increase of Abs_{365} or PM mass or WSOC was NOT observed. Please explain.
Response: We thank the referee's comment. The increase of Abs_{365} or PM mass or WSOC was NOT observed because the metrological condition were favoring for pollutants dispersion (Figure 1). Thus, we provided more detailed explanation at Line 436-440.

Optical properties and molecular compositions of water-soluble and water-insoluble brown carbon (BrC) aerosols in Northwest China

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Abstract

Brown carbon (BrC) contributes significantly to aerosol light absorption, thus can affect the earth's radiation balance and atmospheric photochemical processes. In this study, we examined the light absorption properties and molecular compositions of water-soluble (WS-BrC) and water-insoluble (WI-BrC) BrC in $PM_{2.5}$ collected from a rural site in the Guanzhong Basin – a highly polluted region in Northwest China. Both WS-BrC and WI-BrC showed elevated light absorption coefficients (Abs) in winter (4-7 times of those in summer) mainly attributed to enhanced emissions from residential biomass burning (BB) for house heating. While the average mass absorption coefficients at 365 nm (MAC_{365}) of WS-BrC were similar between daytime and nighttime in summer (0.99±0.17 and 1.01±0.18 $m^2\ g^{-1}$, respectively), the average MAC_{365} of WI-BrC was more than a factor of 2 higher during daytime (2.45±1.14 $m^2\ g^{-1}$) than at night (1.18±0.36 $m^2\ g^{-1}$). This difference was ~~mainly~~ partly attributed to enhanced photochemical formation of WI-BrC species, such as oxygenated polycyclic aromatic hydrocarbons (OPAHs). In contrast, the MACs of WS-BrC and WI-BrC were generally similar in winter and both showed little diel differences. The Abs of wintertime WS-BrC correlated strongly with relative humidity, sulfate, and NO_2, suggesting that aqueous-phase reaction~~s~~ is an important pathway for secondary BrC formation during the winter season in Northwest China. Nitrophenols on average contributed 2.44±1.78% of the Abs of WS-BrC in winter, but only 0.12±0.03% in summer due to faster photodegradation reactions. WS-BrC and WI-BrC were estimated to account for 0.83±0.23% and 0.53±0.33%, respectively, of the total down-welling solar radiation in the UV range in summer, and 1.67±0.72% and 2.07±1.24%, respectively, in winter. The total absorption by BrC in the UV region was about 55-79% relative to the elemental carbon (EC) absorption.

53 Keywords: Brown Carbon (BrC); Organic Aerosol; Optical Property; Molecular Composition

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1. Introduction

Light-absorbing organic matter, termed as “brown carbon (BrC)”, has been recognized as an important climate forcer due to its ability to directly interact with both incoming solar radiation and outgoing terrestrial radiation (Andreae and Gelencser, 2006;Laskin et al., 2015). BrC is a complex mixture of organic compounds, which collectively show a light absorption profile increasing exponentially from the visible (Vis) to the ultraviolet (UV) range. Due to the high abundance of organic aerosol in continental regions, especially in places with intensive anthropogenic pollution, the contribution of BrC to aerosol absorption in the near-UV range is potentially significant (Kirillova et al., 2014b;Huang et al., 2018;Yan et al., 2015a). For example, a model study showed that BrC contributes up to +0.25 W m^{-2} of radiative forcing on a planetary scale, which is approximately 19% of the absorption by anthropogenic aerosols (Feng et al., 2013). Moreover, the strong absorption of BrC in the UV spectral region can reduce the solar actinic flux, and subsequently affect atmospheric photochemistry and tropospheric ozone production (Jacobson, 1998;Mohr et al., 2013).

A thorough understanding of the sources and transformation processes of BrC in the atmosphere is important, but it is still lacking. Biomass/biofuel combustion, including forest fires, and burning of wood and agricultural wastes for residential cooking and heating, has been shown as a particularly important source of BrC (Washenfelder et al., 2015;Desyaterik et al., 2013;Lin et al., 2017). BrC can also be emitted directly from coal burning (Yan et al., 2017), and biogenic release of fungi, plant debris, and humic matter (Rizzo et al., 2013;Rizzo et al., 2011). In addition, recent studies suggested that secondary BrC can be formed through various reaction pathways, including photooxidation of aromatic volatile organic compounds (VOCs) (Lin et al., 2015;Liu et

al., 2016), reactive uptake of isoprene epoxydiols onto preexisting sulfate aerosols (Lin et al., 2014), aqueous oxidation of phenolic compounds and α-dicarbonyls (Chang and Thompson, 2010;Nozière and Esteve, 2005;Smith et al., 2016;Yu et al., 2014;Xu et al., 2018), and reactions of ammonia or amines with carbonyl compounds in particles or cloud droplets (Nozière et al., 2007;Laskin et al., 2010;Updyke et al., 2012;Nguyen et al., 2012;De Haan et al., 2018;Powelson et al., 2014). However, atmospheric oxidation processes may also cause "photobleach" – photodegradation of BrC into less light-absorbing compounds (Lee et al., 2014;Romonosky et al., 2015;Sumlin et al., 2017), which may complicate the understanding of BrC in the atmosphere.

A common way to quantify the absorption properties of BrC is to measure the absorbance of aerosol extracts over a wide wavelength range using spectrophotometers. This approach can differentiate the interference of black carbon (BC) or mineral dust (Hecobian et al., 2010). Most of the studies use ultrapure water to extract organic substance in the aerosol, and thus measure the optical properties of water-soluble BrC (WS-BrC) (Wu et al., 2019;Hecobian et al., 2010;Kirillova et al., 2014b). In addition, some studies analyzed the light absorption of BrC extracted using polar organic solvents such as methanol or acetone (Liu et al., 2013;Huang et al., 2018;Kim et al., 2016). Since such extracts contain both water-soluble and water-insoluble chromophores, little information is available regarding the contribution and formation of water-insoluble BrC (WI-BrC). However, it is important to understand WI-BrC given the facts that some water-insoluble organic compounds, such as polycyclic aromatic hydrocarbons and their derivatives, are effective light absorbers and that the mass absorption of WI-BrC could be even greater than that of the water-soluble fraction (Chen and Bond, 2010;Huang et al., 2018;Sengupta et al., 2018). Thus, it is necessary to extract water-soluble and water-insoluble organic components separately, e.g., via

using solvents with different polarity in sequence. Combining with measurements of BrC molecular compositions, the UV-vis absorption properties of the water-soluble and water-insoluble extracts may help us better understand the sources and formation mechanisms of light-absorbing compounds in the atmosphere.

China has been experiencing serious atmospheric pollution conditions in recent decades, and both model and field results showed elevated light absorption of BrC in most regions of China (Huang et al., 2018;Cheng et al., 2011;Yan et al., 2017;Li et al., 2016b) compared to developed countries such as the U.S. (Hecobian et al., 2010;Washenfelder et al., 2015) and European countries (Mohr et al., 2013;Teich et al., 2017). However, BrC-related data are scarce in the Guanzhong Basin (Shen et al., 2017;Huang et al., 2018), which is one of the most polluted regions in China (van Donkelaar et al., 2010). Here we present measurements of the optical properties of WS-BrC and WI-BrC in $PM_{2.5}$ collected from a rural area of the Guanzhong Basin during winter and summer seasons. We also measured the concentrations of several BrC compounds as well as those of organic carbon (OC), elemental carbon (EC), water-soluble OC (WSOC) and inorganic ions. These data were analyzed to examine the effects of sources emissions, daytime photochemical oxidation, and aqueous-phase chemistry on WS- and WI-BrC components in different seasons.

2. Experimental section

2.1 Sample collection

The sampling was conducted at a small village (namely Lincun, 34º44′ N and 109º32′E, 354m a.s.l.) ~ 40 km northeast to Xi'an, the capital of Shaanxi Province (Figure S1). The sampling site is located in the central part of Guanzhong Basin with no obvious point source of air pollutants in

the surrounding areas. $PM_{2.5}$ samples were collected twice a day (~8 am to ~~20~~ 8 pm and ~~20~~ 8 pm to 8 am) onto prebaked (450 °C, 6-8 hr) quartz fiber filters (Whatman, QM-A, USA) during Aug. 3-23, 2016 and Jan. 20-Feb. 1, 2017 using a TISCH Environmental (USA) $PM_{2.5}$ high volume (1.13 m^3 min^{-1}) sampler. Field blank samples were also collected by mounting blank filters onto the sampler for about 15 min without pumping any air. After sampling, the sample filters were immediately sealed in aluminum foil bags, and then stored in a freezer (−5 °C) prior to analysis. Meteorological conditions, and concentrations of O_3 and NO_2 during this studied period are presented in Figure 1.

2.2 Filter extraction and absorption spectra analysis

For each $PM_{2.5}$ sample, a portion of the filter (~13.384 cm^2) was first extracted in 8 ml of Milli-Q water (18.2 MΩ) through 30 min of sonication at ~ 0°C. The water extract was then filtered via vacuum filtration with a 25mm diameter 5 μm pore hydrophobic PTFE membrane filter (Merck Millipore Ltd, Mitex™ Membrane Filters, USA). Afterwards, the insoluble PM components collected on the PTFE membrane filter and remained on the sample filter were rinsed with 2 ml Milli-Q water, air dried, and then extracted via sonication in 8 ml pure acetonitrile (ACN) (Honeywell Burdick & Jackson, LC/MS Grade, USA). The acetonitrile extract was filtered via a 13 mm diameter 0.45 μm pore syringe filter (PALL, Bulk Acrodisc®, PTFE Membrane Filters, USA). The light absorption spectra of the water and the acetonitrile extracts were measured between 190 nm to 820 nm by a diode-array spectrophotometer (Hewlett Packard 8452A, USA) using quartz cuvettes with 1 cm length path. Field blank filters were extracted and measured in the same manner as the samples. Data presented in this study were corrected for the field blanks (<10% relative to field samples).

2.3 Chemical Analysis

OC and EC were analyzed using DRI Carbon Analyzer (Model 2001, USA). Another piece of the filter sample (~8.6 cm^2) was extracted with Milli-Q water (18.2MΩ), and filtered through a PTFE syringe filter. Then the water-extract was analyzed for water-soluble inorganic ions (SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, F^-, Ca^{2+}, K^+, Na^+ and Mg^{2+}) using a Metrohm Ion Chromatography (Metrohm 940, Switzerland) and WSOC using a Shimadzu TOC analyzer (TOC-L CPH, Japan) and. Concentrations of individual molecules, including levoglucosan, parent-PAHs, Oxygenated-PAHs (OPAHs), nitrophenols, ~~and~~ isoprene and α-/β-pinene derived products, were measured using GC/EI-MS (Agilent 7890A-5975C, USA) calibrated by authentic standards. More details on these measurements can be found in previous publications (Li et al., 2014).

2.4 Data Interpretation

In this study, water-insoluble OC (WIOC) was calculated by the difference between OC and WSOC:

$$M_{WIOC} = M_{OC} - M_{WSOC} \qquad (1)$$

where M_{WIOC}, M_{OC}, and M_{WSOC} correspond to the mass concentration (in μgC m^{-3}) of WIOC, OC, and WSOC, respectively, in the air.

The absorption coefficient of WS-BrC ($Abs_{\lambda,WS\text{-}BrC}$, Mm^{-1}) or WI-BrC ($Abs_{\lambda,WI\text{-}BrC}$, Mm^{-1}) at a given wavelength (λ) is determined from the UV-vis spectrum of the water extract (Hecobian et al., 2010;Laskin et al., 2015)

$$Abs_\lambda = (A_\lambda - A_{700}) \times \frac{V_{solvent}}{V_a \times l} \times \ln(10) \times 100 \qquad (2)$$

where A_λ is the absorbance of the water ($A_{\lambda,WS\text{-}BrC}$) or ACN ($A_{\lambda,WI\text{-}BrC}$) extract at λ, which is corrected for the field blank~~,~~. $V_{solvent}$ (ml) is the volume of solvent (water or ACN) used to

extract the filter (8 mL), and Va (m^3) is the air volume passed through the filter punch. *l* (cm) is the optical length of the quartz cuvettes used for UV-vis measurement and ln(10) is used to convert the logbase-10 (provided by the spectrophotometer) to natural logarithm. 100 is for unit conversion. A_{700} (absorbance at the wavelength of 700 nm) is subtracted to minimize the interference of baseline shift. The mass absorption coefficient of WS-BrC ($MAC_{\lambda,WS\text{-}BrC}$, $m^2\ g^{-1}$) or WI-BrC ($MAC_{\lambda,WI\text{-}BrC}$, $m^2\ g^{-1}$) at wavelength of λ is calculated using eq (3)

$$MAC_\lambda = \frac{Abs_\lambda}{M} \qquad (3)$$

where M is the mass concentration of WSOC or WIOC. Note that since it is possible that not all the WI-BrC was extracted into ACN, the $Abs_{\lambda,WI\text{-}BrC}$ (estimated uncertainty is 32%) and $MAC_{\lambda,WI\text{-}BrC}$ (estimated uncertainty is 33%) reported in this study are likely the lower bound values. Nevertheless, the underestimation is probably insignificant since Chen and Bond (Chen and Bond, 2010) reported that >92% of BrC was extractable by organic solvents (methanol or acetone).

The wavelength dependence for BrC absorption is fit with a power law equation:

$$Abs_\lambda = K \times \lambda^{-AAE} \qquad (4)$$

where K is a constant and AAE stands for absorption Ångström exponent. In this study, the AAE for a given sample is calculated through the linear regression of log(Abs_λ) against log λ between 300−450 nm. This wavelength range is chosen because the fits of all the samples in this study are better than r^2=0.99. Note that slightly higher AAE values (by up to 10%) are obtained using a wider wavelength range (e.g., 300-550 nm; Figure S2).

The fraction of solar irradiance absorbed by particulate BrC at a given wavelength λ is estimated following the Beer−Lambert's law:

$$\frac{I_0 - I}{I_0}(\lambda) = 1 - e^{-b_{ap,\lambda,x} \times h_{ABL}} \quad (5)$$

where *x* denotes WS-BrC or WI-BrC, h_{ABL} is the atmospheric boundary layer height (assuming 1200 m in summer and 600 m in winter) according to the assumption that the ground measurement results are representative of the average values in the whole planetary~~atmospheric~~ boundary layer (~~ABL~~PBL) ~~(Kirchstetter et al., 2004;Kirillova et al., 2014a),~~ (Kirchstetter et al., 2004;Kirillova et al., 2014a). I_0 denotes the incident solar radiance in the form of either actinic flux (in quanta s^{-1} cm^{-2} nm^{-1}) or irradiance (in W m^{-2} nm^{-1}), which were obtained using the TUV Quick Calculator (http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/). (I_0-I) denotes the direct absorption of solar actinic flux or irradiance by BrC.~~and~~ $b_{ap,\lambda,x}$ corresponds to the absorption coefficient ($b_{ap,}$ m^{-1}) of WS-BrC or WI-BrC at wavelength of λ. –The absorption properties of BrC extracted by bulk solution may not entirely reflect the light absorption by ambient aerosols. However, an estimated conversion factor can be calculated from the light absorption of size-resolved samples using the Mie theory. Assuming that particles are of spherical morphology and externally mixed with other light-absorbing components, an imaginary refractive index (*k*, responsible for absorption) could be obtained from MAC using follow equation (Laskin et al., 2015):

$$k_{(\lambda)} = \frac{\rho \times \lambda \times Abs_\lambda}{4\pi \times M_{WSOC}} = \frac{\rho \times \lambda \times MAC_\lambda}{4\pi} \quad (6)$$

where ρ (g/cm3) was particle density and assigned as 1.5, and more details about Mie theory calculations can be referred to the study by Liu et al. (2013). Previous studies showed that the light absorption coefficient of particulate BrC ($b_{ap,\lambda,BrC}$) is around 0.7−2.0 times of that from bulk solution ($Abs_{\lambda,WS\text{-}BrC\ or\ WI\text{-}BrC}$) (Liu et al., 2013;Sun et al., 2007). Here, a conversion factor of 1.3 is applied based on a Mie theory calculation of aerosols in Xi'an (~ 40 km away from the sampling

site) (Wu, 2018). ~~I_0 denotes the incident solar radiance in the form of either actinic flux (in quanta s^{-1} cm^{-2} nm^{-1}) or irradiance (in W m^{-2} nm^{-1}), which were obtained using the TUV Quick Calculator (http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/). (I_0-I) denotes the direct absorption of solar actinic flux or irradiance by BrC.~~

3. Results and Discussion

3.1 Optical absorption characteristics of WS-BrC and WI-BrC

The average absorption spectra of WS-BrC and WI-BrC (λ = 300-700 nm) during daytime and nighttime in different seasons are shown in Figure 2a &b. The absorption Ångström exponents for both WS-BrC ($AAE_{WS\text{-}BrC}$) and WI-BrC ($AAE_{WI\text{-}BrC}$) are generally higher than 5, verifying the contribution of BrC to aerosol absorptivity in the region. The average $AAE_{WS\text{-}BrC}$ are similar between summer (5.43±0.41) and winter (5.11±0.53). Huang et al. (2014) and Shen et al. (2017) reported comparable $AAE_{WS\text{-}BrC}$ values (5.3-5.7) with no significant seasonal change at urban sites of Xi'an, suggesting common characteristics of BrC on a regional scale in the Guanzhong Basin of China. These results are comparable with the data reported in Guangzhou (5.3) (Liu et al., 2018), but much lower than those in Beijing (5.3-7.3) (Cheng et al., 2011;Yan et al., 2015b;Du et al., 2014) and Nanjing (6.7-7.3) (Chen et al., 2018). Moreover, ~~Comparable~~ comparable AAE values were reported for WS-BrC in Switzerland (3.8-5.1) (Moschos et al., 2018) and Nepal (4.2-5.6) (Wu et al., 2019;Kirillova et al., 2016), but higher $AAE_{WS\text{-}BrC}$ were found in ~~Southeastern~~ southeastern US (7 ± 1) (Hecobian et al., 2010), Los Angeles Basin (7.6 ± 0.5) (Zhang et al., 2013), and Korea (5.84-9.17) (Kim et al., 2016)~~, and Beijing (7.0-7.5) (Cheng et al., 2011)~~.

The $AAE_{WI\text{-}BrC}$ shows more obvious seasonal variations with a higher average value in

winter (6.04±0.22) than in summer (5.01±0.58). This difference suggests that the chemical composition of WI-BrC might be more different in different seasons, due to variations in the sources and atmospheric formation and aging processes of light absorbing hydrophobic compounds.

The light absorption properties of WS-BrC and WI-BrC present obvious seasonal variations (Figure 2). The average (±1σ) Abs and MAC values of BrC at 365 nm (i.e., $Abs_{365,WS\text{-}BrC}$, $Abs_{365,WI\text{-}BrC}$, $MAC_{365,WS\text{-}BrC}$, and $MAC_{365,WI\text{-}BrC}$) during daytime and nighttime in winter and summer are summarized in Table 1. 365 nm ~~is~~ was chosen to avoid interferences from inorganic compounds (e.g., nitrate and nitrite) and to be ~~consistence~~ consistent with previous studies (Hecobian et al., 2010;Huang et al., 2018). On average, $Abs_{365,WS\text{-}BrC}$ is significantly higher than $Abs_{365,WI\text{-}BrC}$ in summer (5.00±1.28 Mm^{-1} vs. 2.95±1.94 Mm^{-1}), but the values ~~are comparable~~vary slightly in winter (19.6±8.3 Mm^{-1} vs. 21.9±13.5 Mm^{-1}). The substantially higher BrC absorptions in winter correspond to a much higher organic aerosol concentration – WSOC and WIOC concentrations in winter are on average 4.2 and 14 times of the concentrations in summer (Table 1). Elevated OA (organic aerosols) concentration during winter is due to a combination of lower ~~ABL~~ PBL height and enhanced primary emissions (e.g., from residential heating) in the cold season. It is worth noting that the wavelength-dependent Abs of WS-BrC shows a minor tip at about 360 nm in both seasons (Figure 2), which may be related to the contribution of some specific chromophores. For example, Lin et al. (2015) reported that some nitrogen-containing organic compounds (such as picric acid or nitrophenol) have a maximum absorption at wavelength of ~360 nm. The tip ~~would~~possibly caused an overestimation of average Abs and MAC at wavelength of 365 nm in this study. However, the influence seems

insignificant based on a comparison of average Abs and MAC at wavelength of 340 nm, 350 nm, 360 nm, 370 nm, and 380 nm (Table S1).–

The MACs of WS-BrC are comparable between the two seasons (Figure 2c & d), with the average $MAC_{365,WS\text{-}BrC}$ being 1.00 (±0.18) $m^2\ g^{-1}$ in summer and 0.93 (±0.25) $m^2\ g^{-1}$ in winter (Table 1). As summarized in Table 2, the $MAC_{365,WS\text{-}BrC}$ measured in this study, i.e., at a rural site in the Guanzhong Basin of China, is comparable to or lower than the values observed in Asian cities such Xi'an (Huang et al., 2018), Beijing (Cheng et al., 2011), Seoul (Kim et al., 2016) and New Delhi (Kirillova et al., 2014b), but obviously higher than those in the regional sites of North China Plain (Teich et al., 2017) and the background site of Tibetan Plateau (Xu et al., 2020). ~~However~~Moreover, significantly lower $MAC_{365,WS\text{-}BrC}$ values were observed in the US, including Los Angeles Basin (Zhang et al., 2013), Southeastern US (Hecobian et al., 2010), and Atlanta (Liu et al., 2013).

In winter, the average $MAC_{365,WI\text{-}BrC}$ (0.95±0.32 $m^2\ g^{-1}$) is comparable to $MAC_{365,WS\text{-}BrC}$ (0.93±0.25 $m^2\ g^{-1}$; Table 1). However, in summer the $MAC_{365,WI\text{-}BrC}$ is ~~significantly~~ much higher than $MAC_{365,WS\text{-}BrC}$ (1.82±1.06 vs. 1.00±0.18 $m^2\ g^{-1}$), indicating a relatively stronger light absorption capability of hydrophobic chromophores than hydrophilic chromophores. Further, the fact that the summertime $MAC_{365,WI\text{-}BrC}$ is nearly double the wintertime $MAC_{365,WI\text{-}BrC}$ suggests that more light absorbing molecules are formed in the warm season.

Figure 2 compares the wavelength-dependent light absorptivity (i.e., Abs_λ and MAC_λ) of WS-BrC and WI-BrC between day and night in summer and winter. Higher $Abs_{\lambda,WS\text{-}BrC}$ and $Abs_{\lambda,WI\text{-}BrC}$ occurred during daytime in summer but during nighttime in winter. The MAC_λ of WS-BrC are overall similar between daytime and nighttime in both seasons. However, the MAC_λ

of WI-BrC show a significant daytime increase in summer over the whole wavelength range of 300-700 nm (Figure 2c). The day-night change of BrC light absorptivity can be viewed more obviously in Figure 1e and 1f, where the temporal variations of the Abs_{365} and MAC_{365} of WS-BrC and WI-BrC during summer 2016 (Aug. 3-23) and winter 2017 (Jan. 20 -Feb. 1) are presented. The highest day/night ratio of $MAC_{365,WIOC}$ reached 3.8 in summer and the average daytime $MAC_{365,WI-BrC}$ in summer (2.45±1.14 m^2 g^{-1}) is more than twice the value during nighttime (1.18±0.36 m^2 g^{-1}; Table 1). A possible reason for this observation is that there are additional sources of WI-BrC during summer daytime in this rural region, such as secondary formation of hydrophobic light absorbing compounds.

Figure 3 and 4 present the cross-correlations of $Abs_{365,WS-BrC}$ and $Abs_{365,WI-BrC}$ with major chemical components (e.g., WSOC, WSIC, and sulfate) and molecular tracer species in summer and winter, respectively. In winter, $Abs_{365,WS-BrC}$ correlates strongly with WSOC concentration (r^2=0.80), so does $Abs_{365,WI-BrC}$ with WIOC (r^2=0.76). However, their relationships in summer are much weaker, especially for the correlation between $Abs_{365,WI-BrC}$ and WIOC (r^2=0.50). Considering that secondary OA (SOA) are mainly comprised of water-soluble compounds, such as polyalcohols/polyacids and phenols (Kondo et al., 2007), the much higher WSOC/OC ratio in summer (0.75±0.07) compared to winter (0.50±0.09) confirms more prevalent SOA formation in summer associated with higher ~~air~~ temperature and stronger solar radiation. Formation of secondary organic chromophores may lead to a more complex composition of BrC in summer. More evidences on secondary BrC formation are provided in the subsequent sections.

Numerous studies reported that biomass burning is a dominant source of BrC in the atmosphere (Desyaterik et al., 2013;Washenfelder et al., 2015). In the current study,

297 levoglucosan – a key tracer for biomass burning emissions (Simoneit, 2002) –was determined.
298 As shown in Figure 3 and 4, levoglucosan correlates well with WSOC and WIOC in both
299 summer and winter (r^2=0.45-0.77), suggesting that biomass burning is an important source of OA
300 in the rural region of Guanzhong Basin. For most of the periods in this study, the $MAC_{365,WS\text{-}BrC}$
301 and $MAC_{365,WI\text{-}BrC}$ values are within the range of MAC of biomass burning aerosols (e.g.,
302 1.3−1.8 for corn stalk (Li et al., 2016a), ~1.37 for rice straw (Park and Yu, 2016), ~1.9 for BB
303 smoke particles (Lin et al., 2017)). Also, $Abs_{365,WI\text{-}BrC}$ in both summer and winter correlate well
304 with levoglusocan (r^2=0.74 and 0.62, respectively), demonstrating an important contribution of
305 biomass burning to WI-BrC despite the fact that levoglucosan itself is water soluble. The
306 relationships between the $Abs_{365,WS\text{-}BrC}$ and levoglucosan are much weaker (r^2=0.40 and 0.45 in
307 summer and winter, respectively), suggesting more complex sources of WS-BrC in the region.

308 **3.2 Molecular characterization of BrC aerosols**

309 Five categories of molecular tracer compounds, i.e., parent-polycyclic aromatic
310 hydrocarbons (parent-PAHs), oxygenated-PAHs (OPAHs), nitrophenols, isoprene-derived
311 products (SOA_i), and α-/β-pinene-derived products (SOA_p), were determined by the GC-EIMS
312 technique to investigate the formation pathways of BrC in this study. Their average
313 concentrations as well as daytime and nighttime differences are summarized in Table 1, and the
314 temporal variation profiles of the sum concentrations of each category, together with
315 levoglucosan time series, are presented in Figure S3.

316 PAHs and their ~~derived~~ oxidized products~~compounds~~ are important BrC chromophores,
317 since the large conjugated polycyclic structures are strongly light-absorbing in the near-UV
318 range (Samburova et al., 2016;Huang et al., 2018). A total number of 14 parent PAHs and 5

OPAHs (Table ~~S1~~S2) were determined in this study. Parent-PAHs are unsubstituted PAHs mainly emitted directly from incomplete combustions of coal, biofuel, gasoline or other materials whereas OPAHs can be emitted directly from combustion sources or formed from photochemical oxidation of the parent-PAHs. The time trends of parent-PAHs and OPAHs are highly similar in both seasons (r^2 = 0.90 and 0.98 in summer and winter, respectively, Figure 3 and 4), suggesting that they have common combustion sources. In addition, both parent-PAHs and OPAHs presented good correlations with levoglucosan, particularly in winter (r^2 = 0.69 and 0.73, respectively; Figure 4), indicating that ~~that~~ biomass burning is an important contributor to ~~air~~ ambient particulate PAHs in the region. PAHs, as well as levoglucosan, are elevated during nighttime in winter, corresponding to enhanced biomass burning emissions from heating-related activities as well as reduced boundary layer height at night. In contrast, the average daytime concentrations of parent-PAHs (11.6±5.7 ng m^{-3}) and levoglucosan (142±89 ng m^{-3}) in summer are about 1.95 and 2.58 times, respectively, of the values at night (Table 1). The daytime enhancement of OPAHs concentrations in summer is even more pronounced with an average day/night ratio of ~4.6 and as high as 9.8 for individual OPAH species (e.g., 6H-henzo(cd)pyrene-6-one; Figure S4). Both parent-PAHs and OPAHs, which are hydrophobic thus mainly exist as WIOC, demonstrate a good linear relationship with $Abs_{365,WI-BrC}$ in both winter and summer (r^2 = 0.49-0.83, Figure 3 and 3). However, the good correlation between OPAHs and $Abs_{365,WI-BrC}$ in summer appears to be mainly driven by daytime production, as the correlation coefficient (r^2) is 0.72 for the daytime data but is <0.1 for the nighttime data (Figure S5a). These results suggest that photochemical formation of light-absorption compounds is an important source of BrC during summer in the Guanzhong Basin.

We estimated the potential contribution of parent-PAHs and OPAHs to the light absorption of WI-BrC using a method reported in Samburova et al. (2016). Details on the method are presented in the Supplementary Information (SI). Table ~~S2~~ S3 summarizes the solar-spectrum-weighed mass absorption coefficients for PAHs ($MAC_{PAH,av}$) used in the calculation. As shown in Figure 5, the contribution of parent-PAHs to solar-spectrum-weighed absorption coefficient of WI-BrC varies between 0.55% - 0.66% with slight diurnal or season variations (Table ~~S2~~S3). However, the contribution of OPAHs clearly shows higher daytime values, especially in summer. The average contribution of OPAHs to the solar-spectrum-weighed absorption coefficient of WI-BrC in summer is 0.51±0.28% during daytime and 0.34±0.19% during nighttime. These results indicate that more secondary water-insoluble aromatic chromophores were produced via photochemical oxidation during summertime in the rural region.

Nitrophenols were identified as one of the most important light-absorbing compounds in particles and cloud water influenced by BB emission in China (Desyaterik et al., 2013). These compounds can be either directly emitted from burning of biomass (Xie et al., 2019) or formed in the atmosphere through gas phase and aqueous phase reactions of aromatic precursors including benz[a]pyrene (Lu et al., 2011), naphthalene (Kitanovski et al., 2014), catechol and guaiacol (Ofner et al., 2011), and toluene (Liu et al., 2015) in the presence of NO_x. In this study, only a few nitrophenol compounds were detected in PM (Table ~~S1~~S2) and their average (±1σ) concentration is 0.94 (±0.26) ng m^{-3} in summer and 72.6 (±63.7) ng m^{-3} in winter. The wintertime concentrations of nitrophenols measured in the current study are comparable to those detected in Shanghai (Li et al., 2016b), Mt. Tai in the Shandong province of China (Desyaterik et al., 2013), and Ljubljana of Slovenia (Kitanovski et al., 2012), but the summertime

concentrations observed are more comparable to those detected in the Los Angeles Basin of the U.S. (Zhang et al., 2013). The substantially lower concentration of nitrophenols in summer may be related to rapid photodegradation in the atmosphere. Indeed, according to a laboratory study conducted by Zhao et al. (2015) the timescale for photo-bleaching of nitrophenols can be an hour or less. Furthermore, as shown in Figure S5b, during wintertime, when low temperature and weak solar irradiation suppress photodegradation process, nitrophenols concentration anti-correlates with O_3 mixing ratio in a nonlinear manner (r^2=0.60). On average, concentration of nitrophenols in winter ~~present~~ is 2.5 times higher ~~concentration~~ during nighttime than during daytime whereas the nighttime concentrations of levoglucosan and PAHs are only slightly higher than the daytime concentrations (by 11% and 33%, respectively; Table 1). Levoglucosan and PAHs are less photochemically reactive than nitrophenols. These results confirm that nitrophenols, and other photoreactive BrC compounds, may undergo significant atmospheric degradation during summertime.

Both summertime and wintertime $Abs_{365,WS\text{-}BrC}$ correlated well with the concentrations of nitrophenols (r^2=0.51-0.72, Figure S5c & d), suggesting an important contribution of nitrated aromatic compounds to light absorption of WS-BrC in the study area. Using the MAC of individual nitrophenol reported in Zhang et al. (2013), we calculated that the contributions of nitrophenols to aerosol light absorption are 6.5-27 times higher than their mass contributions to WSOC and that the fractions are much higher in winter (2.44±1.78%) than in summer (0.12±0.03%; Table S3). In addition, due to a significantly higher abundance of nitrophenols during nighttime in winter, their fractional contribution to aerosol absorption is on average 2.5 times higher than during the day (3.47±2.03% vs. 1.41±0.29%).

On a global scale, biogenic VOCs, mostly consisting of isoprene and monoterpenes, are nearly an order of magnitude more abundant than anthropogenic VOCs (Guenther et al., 2006), and their secondary products are estimated to be a predominant contributor to global SOA burden (Heald et al., 2008). Recent studies (Lin et al., 2014;Nakayama et al., 2015;Nakayama et al., 2012) showed that a large amount of biogenic SOA compounds are light absorptive. Some tracers of SOA formed from isoprene (SOA_i) and α-/β-pinene (SOA_p) oxidation were measured in the summertime samples (Table ~~S1~~S2), and their temporal variations are shown in Figure S3. No biogenic SOA tracer species were detectable in the winter samples in this study. Similar results were obtained in our previous study in the Mt. Hua of the Guanzhong Basin (Li, 2011). These findings are consistent with low emissions of biogenic VOCs and low oxidation rates in this region during cold seasons. The average concentrations of SOA_i and SOA_p tracers in summer are 18.6±9.7 and 22.0±6.7 ng m^{-3}, respectively. Neither SOA_i tracers nor SOA_p tracers showed significant correlations with the absorption coefficient of WSOC or WSIC, suggesting a low contribution of biogenic SOA to aerosol light absorption in the region. In addition, compared to the MAC values observed in this study, the MACs of biogenic SOA reported in literature are much lower, on average, by nearly an order of magnitude (Laskin et al., 2015), which further support an insignificant contribution of biogenic sources to BrC in this region. This finding is consistent with the fact that the Guanzhong Basin is a highly polluted region, where the major emission sources of organic aerosols are anthropogenic.

3.3 Variation of BrC during extreme haze events in winter

In recent years, ~~extreme~~extremely severe haze events with very high $PM_{2.5}$ concentrations (up to 500-600 μg m^{-3}) and low visibility (lower than 1 km) occurred frequently during

wintertime in China (Huang et al., 2014). In this study, a heavy~~an extreme~~ haze event occurred during Jan. 21-26 when $PM_{2.5}$ concentration at the rural site increased continuously from ~100 μg m^{-3} to 430 μg m^{-3} and visibility decreased from >10 km to ~1.4 km (Figure 1b & d). Similar to most haze events occurred in Northeast China, this event was associated with stagnant meteorological condition with low wind speed (<1 km s^{-1}), which promotes the accumulation of pollutants. In addition, secondary inorganic aerosol species, e.g., SO_4^{2-}, NO_3^- and NH_4^+, increased sharply (Figure 1d), which indicates secondary aerosol formation was enhanced during the haze event despite the low solar irradiance and low O_3 concertation (e.g., 2 ~ 40 μg m^{-3}; Figure 1c) conditions. Recent studies by Wang et al. (2016) and Cheng et al. (2016) reported dramatic increases of secondary inorganic components, mainly sulfate, nitrate and ammonium (SNA), during haze periods in China and attributed the increases to enhanced aqueous reactions under high relative humidity (RH) conditions with NO_2 being an important oxidant. Moreover, Huang et al. (2014) observed that SOA also increased obviously during haze periods in winter. Indeed, as shown in Figure 4, SO_4^{2-} correlates well with RH (r^2=0.64) and NO_2 (r^2=0.56) in winter. In addition, $Abs_{365,WS\text{-}BrC,}$ which increases continuously during the haze period with a peak value at 43.3 Mm^{-1} (Figure 1e), correlates well with RH (r^2=0.65), sulfate (r^2=0.84) and NO_2 (r^2=0.70) (Figure 4). In contrast, $Abs_{365,WI\text{-}BrC}$ presents obvious diurnal variation during the haze period, and the ~~relationship~~ correlation~~s~~ of RH (r^2=0.40), sulfate (r^2=0.46) and NO_2 (r^2=0.41) with $Abs_{365,WI\text{-}BrC}$ are also much weaker than those with $Abs_{365,WS\text{-}BrC}$. These results suggest that aqueous oxidation has played a role in the formation of WS-BrC (Laskin et al., 2015) during the haze period, although the stagnant meteorological condition with low wind speed can also promote its accumulation. This finding is consistent with ~~with~~ our previous

~~studies~~study conducted in Xi'an (Wu et al., 2020), which also found a secondary formation of BrC in winter by using stable carbon isotope composition analysis ~~have shown that aqueous reactions can be an important pathway of BrC formation in the atmosphere (Laskin et al., 2015)~~. In contrast, a slowly decreasing trend of $MAC_{365,WIOC}$ ~~is~~ was observed during the haze period, suggesting that some of the water-insoluble BrC species were oxidized to form water-soluble chromophores, possibly through aqueous-phase reactions.

It is worthwhile to mention that Jan. 27, 2017 was the Chinese New Year's Eve and a large amount of fireworks were set off for celebration. During this night, the concentrations of $PM_{2.5}$, OC, EC, WSOC and WIOC as well as SNA were ~~actually~~ 25%-51% lower than their wintertime average concentrations due to the higher wind speed favoring for atmospheric dispersion (Figure 1). However, ~~–~~the $MAC_{365,WS-BrC}$ (1.81) increased to about 2 times of its average value in winter, ~~,~~ and $Abs_{365,WS-BrC}$ (20.5 Mm^{-1}) also showed a slight increase. ~~while , OC, EC, WSOC and WIOC as well as SNA were actually 25%-51% lower than their wintertime average concentrations (Figure 1d).~~ Meanwhile, metal ions, which are abundant in fireworks (Wu et al., 2018;Jiang et al., 2015), such as K^+, Mg^{2+}, and Ca^{2+}, ~~,~~increased substantially during the night as well (Figure S6). These results indicate that the increase of $MAC_{365,WSOC}$ during the Chinese New Year's Eve is likely mainly contributed by metal-containing light-absorbing compounds emitted from fireworks (Laskin et al., 2015;Tran et al., 2017).

3.4 Estimation of direct absorption of solar radiation by BrC

Since the light absorption of BrC is mainly in the UV spectral region, an important concern is that BrC can reduce the solar actinic flux and thus affect atmospheric photochemistry and tropospheric ozone production (Jacobson, 1998;Mohr et al., 2013). In this study, the direct

absorptions of solar radiation by both WS-BrC and WI-BrC ~~are~~ were estimated by using Eq 7. Figure S7 presents the incident solar irradiance and actinic flux spectra determined for the region under midday summer (Aug. 10, 2016 13:00 pm Beijing (BJ) time) and winter (Jan. 25, 2017 13:00 pm BJ time) conditions. Note that the local time at Guanzhong is ~ 1 hour later than the BJ time.

Table 3 presents a summary of the calculated direct solar absorptions of BrC. In summer, the direct attenuation of actinic flux by WS-BrC and WI-BrC are estimated at $1.55\times10^{14}\pm0.43\times10^{14}$ and $1.03\times10^{14}\pm0.64\times10^{14}$ quanta s^{-1} cm^{-2}, respectively, in the UV range (300-400 nm), which account for 0.83±0.23% and 0.53±0.33%, respectively, of the total down-welling radiation. In winter, the direct absorptions by BrC are higher with WS-BrC and WI-BrC on average accounting for 1.67±0.72% and 2.07±1.24%, respectively, of the total down-welling radiation in the UV range. These results suggest that BrC may have a significant influence on atmospheric photochemistry in the UV range. In the visible spectral region (400 - 700 nm), the contributions of WS-BrC and WI-BrC to the total down-welling radiation are negligible – 0.10±0.03% and 0.07±0.05% in summer, and 0.15±0.06% and 0.15±0.08% in winter, respectively.

Another concern of BrC is that they can absorb solar irradiance to influence tropospheric temperature in a similar way as black carbon (BC) or elemental carbon (EC) (Feng et al., 2013;Laskin et al., 2015). In our study, the direct absorption of solar irradiance by WS-BrC and WI-BrC are estimated at 0.51±0.14 and 0.34±0.21 W m^{-2} in summer, and 0.57±0.25 and 0.68±0.41 W m^{-2} in winter in the UV range. To evaluate the contribution of BrC to total aerosol absorption, we also estimated the direct absorption of EC based on the Carbon Analyzer data

according to the method described by Kirillova et al. (2014b) and Kirchstetter and Thatcher (2012) (see SI). The estimated contributions of light absorption of BrC relative to EC are shown in Table 3. In the visible region, the contribution is estimated at 10.0±3.52% in summer and 4.99±1.23% in winter for WS-BrC, and 6.19±2.42% and 4.51±1.44%, respectively, for WI-BrC. However, in the UV range, the fractions increase to 49.3±14.5% in summer and 25.9±5.47% in winter for WS-BrC, 29.4±11.0% and 29.0±10.4% for WI-BrC, which are within the range of the values reported in other regions in China (Huang et al., 2018), India (Kirillova et al., 2014b), and Korea (Kirillova et al., 2014a). On the other hand, the direct light absorption of WI-BrC represents a substantive contribution to that of total BrC in this study, which is about 40% in summer and more than 50% in winter in both UV and visible range, emphasizing the important role that WI-BrC likely plays in atmospheric chemistry and the Earth's climate system, especially in China.

4. Summary and Conclusion

Both WS-BrC and WI-BrC showed elevated Abs in winter (4-7 times higher than those in summer), corresponding to much higher concentrations of WSOC and WIOC due to a combination of lower ~~ABL~~PBL height and enhanced primary emissions (e.g., from residential heating) in the cold season. No significant differences were found for the daytime and nighttime MACs of WS-BrC in summer, or for the MACs of WS-BrC and WI-BrC in winter. However, the average daytime $MAC_{365,WI\text{-}BrC}$ was more than twice the nighttime value in summer. We found that the average daytime concentrations of both parent-PAHs and levoglucosan in summer were around 2 times of the values at night and the daytime OPAHs concentration was more than 4 times of the nighttime value. Moreover, OPAHs ~~and~~ well correlated with $Abs_{365,WI\text{-}BrC}$ in summer

~~correlated well~~ during daytime (r^2=0.72) ~~in summer~~ but not during nighttime (r^2<0.1). These results demonstrated that photochemical formation of BrC and enhanced BB emissions (e.g., from cooking) contributed to the higher daytime MACs in summer. In winter, the Abs of WS-BrC correlated strongly with relative humidity, sulfate, and NO_2, suggesting that aqueous-phase reactions played an important role in the formation of secondary BrC. $Abs_{365,WS\text{-}BrC}$ correlated well with the concentrations of nitrophenols in both seasons, suggesting an important contribution of nitrated aromatic compounds to light absorption of WS-BrC. However, this contribution is much lower in summer due to faster photodegradation reactions of these compounds. WS-BrC and WI-BrC were estimated to account for 0.83±0.23% and 0.53±0.33%, respectively, of the total down-welling solar radiation in the UV range in summer, and 1.67±0.72% and 2.07±1.24%, respectively, in winter. The substantive contribution of WI-BrC to total BrC absorption (~40% in summer and >50% in winter) emphasize the important role that WI-BrC likely plays in atmospheric chemistry and the Earth's climate system.

Author Contributions

J.J. Li, Q. Zhang, G.H. Wang, K.F. Ho, and J.J. Cao designed the experiment. J.J. Li, G.H. Wang, and K.F. Ho arranged the sample collection. J. Li, L. Liu and C. Wu collected the samples. J.J. Li, J. Li, J.Y. Wang, W.Q. Jiang, and L.J. Li analyzed the samples. J.J. Li, Q. Zhang, and G.H. Wang performed the data interpretation. J.J. Li, Q. Zhang, and G.H. Wang wrote the paper.

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Table 1 Average (±1σ) values Abs_{365}, MAC_{365}, and AAE of WS-BrC and WI-BrC, as well as concentrations of OC, WSOC, WIOC, and measured organic species in the $PM_{2.5}$ aerosols from the rural site of Guanzhong Basin.

	Summer			Winter		
	Average	Daytime	Nighttime	Average	Daytime	Nighttime
$Abs_{365,WS\text{-}BrC}$ (Mm^{-1})	5.00±1.28	5.64±1.34	4.37±0.83	19.6±8.3	19.2±6.8	19.9±9.5
$Abs_{365,WI\text{-}BrC}$ (Mm^{-1})	2.95±1.94	4.23±1.93	1.67±0.72	21.9±13.5	17.2±8.2	26.7±15.8
$MAC_{365,WS\text{-}BrC}$ ($m^2\ g^{-1}$)	1.00±0.18	0.99±0.17	1.01±0.18	0.93±0.25	0.92±0.21	0.94±0.28
$MAC_{365,WI\text{-}BrC}$ ($m^2\ g^{-1}$)	1.82±1.06	2.45±1.14	1.18±0.36	0.95±0.32	0.85±0.34	1.05±0.28
$AAE_{WS\text{-}BrC}$	5.43±0.41	5.56±0.4	5.30±0.38	5.11±0.53	5.14±0.2	5.07±0.72
$AAE_{WI\text{-}BrC}$	5.01±0.58	4.74±0.19	5.28±0.71	6.04±0.22	5.94±0.12	6.15±0.24
OC (μg m^{-3})	6.78±1.77	7.74±1.73	5.83±1.19	45.9±22.9	44.0±17.2	47.9±27.2
WSOC (μg m^{-3})	5.06±1.11	5.72±1.02	4.39±0.72	21.9±9.3	22.1±8.0	21.7±10.4
WIOC (μg m^{-3})	1.73±0.87	2.02±1.04	1.44±0.53	24.0±14.3	21.9±10.1	26.2±17.3
WSOC/OC	0.75±0.07	0.75±0.09	0.76±0.04	0.50±0.09	0.51±0.08	0.48±0.10
Parent-PAHs (ng m^{-3})	8.81±5.09	11.6±5.7	5.98±1.9	82.3±53.7	70.8±35.4	93.9±65.1
OPAHs (ng m^{-3})	14.0±14.0	23.0±15.1	4.97±1.34	98.3±59.5	89.4±39.8	107±73
Nitrophenols (ng m^{-3})	0.94±0.26	0.87±0.26	1.02±0.24	72.6±63.7	41.1±15.5	104±77
SOA_i [a] (ng m^{-3})	18.6±9.7	15.0±8.0	22.1±9.8	BDL[c]	BDL	BDL
SOA_p [b] (ng m^{-3})	22.0±6.7	25.2±6.7	18.9±5.0	BDL	BDL	BDL
Levoglucosan (ng m^{-3})	98.7±83.7	142±89	55.1±48.7	601±301	569±138	633±401

[a] SOA_i: Tracers of SOA formed from isoprene (SOAi) oxidation, i.e., the sum of 2-methylglyceric acid, 2-methylthreitol, and 2-methylerythritol.

[b] SOA_i: Tracers of SOA formed from α-/β-pinene (SOAp) oxidation, i.e., the sum of pinonic acid, pinic acid, and 3-methyl-1,2,3-butanetricarboxylic acid.

[c] BDL: below detection limit (<0.17 ng m^{-3}) .

Table 2 Comparison of $MAC_{365,WS\text{-}BrC}$ in the present study and those reported in earlier studies in China, India, and the United States (US).

Sampling site	Sampling time	Season	$MAC_{365,WS\text{-}BrC}$ (m^2 g^{-1})	Reference
Lincun, Shaanxi, China	Aug. 3-23, 2016	Summer	1.00±0.18	This study
	Jan. 20-Feb 1, 2017	Winter	0.93±0.25	
Xi'an, China	Jun. 1-Aug. 31, 2009	Summer	0.98 ±0.21	Huang et al. (2018)
	Nov.15, 2008-Mar. 14, 2009	Winter	1.65 ± 0.36	
Beijing, China	Jun. 20-Jul. 20, 2009	Summer	1.8 ± 0.2	Cheng et al. (2011)
	Jan.9-Feb. 12, 2009	Winter	0.7 ± 0.2	
XiangHe, Hebei, China	Jul. 9-14 and Jul. 21-Aug. 1, 2013	Summer	0.38 ± 0.52[a]	Teich et al. (2017)
Wangdu, Hebei, China	Jun. 4-24, 2014	Summer	0.55 ± 0.15[a]	
Mt. Waliguan, Qinghai, China	Jul. 1–31, 2017	Summer	0.48	Xu et al. (2020)
Seoul, Korea	Aug. 13-Sep. 9, 2013	Summer	0.28	Kim et al. (2016)
	Jan. 9-Feb 8, 2013	Winter	1.02	
New Delhi, India	Oct. 24, 2010-Mar. 25, 2011	Winter	1.6 ± 0.5	Kirillova et al. (2014b)
Los Angeles Basin, US	mid-May - mid-June, 2010	~~summer~~Summer	0.71	Zhang et al. (2013)
Southeastern US	2007	~~annually~~Annually	0.3–0.7	Hecobian et al. (2010)
Atlanta, US	May 17-Sep. 29, 2012	~~summer~~ Summer and ~~fall~~Fall	0.14-0.53	Liu et al. (2013)

[a] Data at XiangHe and Wangdu were the averaged MAC of WSOC at wavelength of 370 nm (i.e., $MAC_{370,WS\text{-}BrC}$)

Table 3 Average direct solar absorption of water-soluble and water-insoluble BrC during summer and winter

	WSOC		WIOC	
	Summer	Winter	Summer	Winter
Actinic flux ($\times 10^{14}$ quanta s^{-1} cm^{-2})				
300-400 nm	1.55±0.43	2.14±0.92	1.03±0.64	2.53±1.52
400-700 nm	1.77±0.6	2.67±1.04	1.24±0.8	2.58±1.48
Irradiance (W m^{-2})				
300-400 nm	0.51±0.14	0.57±0.25	0.34±0.21	0.68±0.41
400-700 nm	0.49±0.17	0.57±0.22	0.35±0.23	0.55±0.32
Relative to EC (%)				
300-400 nm	49.4±14.5	25.9±5.47	29.4±11.0	29.0±10.4
400-700 nm	10.0±3.52	4.99±1.23	6.19±2.42	4.51±1.44

Figure Caption

Figure 1 Temporal variation of meteorological parameters (a and b), concentrations of major chemical compositions, Abs_{365}, MAC_{365}, and AAE of water-soluble and water-insoluble BrC in $PM_{2.5}$ from the rural area of Northwest China.

Figure 2 Average spectra of absorption coefficient (Abs_{λ}) (a,b) and mass absorption coefficient (MAC_{λ}) (c,d) of water-soluble (WS-BrC) and water-insoluble (WI-BrC) BrC~~, as well as the ratio of $MAC_{\lambda,WI\text{-}BrC}$ to $MAC_{\lambda,WI\text{-}BrC}$ (e,f)~~ during daytime and nighttime of summer and winter. Absorption Ångström exponent (AAE) is calculated by a linear regression of log Abs_{λ} versus log λ in the wavelength range of 300−450 nm.

Figure 3 Cross correlations between $Abs_{365,WS\text{-}BrC}$, $Abs_{365,WI\text{-}BrC}$, selected chemical compositions, and RH in summer. The numbers at the upper right denote the linear correlation coefficients (r^2) of the corresponding scatter plots.

Figure 4 Cross correlations between $Abs_{365,WS\text{-}BrC}$, $Abs_{365,WI\text{-}BrC}$, selected chemical compositions, and RH in winter. The numbers at the upper right denote the linear correlation coefficients (r^2) of the corresponding scatter plots.

Figure 5 Average contribution of parent-PAHs and OPAHs to the bulk light absorption of WI-BrC (300−700 nm) during daytime and nighttime of summer and winter.

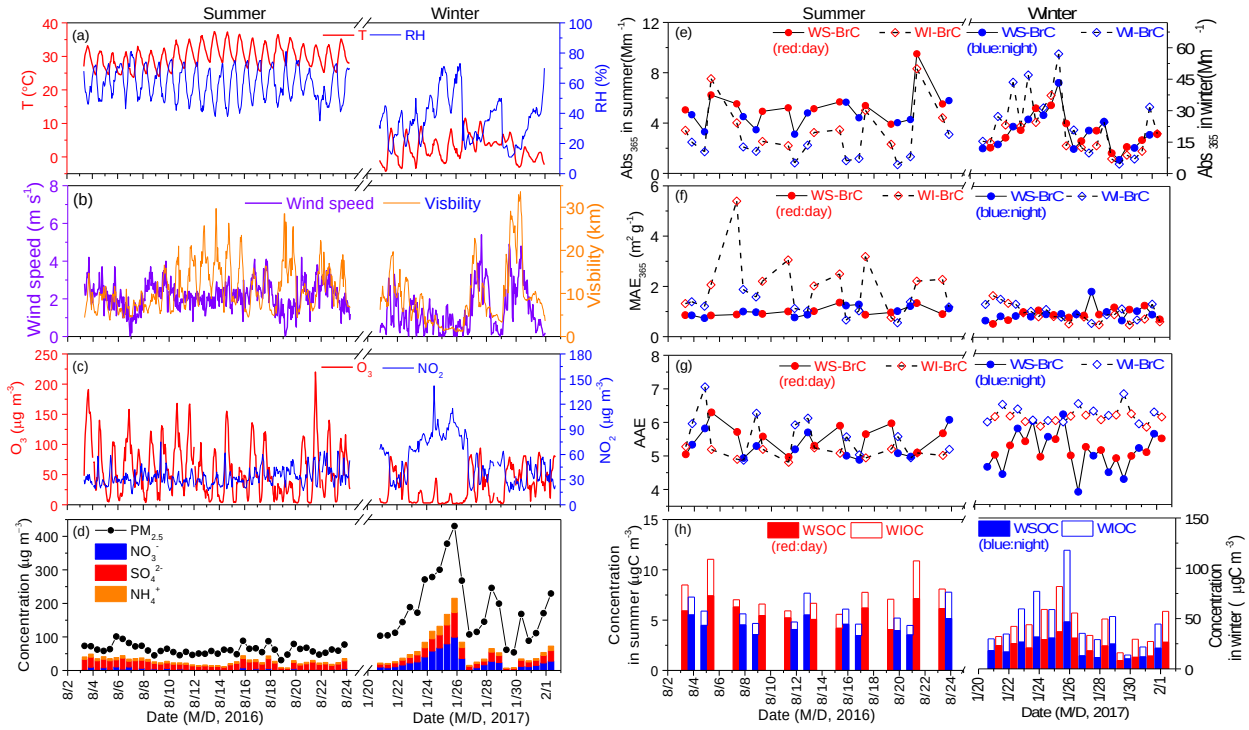
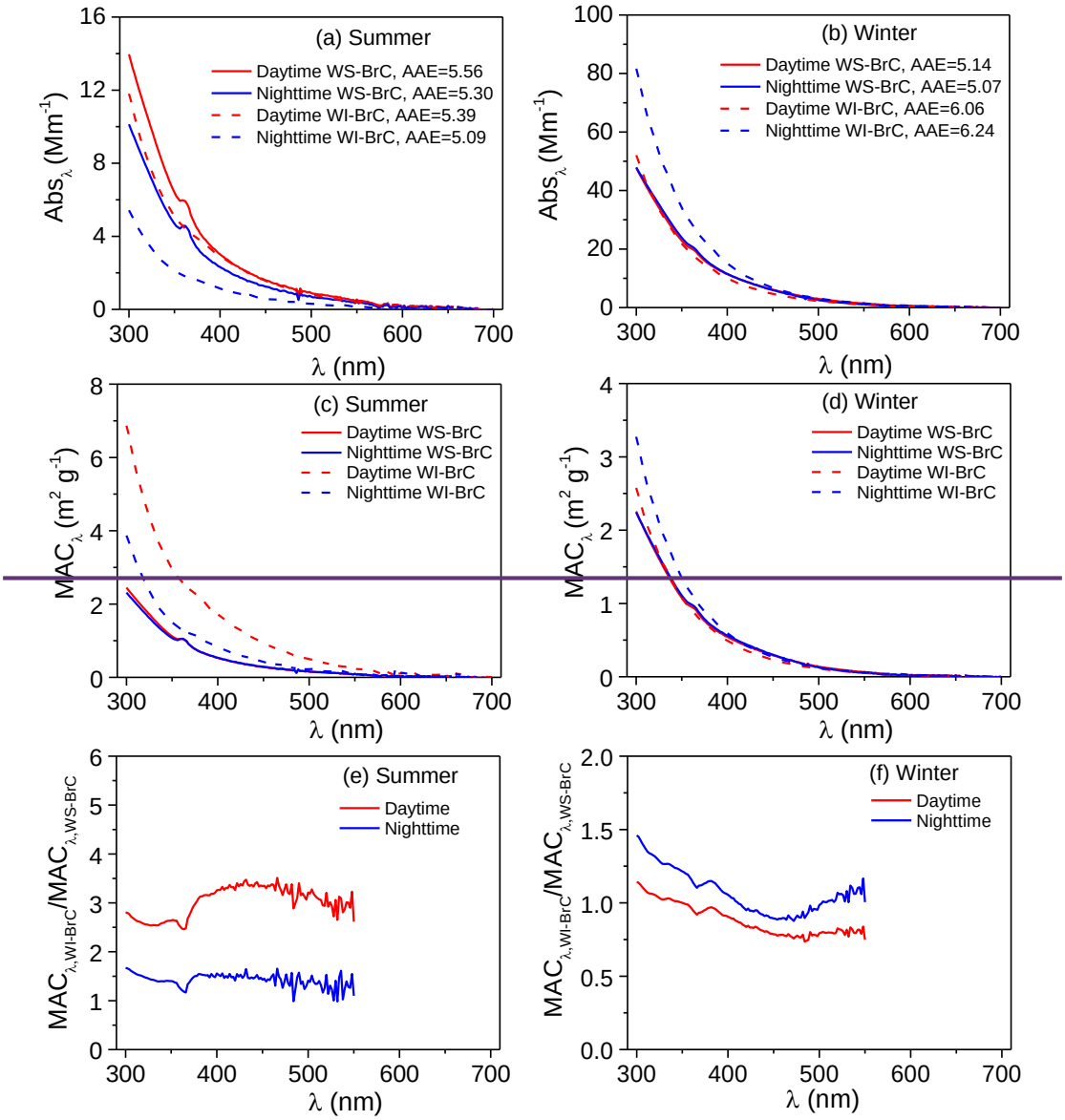


Figure 1 Temporal variation of meteorological parameters (a and b), concentrations of major chemical compositions, Abs_{365}, MAC_{365}, and AAE of water-soluble and water-insoluble BrC in $PM_{2.5}$ from the rural area of Northwest China.


(a) Summer
Daytime WS-BrC, AAE=5.56
Nighttime WS-BrC, AAE=5.30
Daytime WI-BrC, AAE=5.39
Nighttime WI-BrC, AAE=5.09
Abs$_\lambda$ (Mm^{-1})
λ (nm)
(b) Winter
Daytime WS-BrC, AAE=5.14
Nighttime WS-BrC, AAE=5.07
Daytime WI-BrC, AAE=6.06
Nighttime WI-BrC, AAE=6.24
(c) Summer
Daytime WS-BrC
Nighttime WS-BrC
Daytime WI-BrC
Nighttime WI-BrC
MAC$_\lambda$ (m^2 g^{-1})
(d) Winter
(e) Summer
Daytime
Nighttime
MAC$_{\lambda,WI\text{-}BrC}$/MAC$_{\lambda,WS\text{-}BrC}$
(f) Winter

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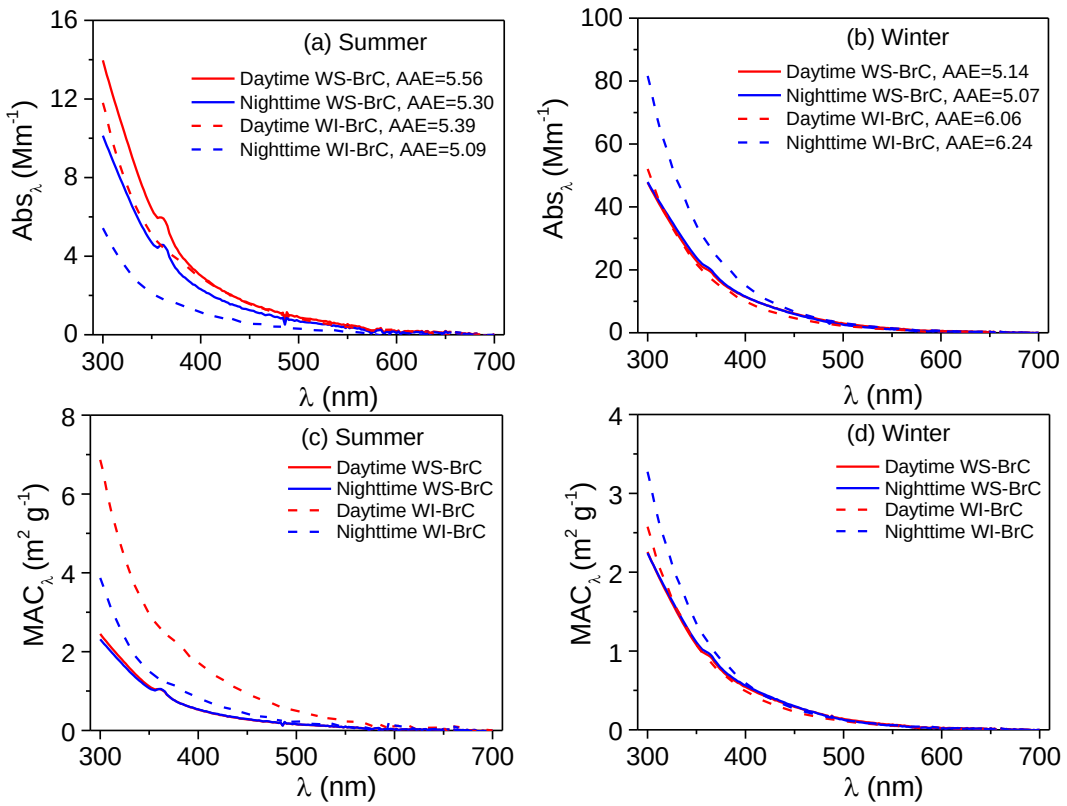


Figure 2 Average spectra of absorption coefficient (Abs$_\lambda$) (a,b) and mass absorption coefficient (MAC$_\lambda$) (c,d) of water-soluble (WS-BrC) and water-insoluble (WI-BrC) BrC~~, as well as the ratio of MAC$_{\lambda,\text{WI-BrC}}$ to MAC$_{\lambda,\text{WI-BrC}}$ (e,f)~~ during daytime and nighttime of summer and winter. Absorption Ångström exponent (AAE) is calculated by a linear regression of log Abs$_\lambda$ versus log λ in the wavelength range of 300−450 nm.

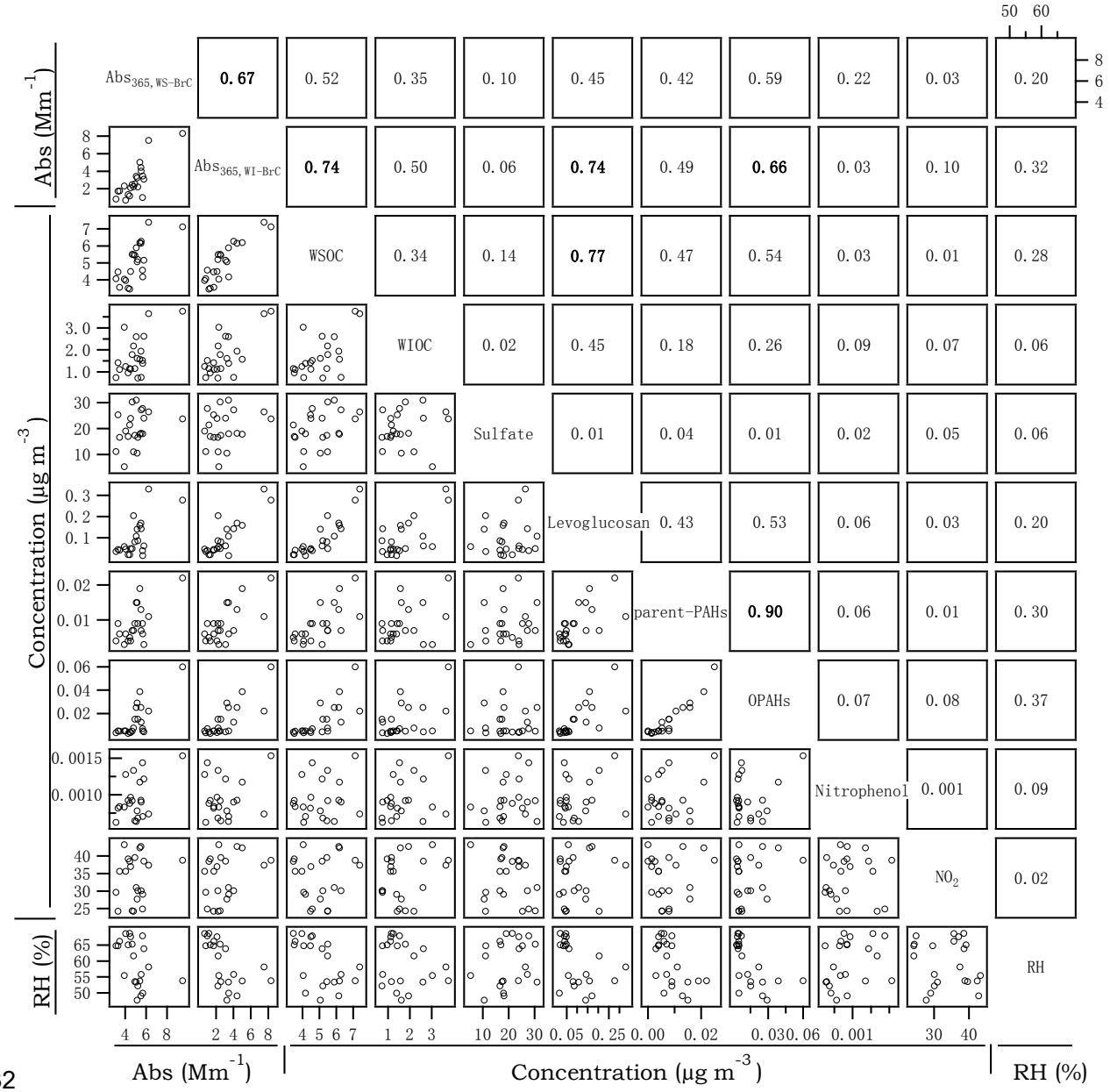
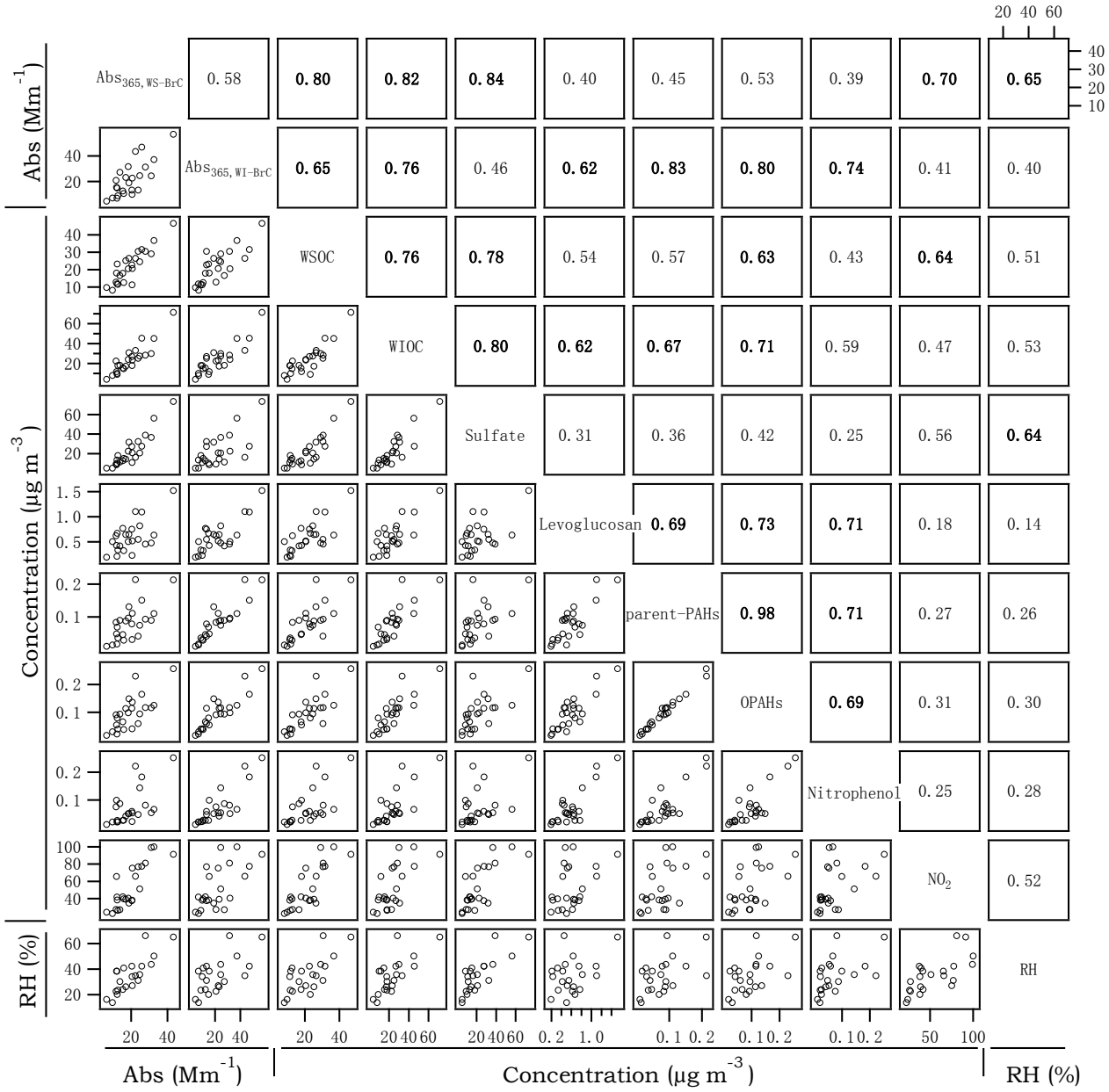


Figure 3 Cross-correlations between $Abs_{365,WS\text{-}BrC}$, $Abs_{365,WI\text{-}BrC}$, selected chemical components, and RH in summer. The numbers at the upper right denote the linear correlation coefficients (r^2) of the corresponding scatter plots.



837

838 Figure 4 Cross-correlations between $Abs_{365,WS\text{-}BrC}$, $Abs_{365,WI\text{-}BrC}$, selected chemical components, and RH in
839 winter. The numbers at the upper right denote the linear correlation coefficients (r^2) of the corresponding
840 scatter plots.

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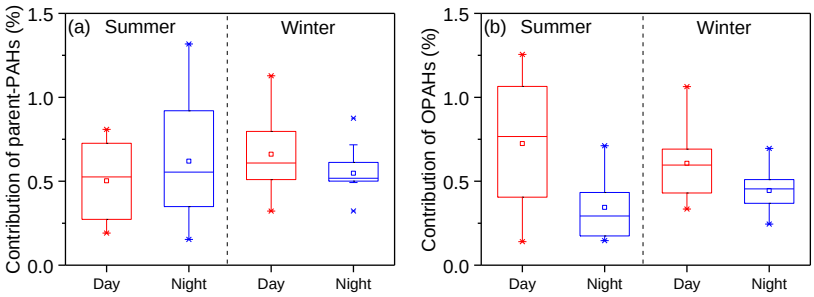

842

843 Figure 5 Average contribution of parent-PAHs and OPAHs to the bulk light absorption of WI-BrC (300−700
844 nm) during daytime and nighttime of summer and winter.

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Supporting information

Optical properties, molecular compositions and secondary formation of Brown carbon (BrC) in a rural area of Guanzhong Basin, China

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Estimation of contribution of parent-PAHs and OPAHs to the light absorption of water-insoluble BrC

Average mass absorption coefficient of individual PAH (parent-PAH or OPAH) ($MAC_{PAH,AV}$) in the wavelength range of 300-700 nm in this study is cited from Samburova et al. (Samburova et al., 2016) and Huang et al. (Huang et al., 2018), who use authentic standard to measure the absorption of each individual PAH, and then calculated the $MAC_{PAH,AV}$ by multiplying MAC_{λ} of individual PAHs with the power distribution of the solar spectrum and spectrally integrated (eq S1).

$$MAC_{PAH,AV} = \frac{\int_{300}^{700} MAC_{\lambda} \times I_0(\lambda) d_{\lambda}}{\int_{300}^{700} I_0(\lambda) d_{\lambda}} \qquad (eq\ S1)$$

where $I_0(\lambda)$ is the clear sky Air Mass 1 Global Horizontal solar irradiance (Levinson et al., 2010). Then the $MAC_{PAH,AV}$ were used to calculated the contribution of individual PAH to solar-spectrum-weighed absorption coefficient of WI-BrC.

Estimation of light absorption of elemental carbon

The light absorption of elemental carbon (EC) were estimated by the output data of thermal/optical carbon analyzer, which is similar to the determination of black carbon (BC) light absorption by Aethalometer(Ram and Sarin, 2009). At first, the optical-attenuation (ATN) at wavelength of 632 nm (wavelength used in carbon analyzer) caused by EC is governed by the Beer-Lambert's law, according to the eq S2.

$$ATN_{632,EC} = -\ln\left(\frac{I}{I_0}\right) \qquad (eq\ S2)$$

where I_0 and I is the intensity of incident light and transmitted light through the filter substrate and aerosols.

Then $b_{ap,632,EC}$ can be obtained after correcting the multiple scattering and shadowing effects following by eq S4:

$$b_{ap,632,EC} = \frac{ATN_{632,EC}}{C \times R(ATN)} \times \frac{A}{V} \qquad \text{(eq S3)}$$

where A is the effective filter area (414 cm^2), *V* is the volume of air sampled (m3). *C* depends on absorbing material, mixing state of aerosols, and filter substrate, and a value of 2.14 was suggested for quartz filters (Weingartner et al., 2003;Bond and Bergstrom, 2006). *R*(ATN) is determined by eq S4:

$$\mathrm{R(ATN)} = \left(\frac{1}{f} - 1\right) \times \frac{lnATN_{632,EC} - ln10\%}{ln50\% - ln10\%} + 1 \qquad (eq\ S4)$$

where f is set as 1.103 for wintertime and 1.114 for summertime(Sandradewi et al., 2008).

At last, light absorption coefficient of EC at wavelength of λ ($b_{ap,\lambda,EC}$) can be calculated by eq S5:

$$b_{ap,\lambda,EC} = b_{ap,632,EC} \times \left(\frac{632}{\lambda}\right)^{AAE} \qquad \text{(eq S5)}$$

where AAE is the absorption Ångström exponent of EC. Previous study suggested that AAE of EC is in the range of 0.8 and 1.4(Lack et al., 2013), and a value of 1.0

were used in this study.

Then the contribution of BrC relative to EC ($f_{BrC/EC}$, %) can be calculated by eq S6:

$$f_{BrC/EC} = \frac{\int I_0(\lambda)(1-e^{-b_{ap,\lambda,BrC}\times h_{ABL}})d_\lambda}{\int I_0(\lambda)(1-e^{-b_{ap,\lambda,EC}\times h_{ABL}})d_\lambda} \times 100 \qquad \text{(eq S6)}$$

Table S1 Average (±1σ) values Abs and MAC of WS-BrC and WI-BrC at the wavelength of 340 nm, 350 nm, 360 nm, 370 nm, and 380 nm in the $PM_{2.5}$ aerosols from the rural site of Guanzhong Basin.

	340 nm		350 nm		360 nm		370 nm		380 nm	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
$Abs_{WS\text{-}BrC}$ (Mm^{-1})	6.55±1.91	27.5±12.4	5.55±1.61	23.36±10.6	5.27±1.36	20.7±9.02	4.34±1.17	17.8±7.59	3.55±0.99	15.07±6.41
$Abs_{WI\text{-}BrC}$ (Mm^{-1})	4.22±2.67	33.6±20.5	3.61±2.3	28.0±17.1	3.19±2.04	23.9±14.61	2.87±1.81	20.1±12.4	2.63±1.64	17.5±10.8
$MAC_{WS\text{-}BrC}$ ($m^2\ g^{-1}$)	1.29±0.22	1.29±0.34	1.10±0.19	1.09±0.29	1.05±0.18	0.97±0.26	0.87±0.15	0.85±0.23	0.71±0.13	0.71±0.2
$MAC_{WI\text{-}BrC}$ ($m^2\ g^{-1}$)	2.60±1.42	1.46±0.51	2.23±1.24	1.21±0.42	1.97±1.11	1.03±0.35	1.79±1.00	0.87±0.29	1.64±0.92	0.76±0.25

Table ~~S1~~ S2 Molecular concentrations of the measured parent-PAHs, OPAHs, nitrophenols, and isoprene and α-/β-pinene derived products in the $PM_{2.5}$ samples in the rural site of Northwest China during summer and winter.

	Summer			Winter		
	Average	Daytime	Nighttime	Average	Daytime	Nighttime
(a) parent-PAHs						
phenanthrene	0.68±0.33	0.64±0.39	0.73±0.26	6.67±3.78	5.64±2.02	7.7±4.73
anthracene	0.05±0.01	0.05±0.01	0.05±0.02	0.38±0.14	0.38±0.14	0.38±0.14
fluoranthene	0.36±0.13	0.36±0.12	0.37±0.14	5.92±3.29	5.68±2.78	6.15±3.71
pyrene	0.34±0.12	0.36±0.14	0.32±0.1	5.84±3.4	5.4±2.6	6.28±4
benz(a)anthracene	0.29±0.13	0.33±0.13	0.26±0.12	5.39±4.18	4.09±2.25	6.69±5.15
chrysene / triphenylene	0.61±0.23	0.63±0.23	0.58±0.22	9.55±6.35	8.32±4.5	10.78±7.57
benzo(b)fluoranthene	1.33±0.87	1.76±1.03	0.9±0.31	13.88±9.11	11.8±6.07	15.96±10.97
benzo(k)fluoranthene	0.38±0.24	0.51±0.28	0.26±0.09	3.51±2.24	3.03±1.52	3.98±2.69
benzo(e)pyrene	1.06±0.65	1.38±0.74	0.74±0.31	8.43±5.56	7.23±3.77	9.63±6.7
benzo(a)pyrene	0.66±0.45	0.94±0.47	0.39±0.17	5.21±3.7	4.23±2.28	6.19±4.5
perylene	0.13±0.09	0.19±0.09	0.07±0.03	1.12±0.85	0.84±0.45	1.39±1.04
indeno[123-cd]pyrene	1.41±1.23	2.24±1.27	0.58±0.2	7.72±5.55	6.65±3.55	8.79±6.83
dibenz(a,h)anthracene	0.25±0.17	0.34±0.18	0.16±0.09	1.77±1.38	1.49±0.84	2.05±1.71
benzo(ghi)perylene	1.25±0.98	1.91±1	0.58±0.23	6.95±4.87	6.06±3.24	7.85±5.95
(b) OPAHs						
anthraquinone	1.84±0.36	1.67±0.29	2.01±0.34	34.33±14.3	32.3±10.16	36.35±17.25
benzathrone	1.89±2.11	3.13±2.39	0.64±0.22	14.9±9.84	13.44±6.89	16.36±11.91
benzo(a)anthracene-7,12-dione	0.61±0.35	0.79±0.38	0.43±0.17	6.05±3.81	5.15±2.49	6.95±4.61
5,12-naphthacenequione	0.32±0.24	0.48±0.26	0.17±0.06	4.14±3.14	3.09±1.78	5.18±3.79
6H-benzo(cd)pyrene-6-one	9.33±11.44	16.95±12.05	1.72±0.67	38.84±29.42	35.42±19.46	42.26±36.45
(c) Nitrophenols						
4-nitrophenol	0.52±0.16	0.45±0.12	0.59±0.17	15.2±10.17	11.08±4.26	19.32±12.44
3-methyl-4-nitrophenol	BDL*	BDL	BDL	9.69±6.18	6.54±1.77	12.84±7.31
4-nitrocatechol	0.42±0.15	0.42±0.16	0.43±0.14	37.79±38.93	18.67±9.87	56.92±46.92
4-methyl-5-nitrocatechol	BDL	BDL	BDL	9.92±10.76	4.78±2.56	15.05±13.12
(d)Isoprene-derived products						
2-methylglyceric acid	4.15±1.35	3.58±1.04	4.73±1.38	BDL	BDL	BDL
2-methylthreitol	3.55±2.3	2.48±1.65	4.61±2.36	BDL	BDL	BDL
2-methylerythritol	10.84±6.31	8.9±5.65	12.79±6.33	BDL	BDL	BDL
(e) α-/β-Pinene derived products						
pinonic acid	3.92±0.97	3.35±0.68	4.5±0.88	BDL	BDL	BDL
pinic acid	3.85±0.96	3.8±0.54	3.9±1.24	BDL	BDL	BDL
3-methyl-1,2,3-butanetricarboxylic acid	14.27±6.38	18±6.16	10.53±3.94	BDL	BDL	BDL

*BDL: below detection limit.

Table ~~S2~~ S3 The solar-spectrum-weighed individual $MAC_{PAH,av}$, and the contributions of individual parent-PAH and OPAH to WI-BrC light absorption.

	$MAC_{PAH,av}$ (m^2 g^{-1})	Contribution to WI-BrC light absorption (%)			
		Summer		Winter	
		Daytime	Nighttime	Daytime	Nighttime
(a) parent-PAHs					
phenanthrene	0.0256 [a]	0.004±0.004	0.005±0.003	0.003±0.001	0.003±0.001
anthracene	0.2801 [a]	0.003±0.003	0.004±0.002	0.003±0.001	0.002±0.001
fluoranthene	0.2834 [a]	0.019±0.018	0.026±0.016	0.037±0.014	0.026±0.004
pyrene	0.353 [a]	0.021±0.018	0.028±0.016	0.044±0.016	0.032±0.006
benz(a)anthracene	0.2842 [a]	0.014±0.01	0.018±0.01	0.025±0.01	0.025±0.01
chrysene / triphenylene	0.0883 [a]	0.009±0.007	0.012±0.007	0.016±0.006	0.013±0.003
benzo(b)fluoranthene	0.3475 [a]	0.064±0.045	0.076±0.042	0.092±0.031	0.078±0.018
benzo(k)fluoranthene	0.3475 [b]	0.019±0.014	0.022±0.013	0.024±0.008	0.02±0.004
benzo(e)pyrene	0.7709 [c]	0.109±0.072	0.135±0.073	0.124±0.04	0.104±0.024
benzo(a)pyrene	0.7709 [a]	0.07±0.046	0.074±0.046	0.071±0.027	0.063±0.021
perylene	1.7942 [a]	0.032±0.02	0.032±0.02	0.033±0.014	0.032±0.012
indeno[123-cd]pyrene	1.0711 [d]	0.171±0.095	0.152±0.085	0.156±0.057	0.122±0.045
dibenz(a,h)anthracene	0.2842 [a]	0.027±0.014	0.025±0.013	0.024±0.009	0.019±0.006
benzo(ghi)perylene	0.1821 [a]	0.01±0.006	0.011±0.007	0.009±0.004	0.007±0.003
subtotal		0.57±0.35	0.62±0.34	0.66±0.23	0.55±0.15
(b) OPAHs					
anthraquinone	0.1032 [a]	0.037±0.03	0.051±0.025	0.083±0.023	0.064±0.017
benzathrone	0.4385 [a]	0.082±0.043	0.068±0.04	0.131±0.049	0.097±0.028
benzo(a)anthracene-7,12-dione	0.3069 [e]	0.028±0.02	0.032±0.019	0.036±0.014	0.032±0.006
5,12-naphthacenequione	0.3069 [a]	0.013±0.007	0.013±0.007	0.021±0.008	0.021±0.008
6H-benzo(cd)pyrene-6-one	0.4385 [f]	0.345±0.243	0.181±0.1	0.336±0.142	0.231±0.101
subtotal		0.51±0.28	0.34±0.19	0.61±0.21	0.44±0.13

[a] MAC_{PAH_av} values comes from Samburova et al. (2016) (Samburova et al., 2016); [b] use value from benzo(b)fluoranthene; [c] use value from benzo(a)pyrene; [d] use value from indeno[1,2,3-cd] fluoranthene; [e] use value from 5,12-naphthacenequione; [f] use value from benzathrone.

Table S3 The contribution (%) of detected individual nitrophenol to light absorption of water-soluble BrC at the wavelength of 365 nm.

	Summer			Winter		
	Average	Daytime	Nighttime	Average	Daytime	Nighttime
4-nitrophenol	0.06±0.02	0.04±0.01	0.07±0.02	0.41±0.16	0.32±0.13	0.49±0.14
3-methyl-4-nitrophenol	BDL[a]	BDL	BDL	0.28±0.13	0.20±0.06	0.36±0.13
4-nitrocatechol	0.06±0.02	0.05±0.01	0.07±0.02	1.30±1.16	0.66±0.25	1.93±1.35
4-methyl-5-nitrocatechol	BDL	BDL	BDL	0.46±0.43	0.23±0.10	0.68±0.50
Total nitrophenols	0.12±0.03	0.10±0.02	0.14±0.02	2.44±1.78	1.41±0.29	3.47±2.03

[a] BDL: below detection limit.

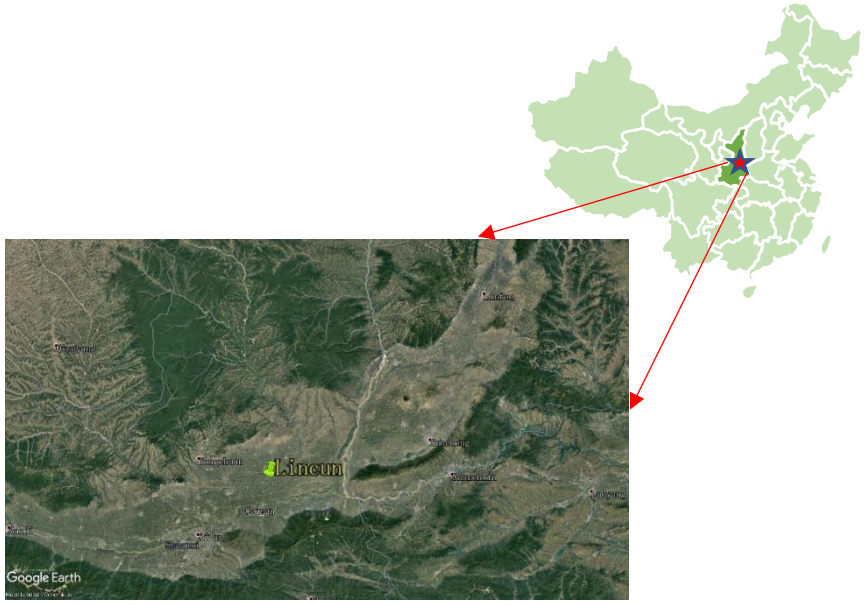

Figure S1 Location of the sampling site (Map data copyright @2019 Google).

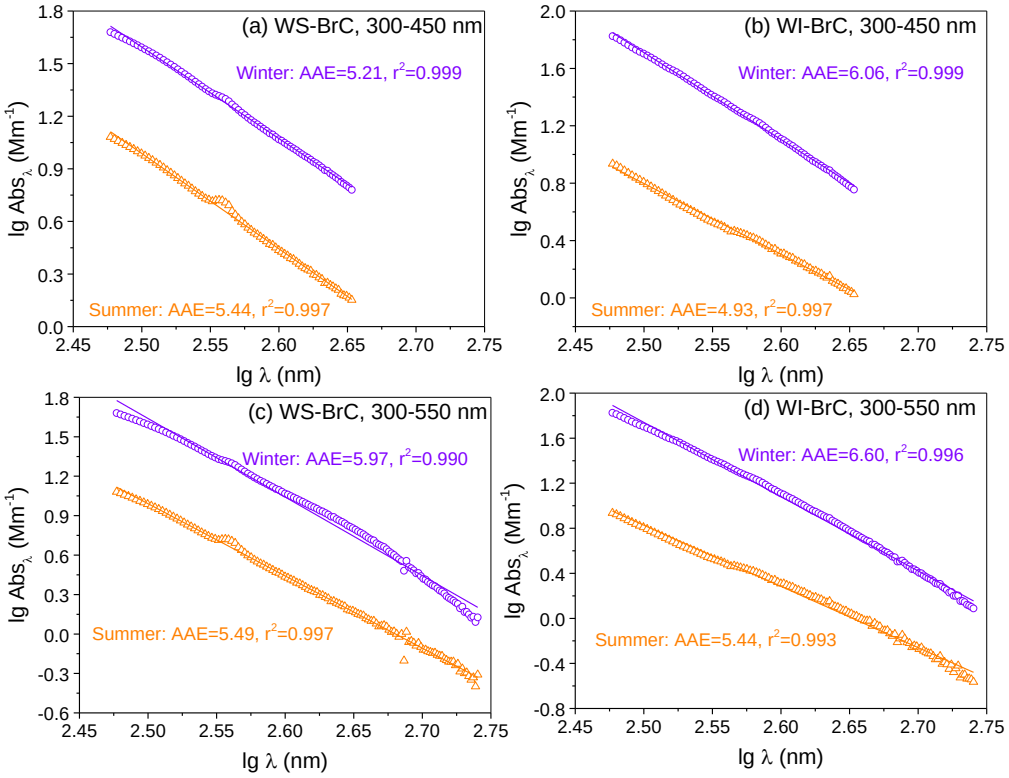

Figure S2 Comparison of Absorption Ångström exponent (AAE) calculation for average absorption spectrums in summer and winter in the wavelength of 300-450 nm (a and b) and 300-550 nm (c and d).

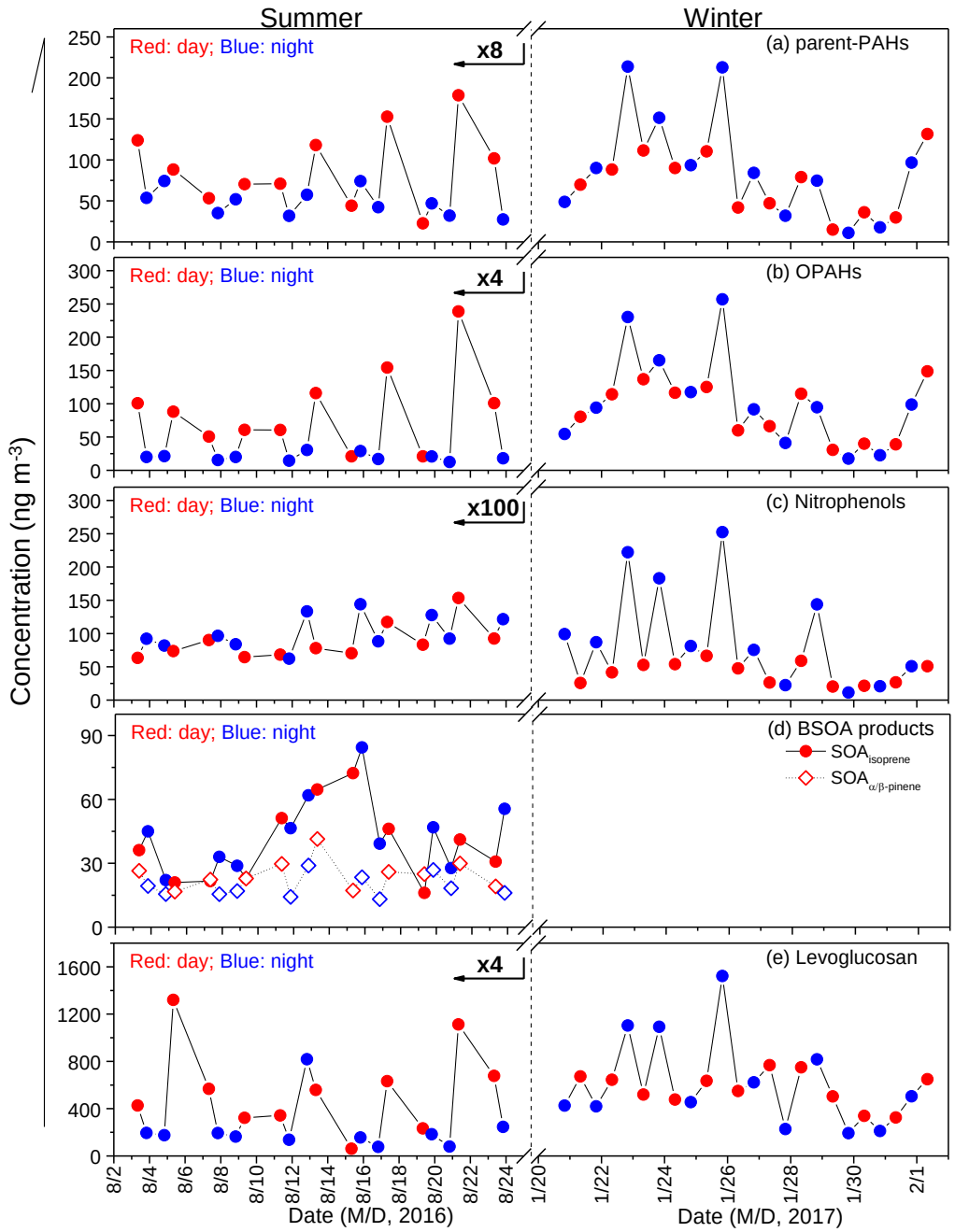

Figure S3 Temporal variation of subtotal concentrations of the measured parent-PAHs (a), OPAHs (b), nitrophenols (c), secondary products derived from isoprene ($SOA_{isoprene}$) and α-/β-pinene ($SOA_{\alpha-/\beta-pinene}$) (d), and levoglucosan (e) in $PM_{2.5}$.

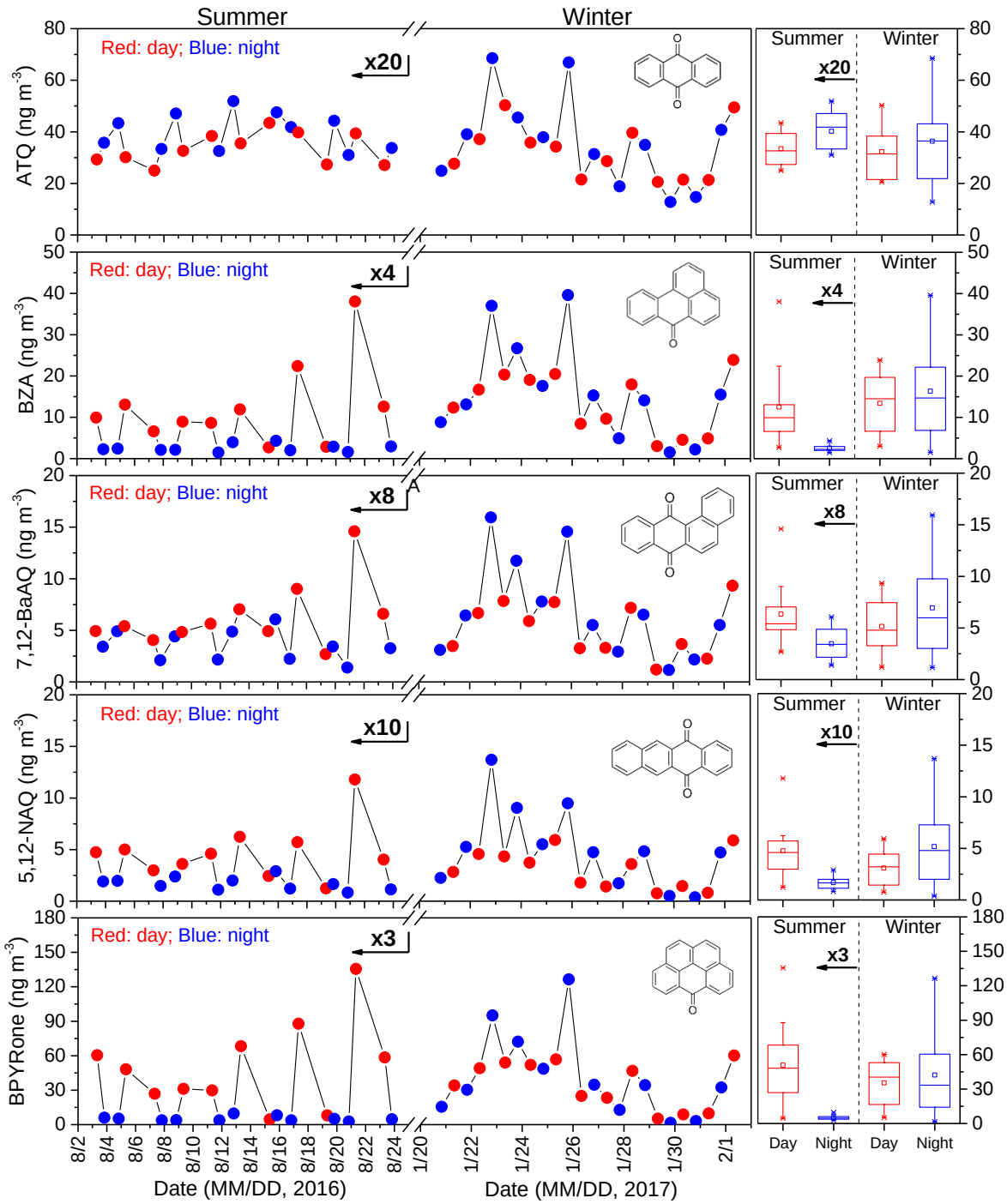

Figure S4 Time series and box charts of the five detected individual oxygenated-PAHs during the sampling period. The number of "×n" in the figures means summer concentrations were lower than winter data by a factor of n.

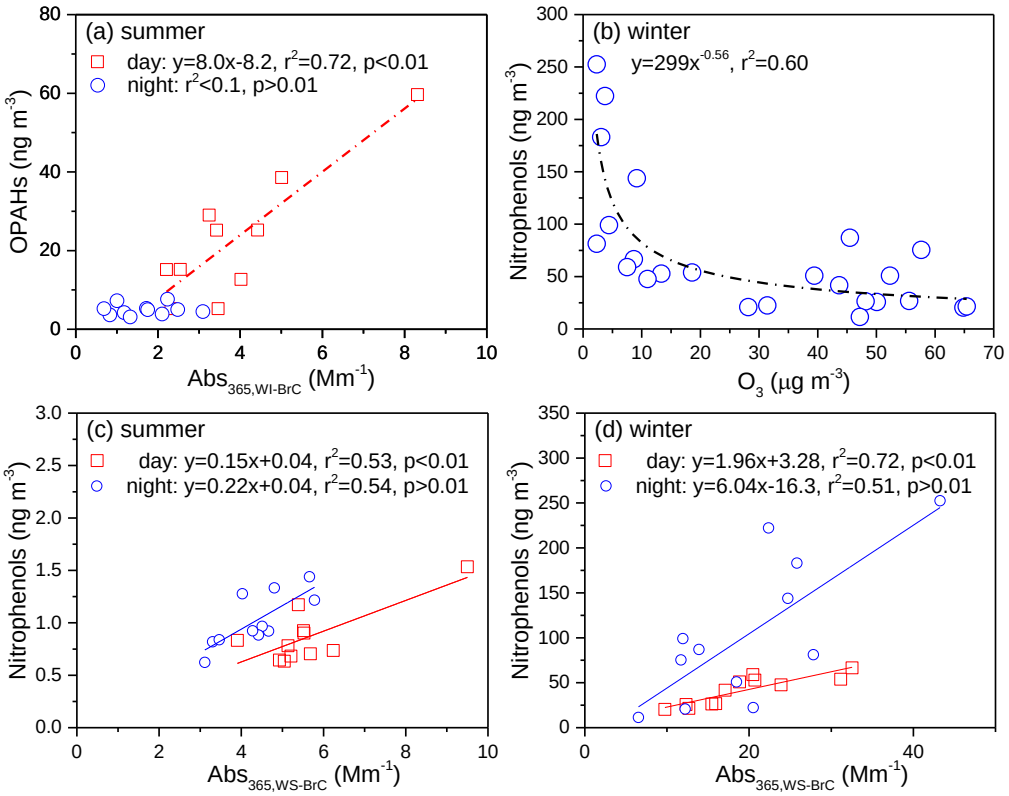

Figure S5 Relationships of OPAHs with $Abs_{365,WI\text{-}BrC}$ during daytime and nighttime in summer (a), nitrophenols with O_3 in winter (b), and nitrophenols with $Abs_{365,WS\text{-}BrC}$ during daytime and nighttime in summer (c) and winter (d).

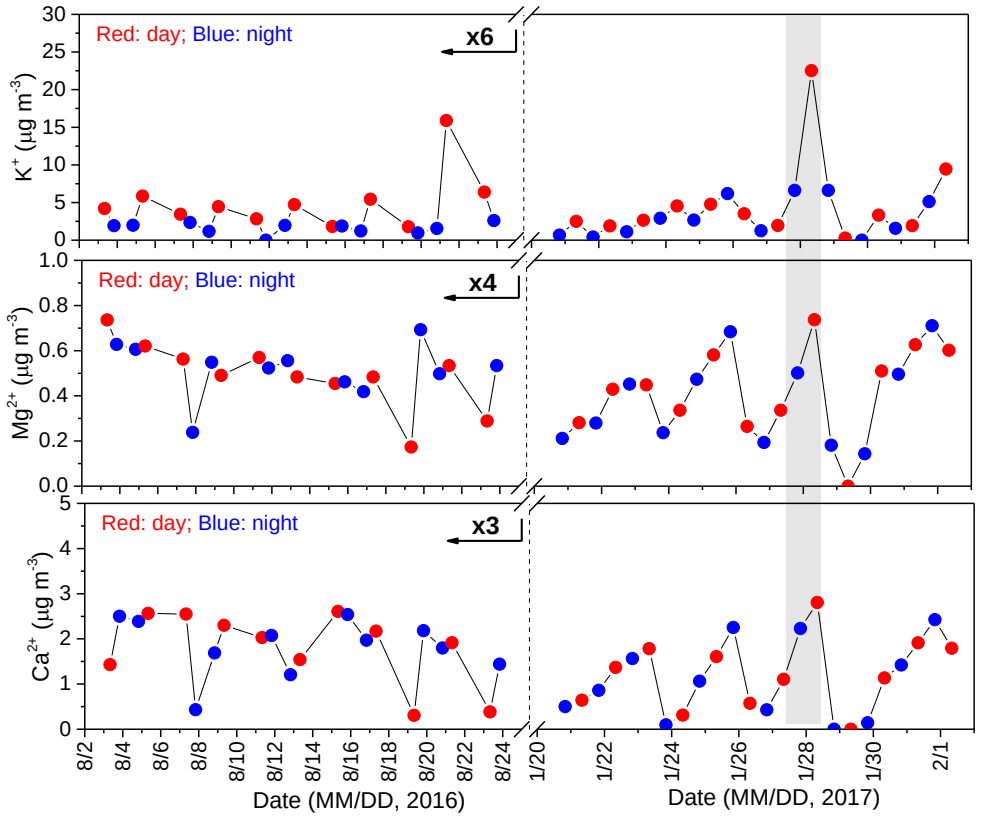

Figure S6 Temporal variation of water-soluble metal ions in $PM_{2.5}$ from the rural area of

Guanzhong Basin. Shadow denotes Chinese New Year eve and Spring festival, during which a large amount of fireworks were set off for celebration.

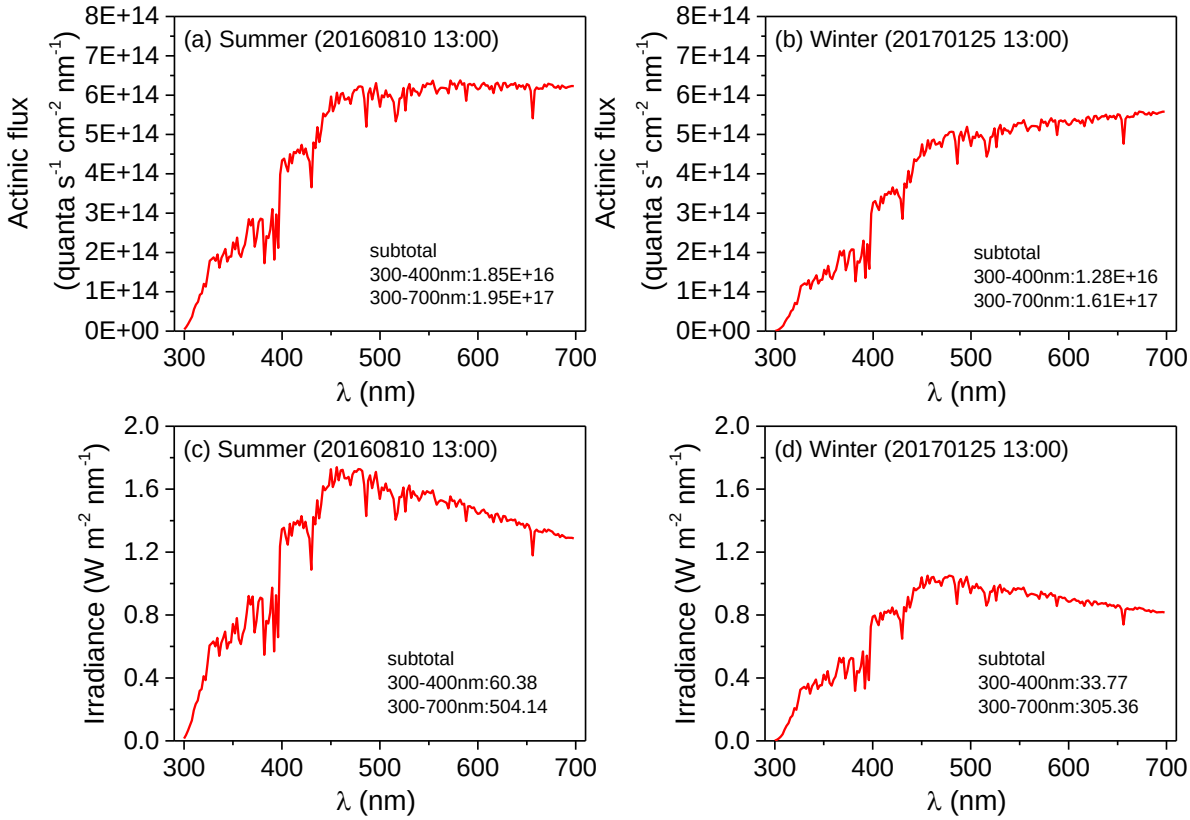

Figure S7 Total down-welling solar spectrum of actinic flux (a and b) and irradiance (c and d) at the sampling site at 20160810 13:00 and 20170125 13:00 (Beijing time) arrived. Data were provided by NCAR TUV Quick Calculator (http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/), assuming no cloud effect. Ground elevation is 0.4 km a.s.l. (about 50 m above ground level).

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