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Non-negligible secondary contribution to brown carbon in autumn and winter: inspiration from particulate nitrated and oxygenated aromatic compounds in urban Beijing

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Abstract

Nitrated aromatic compounds (NACs) and oxygenated derivatives of polycyclic aromatic hydrocarbons (OPAHs) play vital roles within brown carbon (BrC), influencing both climate dynamics and human health to a certain degree. The concentrations of these drug classes were analyzed in $PM_{2.5}$ from an urban area in Beijing during the autumn and winter of 2017–2018. There were four heavy haze episodes during the campaign; two of which happened prior to heating whereas the other two after heating. During the entire course of sampling, the mean total concentrations of the nine NACs and the eight OPAHs were 1.2-263 and 2.1-234 ng m^{-3}, respectively. The concentrations of both NACs and OPAHs were approximately 2-3 times higher in the heating period than before heating. For NACs, the relative molecular composition did not change significantly before and during heating, with 4-nitrocatechol and 4-nitrophenol demonstrating the highest abundance. For OPAHs, 1-Naphthaldehyde was the most abundant species before and during heating, while the relative proportion of Anthraquinone increased by more than twice, from 13% before heating to 31% during the heating. In Beijing's urban area during autumn and winter, significant sources of NACs and OPAHs have been traced back to automobile emissions and biomass-burning activities. Interestingly, it was observed that the contribution from coal combustion increased notably with the onset of heating during this period. It is worth noticing that the secondary generation of BrC was important throughout the whole sampling period, which was manifested by the photochemical reaction before

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heating and the aqueous reaction during heating. It was further found that the haze in autumn and winter was nitrate-driven before heating and SOC-driven when heating began, and the secondary formation of BrC increased significantly in pollution events, particularly during heating.

1 Introduction

As an important light-absorbing material, brown carbon (BrC) has garnered increasing attention in recent years (Jiang et al., 2023; Yi Chen et al., 2022; Song et al., 2022; Cai et al., 2022; Zhang et al., 2021; Liu et al., 2023; Ren et al., 2023; Ren et al., 2022). BrC could not only directly absorb solar energy, but also indirectly contribute to climate change by promoting the evaporation of water and the dispersal of clouds (Laskin et al., 2015; Huang et al., 2018). In addition to its significant climate effects, BrC also has potential adverse effects on human health on account of its strong mutagenic, cytotoxic, and carcinogenic properties (Teich et al., 2016).

Primary as well as secondary sources contribute to the atmospheric accumulation of BrC (Zhu et al., 2021). Direct emissions of primary BrC come from burning biomass and combustion of fossil fuels (Ni et al., 2021; Wang et al., 2020a; Lu et al., 2019a; Lu et al., 2019b). Oxidation and aging processes in the atmosphere produce secondary BrC (Wang et al., 2019; Wang et al., 2020c; Cheng et al., 2021; Jiang et al., 2023; Cai et al., 2022). Toluene, phenol, benzene, and other aromatic hydrocarbons can be oxidized by NO_3 or OH radical vapor phase in the presence of NO_x to produce nitrophenol or

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nitrocatechol (Olariu et al., 2002; Sato et al., 2007; Iinuma et al., 2010; Ji et al., 2017). VOCs emitted during biomass combustion and pyrolysis (such as cresol, catechol, methyl catechol, etc.) can be oxidized to produce nitro-aromatic hydrocarbons (Iinuma et al., 2010; Claeys et al., 2012; Finewax et al., 2018). Research on the source analysis of brown carbon (BrC) frequently focuses on examining two key constituents: the carbon component within humic-like substances (HULIS-C) and water-soluble organic carbon (WSOC). These components are often studied to understand the origins and properties of BrC in various environmental contexts. Secondary generation and burning of biomass are the two main sources of HULIS in Guangzhou and Shanghai (Fan et al., 2016; Zhao et al., 2016). In comparison with the water-insoluble BrC in the winter, the contribution of non-fossil sources (for instance burning biomass) to water-soluble BrC is 67% (Liu et al., 2018; Song et al., 2018). Coal combustion is presumably a significant source of HULIS in the winter, in addition to burning biomass and secondary generation (Tan et al., 2016). According to multiple studies conducted in Beijing, the primary contributor to WSOC is secondary generation, accounting for 54% of its composition. Following this, biomass burning contributes approximately 40%, while other primary emission sources contribute a smaller proportion, making up only 6% (Du et al., 2014). In Beijing, the percentages of biomass burning, coal combustion, and secondary generation that contribute to atmospheric HULIS are 47%, 15%, and 39%, respectively. The primary origins of HULIS show minimal association with motor vehicles and industrial emissions (Li et al., 2019). According to Ma et al., secondary generation is responsible for over 50% of HULIS in the non-heating season. Biomass burning

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represents 21% of the HULIS content during this period. However, in the heating season, approximately 40% of HULIS originates from biomass burning, while the remaining 60% is contributed by diverse combustion sources like coal burning, waste incineration, and vehicular emissions. Within this season, secondary generation accounts for about 19% of the HULIS content (Ma et al., 2018).

The research suggests that various sources contribute to BrC, but their relative impact varies depending on time and location. As a result, the chemical makeup, light absorption characteristics, and concentrations of BrC show considerable variability. This variability poses challenges in accurately assessing and forecasting the influence of these sources on radiation and climate changes (Wang et al., 2020b; Yan et al., 2018; Laskin et al., 2015). However, until recently, there was only a limited volume of research pertaining to the sources and pathways of BrC leading to their generation in the densely populated city environment. NACs and OPAHs are the primary focus of this study because several studies have noted that nitrogen-containing aromatics, polycyclic aromatic hydrocarbons (PAHs), and their derivatives are significant BrC chromophores (Huang et al., 2018; Cai et al., 2022; Yi Chen et al., 2022; Wu et al., 2020; Liu et al., 2023; Wang et al., 2020b). It is well-established that residential heating plays a significant role in the substantial increase of anthropogenic pollutant emissions during the winter season. From autumn to winter, there is a substantial rise in the emission of aromatics-derived secondary organic aerosol (Ding et al., 2017), and particle BrC is often detected especially in haze periods during the autumn and winter (Liu et al., 2023). This study was conducted in the autumn and winter of 2017-2018 in

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Beijing. Nine NACs and eight OPAHs were measured in $PM_{2.5}$ samples, with a focus on examining their sources, compositions, and concentration variations under various air conditions. Specifically, emphasis was placed on investigating the contribution of secondary generation to these two typical BrC species, particularly their involvement in particle pollution processes during autumn and winter.

2 Materials and Methods

2.1 Field observations

$PM_{2.5}$ was sampled at a height of 10m on the rooftop of a building at the Chinese Research Academy of Environmental Sciences (CRAES), Beijing, China (40º02′N, 116º24′E). Using a high-volume sampler (1.13 m^3 min^{-1}, Thermofisher Co., USA), $PM_{2.5}$ specimens were collected in the autumn and winter of 2017/2018. The sampling process was executed from 8:00 to 19:30 during the day and from 20:00 to 7:30 in the subsequent morning. The specimens and blanks were gathered using a pre-combusted quartz fiber filter (at 450 °C for 6 h). A total of 4 field blanks and 122 $PM_{2.5}$ samples were acquired. Individual filters were sealed in a bag made from an aluminum foil bag before sampling and analysis and placed in a freezer set at a temperature of -20 °C.

Using automatic equipment (CRAES Supersite for Comprehensive Urban Air Observation and Research), meteorological parameters such as air temperature (T, °C) and relative humidity (RH, %) along with gaseous pollutants (SO_2, NO_2, O_3, and CO) were observed and measured at the same time.

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2.2 Chemical analysis

The present study employed a pre-treatment comprising ultrasonic extraction and derivatization in an attempt to analyze the organic species in the specimens. The details of specimen extraction and derivatization have already been published (Wang et al., 2009; Ren et al., 2021; Ren et al., 2023). In brief, filter aliquots were sectioned and extracted with a methanol and dichloromethane (1:2 v/v,) mixture. Following the concentration of the extracts to dryness, derivatization was carried out using a mixture of N, O-bis-(trimethylsilyl) trifluoroacetamide [BSTFA+TMCS, (99:1), v/v] and pyridine (5:1, v/v). Lastly, the derivatized samples were examined using gas chromatography coupled with a mass spectroscopy detector (GC/MS: HP 7890A, HP 5975C, Agilent Co., USA). The extraction and derivatization methods described above allowed for the simultaneous measurement of the samples' polar and non-polar constituents.

Given that OPAHs and NACs were the main points of focus, this study investigated a total of eight OPAHs and nine NACs. The nine NACs included 2,4-dinitrophenol (2, 4-DNP), 4-nitrophenol (4NP), 3-methyl-4-nitrophenol (3M4NP), 4-nitrocatechol (4NC), 4-methyl-5-nitrocatechol (4M5NC), 4-nitroguaiacol (4NGA), 5-nitroguaiacol (5NGA), 3-nitro-salicylic acid (3NSA), and 5-nitro-salicylic acid (5NSA), while the eight OPAHs encompassed 9-fluorenone (9-FO), benzanthrone (BZA), 1-Naphthaldehyde (1-NapA), anthraquinone (ATQ), 1,4-chrysenequione (1,4-CQ), benzo(a)anthracene-7,12-dione (7,12-BaAQ), 5,12-naphthacenequione (5,12-NAQ) and 6H-benzo(cd)pyrene-6-one (BPYRone).

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The elemental carbon (EC) and organic carbon (OC) content of individual $PM_{2.5}$ filter samples were analyzed using an Atmoslytic Inc. DRI model 2001 Carbon Analyzer. This analysis followed the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol, involving the examination of a 0.526 cm^2 punch from each specimen. The specifics of the above-described techniques have been documented in literature (Li et al., 2016; Ren et al., 2021).

2.3 Evaluation of secondary BrC

In this study, the contributions of secondary oxidation to the detected NACs and OPAHs were evaluated by using a CO-tracer method, which is comparable to the EC-tracer used for secondary OC quantification. Various methodologies have been similarly adopted successfully in other studies (Liu et al., 2023; Cai et al., 2022). Equation 1 and Equation 2 were respectively used to evaluate the secondary formation of NACs and OPAHs.

$$[NACs]_s = [NACs]_t - ([NACs]_t/[CO])_{pri} \times [CO] \quad (1)$$

$$[OPAHs]_s = [OPAHs]_t - ([OPAHs]_t/[CO])_{pri} \times [CO] \quad (2)$$

$[NACs]_s$ and $[NACs]_t$ in Equation 1 refer to the NACs concentration produced by secondary oxidation and the total amount of NACs, respectively. $([NACs]_t/[CO])_{pri}$ represents the primary emission ratio of NACs in relation to combustion. This calculation assumes that the primary source was predominant during the period, with minimal secondary production. The $([NACs]_t/[CO])_{pri}$ was calculated in this work by fitting the 15% lowest $[NACs]_t/[CO]$ ratios observed during the entire sampling

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duration. In equation 2 the concentration of OPAHs produced by secondary oxidation and the total observed OPAHs are denoted by $[OPAHs]_s$ and $[OPAHs]_t$ respectively. The concentration of CO is denoted by [CO], while the primary emission ratio of OPAHs in relation to combustion is represented by $([OPAHs]/[CO])_{pri}$, which was calculated by fitting the lowest 15% $[OPAHs]_t/[CO]$ ratios observed in the entire sample interval.

3 Results and discussion

3.1 Variations in major components of $PM_{2.5}$ with respect to meteorological conditions and gaseous pollution

Based on the Beijing heating time, the entire period of the study was divided into two phases: before heating (18 October to 14 November 2017) and during heating (15 to 23 November 2017; 23 December 2017 to 17 January 2018). Table 1 and Fig. 1 present the temporal fluctuations in meteorological factors, gaseous pollutant concentrations, and the main $PM_{2.5}$ components in the two phases. The temperature (T) and relative humidity (RH) were higher before heating (11 ± 3.8 ℃ and 49 ± 26%) than during heating (1.9 ± 4.4 ℃ and 23 ± 15%), with average values amounting to 5.9 ± 5.9 ℃ and 35 ± 25%, respectively. SO_2 concentrations during heating (4.3 ± 1.5 ppb) were more than twice that before heating (2.1 ± 0.8 ppb), presumably because of the increase in household coal burning for heating. The levels of NO_2 and NO remained consistent before and during heating, suggesting that these pollutants were minimally

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impacted by heating and were primarily influenced by mobile sources in Beijing. This pattern seems to remain stable in the short term.

Fig.2 shows the variation in the chemical makeup of $PM_{2.5}$ in the entire sampling period, before and during hearting, respectively. Secondary inorganic aerosols (SIA, i.e. SO_4^{2-}, NH_4^+, and NO_3^-) were identified as the leading constituents of $PM_{2.5}$, followed by OM (1.6 times OC), with an average of 31.5% and 20.4% in the whole sampling, respectively (Fig. 2a). Even though the $PM_{2.5}$ concentrations remained relatively stable during this period (as indicated in Table 1 and Fig. 2), there were significant changes observed in the concentrations of SIA and OM, as well as their relative contributions to $PM_{2.5}$. Before heating, SIA accounted for 41.9% of $PM_{2.5}$, which notably decreased to 23.1% during heating. This decline was primarily evident in the reduction of NO^{3-}. Specifically, SO_4^{2-}, NO_3^-, and NH_4^+ were measured at 5.5, 16, and 5.4 μg m^{-3}, respectively, according to Table 1. These values constituted 8.7%, 24.7%, and 8.5% of $PM_{2.5}$ before heating, as shown in Fig. 2b. Their concentrations decreased to 4.3, 6.8, and 4.2 μg m^{-3} (Table 1). The relative contributions of NO_3^- to $PM_{2.5}$ dropped dramatically to 10.3% during heating, amounting to a drop of nearly 60%. Both SO_4^{2-} and NH_4^+ experienced a roughly 25% decrease in their relative contributions to $PM_{2.5}$, as illustrated in Fig. 2c. The relative abundance of OM to $PM_{2.5}$ increased from 18.6% before heating to 21.9% during heating, with the average mass concentration of OC showing an increase from 7.4 to 9.1 μg m^{-3} in the corresponding duration. The OC/EC ratio also increased by 63% from 2.7 ± 3.3 before heating to 4.4 ± 3.7 during heating. These significant changes in SIA and OM, including concentrations and the relative

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209 contributions to $PM_{2.5}$, showed that primary organic aerosols and/or VOCs emissions
210 were the leading contributors during the heating seasons due to household heating (Tan
211 et al., 2018). The rise in mass concentrations of K^+ and Cl^- indicated additional burning
212 activities occurring during heating, aside from coal combustion, such as biomass
213 burning (Bai et al., 2023; Li et al., 2022).

214

Table 1. Gaseous pollution concentrations and meteorological parameters and chemical constituents of $PM_{2.5}$ during the sampling periods in Beijing.

	The whole sampling	Before heating period	During heating period
	N=122	18/10–14/11, 2017	15/11–23/11, 2017 23/12, 2017–17/1, 2018
		N=56	*N*=66
Meteorological parameters			
Temperature, ℃	5.9 ± 5.9 ((-7.5) – 16)	11 ± 3.8 (1.2 – 16)	1.9 ± 4.4 ((-7.5) – 11)
Relative humidity, %	35 ± 25 (7.1 – 99)	49 ± 26 (11 – 99)	23 ± 15 (7.1 – 67)
Gaseous pollutants, ppb			
SO_2	3.2 ± 1.6 (1.1 – 7.9)	2.1 ± 0.8 (1.1 – 4.8)	4.3 ± 1.5 (2.2 – 7.9)
NO_2	26 ± 13 (4.6 – 56)	25 ± 11 (4.6 – 43)	26 ± 14 (5.5 – 56)
NO	26 ± 28 (2.4 – 136)	28 ± 30 (2.4 – 136)	25 ± 26 (2.7 – 116)
CO	0.64 ± 0.55 (0.03 – 2.7)	0.81 ± 0.42 (0.12 – 1.6)	0.50 ± 0.61 (0.03 – 2.7)
Major components of $PM_{2.5}$, μg m^{-3}			
$PM_{2.5}$	65 ± 40 (6.1 – 195)	64 ± 39 (6.1 – 175)	66 ± 41 (8.6 – 195)
OC	8.3 ± 5.0 (0.99 – 26)	7.4 ± 3.9 (1.0 – 18)	9.1 ± 5.8 (1.8 – 26)
EC	4.7 ± 4.7 (0.11 – 25)	4.9 ± 3.8 (0.11 – 17)	4.5 ± 5.3 (0.18 – 25)
OC/EC	3.7 ± 3.6 (0.96 – 21)	2.7 ± 3.3 (0.96 – 21)	4.4 ± 3.7 (1.0 – 17)
SO_4^{2-}	4.8 ± 4.2 (0.85 – 25)	5.5 ± 3.5 (0.86 – 13)	4.3 ± 4.7 (0.85 – 25)
NO_3^-	11 ± 14 (0.09 – 58)	16 ± 16 (0.09 – 58)	6.8 ± 8.8 (0.29 – 37)
NH_4^+	4.7 ± 4.9 (0.02 – 20)	5.4 ± 5.4 (0.02 – 20)	4.2 ± 4.5 (0.19 – 20)
K^+	0.43 ± 0.39 (0.02 – 2.2)	0.38 ± 0.27 (0.03 – 1.1)	0.48 ± 0.46 (0.02 – 2.2)
Cl^-	1.5 ± 1.6 (0.06 – 9.2)	1.0 ± 0.98 (0.06 – 4.5)	1.9 ± 2.0 (0.13 – 9.2)

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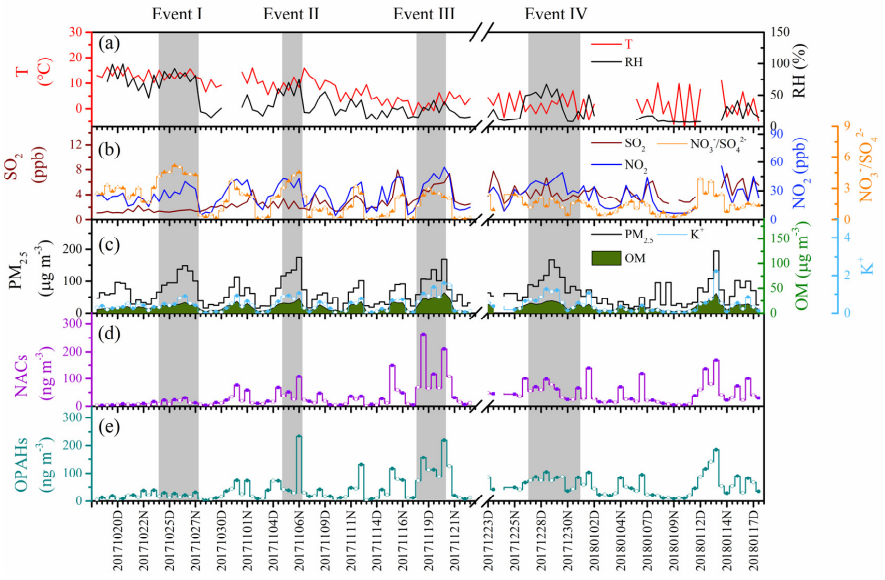

Time (YYYYMMDD; D: daytime, N: nighttime)

Fig.1 Time series of (a) RH and T, (b) SO_2 and NO_2, (c) $PM_{2.5}$, OM, and K^+, (d) NACs and (e) OPAHs in the autumn and winter of urban Beijing. (Daytime is denoted by empty marks and the nighttime is represented by solid marks in the panel b–e. The pollution episodes, with elevated concentrations of daily $PM_{2.5}$ more than 75μg m^{-3} in two successive days, have been marked in light gray).

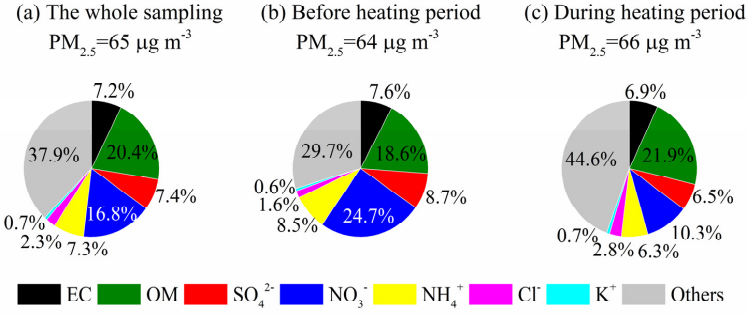

Fig.2 Chemical constitution of $PM_{2.5}$ in the entire sampling period (a), before (b), and during (c) heating periods, respectively.

3.2 Concentration and composition variations of BrC compounds

This work quantified nine NACs and eight OPAHs. The corresponding

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concentrations and compositions have been presented in Fig. 3 and Table S1 (supporting information).

As seen in Table S1, during the entire sampling, the total concentrations of NACs (∑9NACs) and their corresponding contribution to OM (∑9NACs/OM) respectively averaged to 38 (1.2–263) ng m^{-3} and 0.25 (0.03–0.86) %. ∑9NACs and ∑9NACs/OM respectively averaged 53 (4.5–263) ng m^{-3} and 0.33 (0.09–0.86) % during heating, both values are two times higher in magnitude in comparison to those measured before heating (averaged 20 (1.2–108) ng m^{-3} and 0.15 (0.03–0.4) %, respectively). ∑9NACs exhibited a nighttime increase, reaching approximately twice the levels observed during daytime throughout the entire campaign (Fig. 3a). The observed difference between day and night is consistent with our previous research (Ren et al., 2022). However, the relative molecular composition of the total nine NACs in $PM_{2.5}$ did not manifest any significant change (Fig.4a, c), 4-Nitrophenol (4NP) was found to have the highest concentration among all species, accounting for 44% and 42% of the total NACs before and during heating, followed by 4-nitrocatechol (4NC) which accounted for 21% before heating and 23% during heating. These findings align with the dominant species observed in previous studies (Ren et al., 2022; Ren et al., 2023; Li et al., 2020) however the values were much higher in comparison to those found in our earlier work (Ren et al., 2022) at the same sample site during the spring (8.6 (0.48–27) ng m^{-3}) and summer (8.5 (1.0–16) ng m^{-3}). It's plausible that seasonal variations in NACs are linked to emission sources, formation pathways, and weather conditions. In this study, the overall abundance of the ∑9NACs appeared to align closely with measurements from earlier

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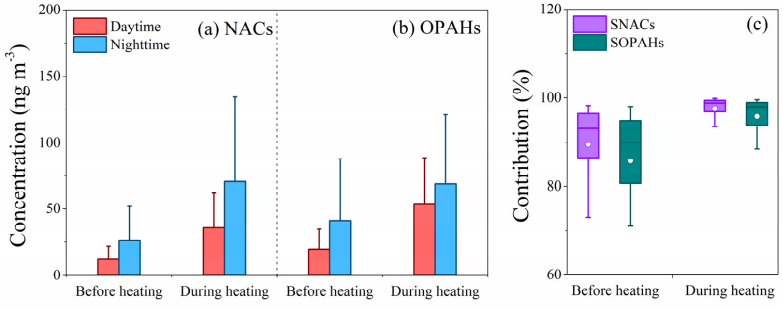
252 studies conducted during winter in Beijing (74 ± 51 ng m^{-3} in winter, 20 ± 12 ng m^{-3} in
253 autumn) (Li et al., 2020) and Jinan (48 ± 26 ng m^{-3} in winter, 9.8 ± 4.2 ng m^{-3} in autumn,)
254 (Wang et al., 2018), but are significantly higher than those measured for Xi'an (17 ± 12
255 ng m^{-3}) and Hong Kong (12 ± 14 ng m^{-3}) in winter (Wu et al., 2020; Chow et al., 2015).
256 In contrast to studies conducted abroad, the levels of ∑9NACs in this particular study
257 tended to be higher Germany showed 16 ng m^{-3}, while in the UK, levels were around
258 19 ng m^{-3}. Belgium recorded levels of 32 ng m^{-3} in winter and 13 ng m^{-3} in autumn.
259 (Teich et al., 2017; Mohr et al., 2013; Kahnt et al., 2013). This indicates that it is urgent
260 to further reduce the concentration of contaminant precursors in China.



261
262 Fig.3 NACs and OPAHs concentrations (a,b) and contributions of secondary
263 formation (SNACs, SOPAHs) to the total (c) before and during heating periods.

264 Throughout the sampling, the total concentrations of OPAHs (∑8OPAHs)
265 averaged 47 (1.2–234) ng m^{-3} whereas the mean value for their total contribution to OM
266 (∑8OPAHs/OM) was 0.33 (0.06–0.81) % (Table S1). These values were both slightly
267 higher than those of NACs in this work. ∑8OPAHs and ∑8OPAHs/OM respectively
268 averaged 61 (6.9–218) ng m^{-3} and 0.40 (0.18–0.58) % during heating. These values are
269 almost twice as much as those measured before heating (averaging 31 (2.1–234) ng m^{-3}
270 and 0.24 (0.06–0.81) %, respectively). Like the ∑9NACs, the combined levels of

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∑8OPAHs were higher during nighttime compared to daytime, averaging about twice as high before heating and 1.3 times during heating, as indicated in Fig. 3b. Among the eight OPAHs studied, 1-NapA constituted the highest proportion before (60%) and during (36%) heating. However, the relative proportion of ATQ more than doubled, increasing from 13% before heating to 31% during heating, as depicted in Fig. 4b and d. The average concentrations of ∑8OPAHs were higher than those recorded for other Chinese urban sites, including Guangzhou (23 ng m^{-3}) and Xi'an (54 ng m^{-3}) (Ren et al., 2017) as well as higher than those documented for the south (41.8 ng m^{-3}, traffic site) (Alves et al., 2017) and central (~10 ng m^{-3}) European cities (Lammel et al., 2020). The average concentrations of ∑8OPAHs were also higher than those recorded for Mainz, Germany (0.047-1.6 ng m^{-3}) and Thessaloniki, Greece (0.86-4.3 ng m^{-3}) (Kitanovski et al., 2020).

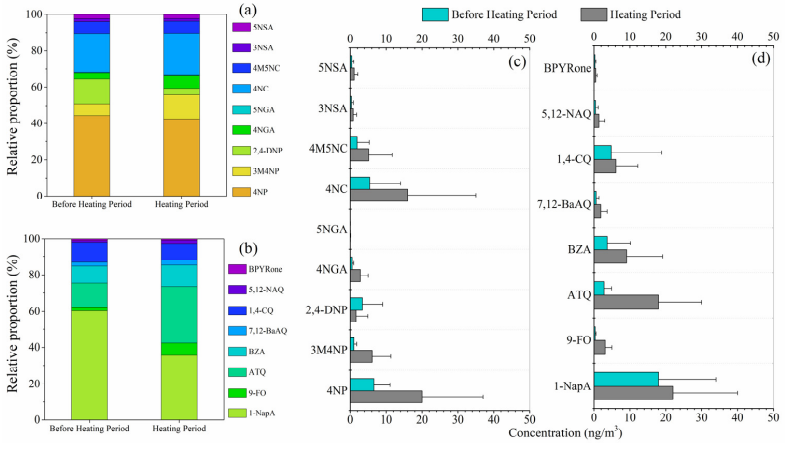

Fig.4 Comparison of measurements before and during the heating period at the urban site of Beijing, including (a) Relative proportion of NAC species, (b) Relative proportion of OPAH species, (c) NAC concentrations, and (d) OPAH concentrations. (4NP: 4-nitrophenol, 3M4NP: 3-methyl-4-nitrophenol, 2, 4-DNP: 2,4-dinitrophenol, 4NGA: 4-nitroguaiacol, 5NGA: 5-nitroguaiacol, 4NC: 4-nitrocatechol, 4M5NC: 4-

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methyl-5-nitrocatechol, 3NSA: 3-nitro-salicylic acid, 5NSA: 5-nitro-salicylic acid; 1-NapA: 1-Naphthaldehyde, 9-FO: 9-fluorenone, ATQ: anthraquinone, BZA: benzanthrone, 7,12-BaAQ: benzo(a)anthracene-7,12-dione, 1,4-CQ: 1,4-chrysenequione, 5,12-NAQ: 5,12-naphthacenequione, and BPYRone: 6H-benzo(cd)pyrene-6-one)

3.3 Sources and formation of BrC compounds

The relation between individual and total species and the associated pollutants—levoglucosan, K^+, SO_2, NO_2, O_3, RH, and SIA—was examined according to the data findings for the Pearson correlations shown in Table 2 (for NACs) and Table 3 (for OPAHs) to provide additional clarity regarding the source and formation of NACs and OPAHs. The strong correlations observed throughout the entire campaign between levoglucosan (an organic tracer associated with biomass burning), K^+ (an inorganic tracer linked to biomass burning), and NO_2 with total NACs and all identified NAC species indicate that both automobile emissions and biomass burning played significant roles in the accumulation of NACs in urban Beijing during autumn and winter. The correlation between NACs and SO_2 was significantly higher during heating ($r=0.275$, $p<0.05$) compared to pre-heating, indicating that coal combustions play a more significant role in NAC formation after heating commences.

In addition to these primary pollutants, NACs were also significantly correlated with some secondary pollutants. Before heating, there existed a strong positive association ($r=0.692$, $p<0.01$) between NACs and O_3. However, this association changed considerably after heating, becoming notably negative ($r=-0.303$, $p<0.05$). NACs and RH concurrently displayed a strong positive correlation ($r=0.548$, $p<0.01$)

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312 during heating. Along with SO_4^{2-}, NO_3^-, and NH_4^+, total NACs also exhibited high
313 positive correlation, particularly while heating (r=0.373, p<0.01; r=0.504, p<0.01;
314 r=0.513, p<0.01, respectively). The overall concentrations of OPAHs and NACs
315 throughout the campaign exhibited substantial correlations (r=0.830, p<0.01 before
316 heating; r=0.895, p<0.01 during heating) (Table 3, Fig. S1). This suggests that their
317 sources and/or influencing variables were comparable. Specifically, throughout the
318 entire campaign, both total OPAHs and all identified OPAH species exhibited a strong
319 correlation with levoglucosan, K^+, and NO_2. This implies that automobile emissions
320 and biomass burning played significant roles as sources of OPAHs. OPAHs and SO_2
321 (r=0.365, p<0.01) were determined to be more strongly correlated during heating than
322 before heating, suggesting the contribution of coal combustions to OPAHs becomes
323 significant when heating begins. Moreover, the correlation between OPAHs and O_3 was
324 significantly positive before heating (r=0.563, p<0.01), whereas it was significantly
325 negative during heating (r=-0.385, p<0.01). Furthermore, it was discovered that
326 throughout the heating phase, OPAHs and RH had a substantial positive correlation
327 (r=0.578, p<0.01). Total OPAHs also showed good correlations with SO_4^{2-}, NO_3^-, and
328 NH_4^+, especially during heating period (r=0.477, p<0.01; r=0.658, p<0.01; r=0.658,
329 p<0.01; respectively).

330 The observed phenomena, involving photooxidation before heating and aqueous
331 reactions during heating, strongly suggest a significant role in the secondary creation
332 of BrC throughout the entire sampling period. Earlier studies have highlighted that in
333 certain regions, the primary mechanism driving the formation of nitro-aromatic

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hydrocarbons involves the gaseous phase oxidation of VOC precursors from anthropogenic sources, such as toluene and benzene (Olariu et al., 2002; Sato et al., 2007; Yuan et al., 2016; Ji et al., 2017; Liu et al., 2023). According to a recent study, for instance, NACs are mostly generated at a rural location on China's Chongming Island through gaseous-phase photooxidation (Liu et al., 2023). Aqueous reaction is also a key pathway for the formation of BrC (Zhang et al., 2020; Cheng et al., 2021; Jiang et al., 2023). Zhang et al., suggested that the aqueous formation of anthropogenic secondary organic carbon was a key source of atmospheric BrC in Xi'an (Zhang et al., 2020). Wang et al.'s field observations in urban Beijing revealed that the aqueous reaction is a significant mechanism for the secondary synthesis of nitro-aromatic hydrocarbons during summer temperatures with high relative humidity (Wang et al., 2019).

Table 2 Correlations between NACs and meteorological parameters, gas pollutants, and aerosol components before (n=56) and during the heating period (n=66).

Before heating period		levoglucosan	K^+	SO_2	NO_2	O_3	RH	SO_4^{2-}	NO_3^-	NH_4^+
NACs	∑9NACs	0.897**	0.738**	0.210	0.714**	0.692**	0.170	0.359**	0.369**	0.190
	4NP	0.784**	0.699**	0.249	0.715**	0.649**	0.118	0.345**	0.372**	0.207
	3M4NP	0.752**	0.526**	0.290*	0.575**	0.511**	-0.011	0.184	0.191	0.029
	2,4-DNP	0.436**	0.353**	0.310*	0.463**	0.492**	-0.151	0.034	-0.048	-0.166
	4NGA	0.545**	0.361**	0.438**	0.560**	0.524**	-0.137	-0.016	-0.025	-0.131
	5NGA	0.582**	0.355**	0.114	0.343**	0.433**	0.005	0.120	0.139	0.044
	4NC	0.897**	0.748**	0.064	0.641**	0.617**	0.308*	0.448**	0.486**	0.325*
	4M5NC	0.885**	0.668**	0.076	0.579**	0.577**	0.252	0.364**	0.413**	0.261
	3NSA	0.791**	0.678**	0.129	0.553**	0.495**	0.214	0.457**	0.515**	0.331*
	5NSA	0.737**	0.596**	0.219	0.594**	0.553**	0.085	0.279*	0.316*	0.125
During heating period		levoglucosan	K^+	SO_2	NO_2	O_3	RH	SO_4^{2-}	NO_3^-	NH_4^+
NACs	∑9NACs	0.888**	0.786**	0.275*	0.481**	-0.303*	0.548**	0.373**	0.504**	0.513**
	4NP	0.812**	0.725**	0.262*	0.471**	-0.296*	0.586**	0.390**	0.489**	0.511**
	3M4NP	0.756**	0.655**	0.248	0.374**	-0.225	0.613**	0.318**	0.397**	0.462**

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	2,4-DNP	0.537**	0.495**	0.280*	0.417**	-0.304*	0.199	0.136	0.247*	0.136
	4NGA	0.672**	0.406**	0.229	0.274*	-0.206	0.201	-0.047	0.074	0.081
	5NGA	0.275*	0.208	-0.028	0.190	0.026	-0.006	0.114	0.100	0.125
	4NC	0.894**	0.804**	0.248	0.454**	-0.290*	0.520**	0.378**	0.523**	0.530**
	4M5NC	0.882**	0.736**	0.246	0.434**	-0.244	0.430**	0.283*	0.421**	0.422**
	3NSA	0.788**	0.910**	0.348**	0.681**	-0.410**	0.577**	0.707**	0.888**	0.828**
	5NSA	0.820**	0.866**	0.268*	0.629**	-0.377**	0.599**	0.680**	0.846**	0.828**

**significant correlation at the 0.01 level;

*significant correlation at the 0.05 level;

From the above analysis, it is evident that there is a good correlation between these two aromatic compounds and levoglucosan, as well as SO_2. Since levoglucosan and SO_2 are long-lived and inert chemicals in the atmosphere (Cai et al., 2022), it was not possible to determine with certainty whether NACs and OPAHs originated predominantly from direct emission from the coal and biomass combustion or by secondary oxidation of the precursors produced as a result of these processes. Equations 1 and 2's outcomes indicated that in Beijing's urban areas during fall and winter, NACs and OPAHs were predominantly of secondary origin. Throughout the entire sampling period, secondary formation accounted for 17% to 99% (average of 80%) of NACs and 8.9% to 99% (average of 73%) of OPAHs, as depicted in Fig. 3c. Notably, the secondary fraction for OPAHs increased by 10.4% from 86% to 96%, while the secondary fraction for NACs rose by 8.9% from 90% before heating to 98% during heating. Earlier studies have highlighted the presence of significant levels of secondary particle BrC during autumn and winter, particularly during haze periods (Ding et al., 2017; Liu et al., 2023), and the results of this work corroborate well with the earlier studies. Moreover, the good correlations between OPAHs and NACs with O_3 before heating and with RH during heating, confirm the importance of photochemical and aqueous oxidation in these two

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364 different periods.

365

Table 3 Correlations between OPAHs and meteorological parameters, gas pollutants, and aerosol components before (n=56) and during the heating period (n=66).

Before heating period		∑9NACs	levoglucosan	K^+	SO_2	NO_2	O_3	RH	SO_4^{2-}	NO_3^-	NH_4^+
OPAHs	∑8OPAHs	0.830**	0.865**	.605**	0.188	0.563**	0.563**	0.143	0.244	0.283*	0.139
	1-NapA	0.844**	0.870**	.621**	0.211	0.640**	0.622**	0.174	0.213	0.238	0.096
	9-FO	0.775**	0.785**	.646**	0.283*	0.558**	0.573**	0.059	0.183	0.235	0.119
	ATQ	0.633**	0.694**	.497**	0.392**	0.477**	0.483**	-0.018	0.042	0.061	-0.024
	BZA	0.686**	0.759**	.573**	0.232	0.537**	0.594**	0.110	0.177	0.206	0.117
	7,12-BaAQ	0.821**	0.865**	.685**	0.189	0.591**	0.622**	0.187	0.325*	0.356**	0.224
	1,4-CQ	0.636**	0.646**	.406**	0.041	0.303*	0.290*	0.102	0.259	0.309*	0.174
	5,12-NAQ	0.694**	0.752**	.563**	0.227	0.511**	0.559**	0.091	0.184	0.214	0.110
	BPYRone	0.827**	0.870**	.662**	0.131	0.590**	0.616**	0.226	0.345**	0.398**	0.255
Heating period		∑9NACs	levoglucosan	K^+	SO_2	NO_2	O_3	RH	SO_4^{2-}	NO_3^-	NH_4^+
OPAHs	∑8OPAHs	0.895**	0.931**	0.877**	0.365**	0.678**	-0.385**	0.578**	0.477**	0.658**	0.658**
	1-NapA	0.752**	0.774**	0.659**	0.248	0.547**	-0.378**	0.332*	0.332**	0.498**	0.446**
	9-FO	0.478**	0.457**	0.342**	0.305*	0.302*	-0.020	0.131	-0.013	0.167	0.250*
	ATQ	0.780**	0.797**	0.815**	0.426**	0.668**	-0.372**	0.656**	0.466**	0.642**	0.684**
	BZA	0.840**	0.881**	0.829**	0.332**	0.570**	-0.273*	0.577**	0.431**	0.568**	0.577**
	7,12-BaAQ	0.801**	0.856**	0.896**	0.391**	0.633**	-0.299*	0.655**	0.531**	0.689**	0.710**
	1,4-CQ	0.703**	0.780**	0.791**	0.244	0.597**	-0.282*	0.624**	0.560**	0.647**	0.675**
	5,12-NAQ	0.777**	0.818**	0.869**	0.365**	0.601**	-0.293*	0.535**	0.444**	0.619**	0.614**
	BPYRone	0.858**	0.857**	0.845**	0.339**	0.588**	-0.320*	0.478**	0.396**	0.612**	0.568**

**significant correlation at the 0.01 level;

*significant correlation at the 0.05 level;

366

367 **3.4 Different pollution characteristics in haze events**

368 From Fig.1, it can be found that $PM_{2.5}$ shows four equivalent maxima lasting for
369 two to five days. Among the four pollution events, two occurred before heating (24-27,
370 October and 5-6, November) and the other two occurred during heating (18-20,
371 November and 27-31 December). $PM_{2.5}$ was significantly different in terms of its
372 chemical constituents before and during heating although the mass concentration of

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$PM_{2.5}$ was rather similar (respectively averaging 107, 115, 113, and 108 μg m^{-3} for Event I, II, III, and IV) (Fig. 5a). In the two events before heating, OM existed as the second most dominant species in $PM_{2.5}$, with the respective relative abundance of 15.5% and 16.2% in Events I and II. In contrast, OM surfaced as the most dominant species of $PM_{2.5}$ during heating. The relative abundance of OM (26.5%) during Event III was higher (17.8%) than that during Event IV (Fig.5a). The ratios of $NO_3^-/PM_{2.5}$ were higher in Events I and II as compared to Events III and IV, with the ratios of SOC/OC showing the opposite trend (Fig.5b), suggesting a significant increase in the concentration of secondary organic compounds after heating. In the context of fossil fuel combustion, PAHs serve as markers for coal burning, while levoglucosan acts as a significant tracer for biomass smoke. Figure 5c shows that the ratios of PAHs to organic carbon mass in $PM_{2.5}$ (PAHs/OC) were higher during Events III and IV compared to Events I and II. This underscores the heightened emissions from household burning of coal for heating purposes. Levoglucosan/OC, the mass ratio of levoglucosan to OC in $PM_{2.5}$, did not, however, rise considerably over the same period (Fig. 5c), indicating a similar degree of emissions from burning biomass before and during heating. This result was consistent with our earlier research from the 2014 APEC meeting (Wang et al., 2017).

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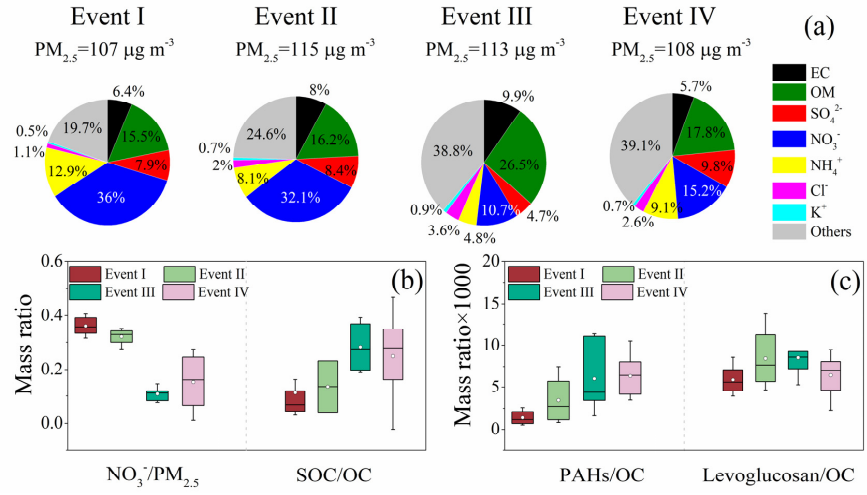

Fig.5 Comparative analysis of the chemical composition of $PM_{2.5}$ during four distinct events of air pollution. (a) Relative percentages of major species in $PM_{2.5}$; (b, c) mass ratios of the key species and organic tracers in $PM_{2.5}$.

According to the majority of research, Beijing's haze is distinguished by intense secondary formation (Zhang et al., 2018; Xu et al., 2017; Sun et al., 2016; Guo et al., 2014). According to several research studies, organic materials (OM) predominates in the autumn and winter, while secondary SIA is the most prevalent species in the summer (Renhe et al., 2014). Additionally, according to a few investigators, SIA has a major role in wintertime pollution episodes (Guo et al., 2014; Wang et al., 2016). Furthermore, a recent investigation identified the species responsible for Beijing haze, and listed distinct haze-driving species operative over the year: The haze is primarily OM-driven during winter and late fall, nitrate-driven in early fall, sulfate-driven in summer, whereas it is driven primarily by nitrates during spring (Tan et al., 2018). Table 4 and Fig.5a depict that $PM_{2.5}$ was enriched with SIA especially NO_3^- during Events I and II, but enriched OM with higher levels of SOC was observed during Events III and IV. The findings strongly indicated that haze during fall and winter in urban Beijing

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was primarily influenced by nitrate before heating and shifted to being driven by SOC during heating. Table 4 illustrates that T (temperature) and RH (relative humidity) were notably higher during Events I and II compared to Events III and IV. These warmer and moister conditions favored photochemical oxidation, leading to an increased abundance of SIA during the same period. Home heating activities, such as burning residential coal, were increased during the heating period. This resulted in massive emissions of SO_2, NO_x, VOCs, and primary particles, all of which were conducive to the generation of SOC. As a result, during Events III and IV, SOC concentrations and relative abundances were higher than during Events I and II. Furthermore, Fig. 6a shows that the NACs/OC and OPAHs/OC ratios were significantly higher in Events III and IV compared to Events I and II. Figure 6b displays a parallel trend in the relative contributions of secondary formation for both events, highlighting a notable increase in the secondary formation of BrC during pollution events, particularly evident during heating periods.

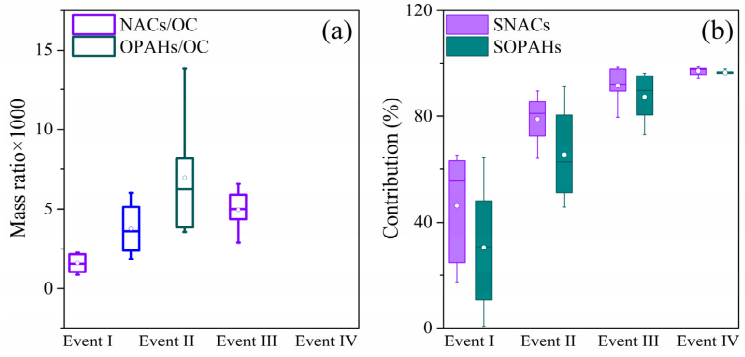

Fig. 6 Comparative analysis of the chemical composition of BrC during four distinct air pollution events. (a) Mass ratios of NACs and OPAHs to OC in $PM_{2.5}$. (b) Relative contributions of secondary formation (SNACs/OPAHs) to the total NACs/OPAHs in the fine particulate.

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Table 4. Meteorological parameters, chemical components (μg m^{-3}) of $PM_{2.5}$, and concentrations of gaseous pollutants (ppb) among four pollution episodes in Beijing.

	Before Heating Period		During Heating Period	
	Event I	Event II	Event III	Event IV
	24/10–27/10	5/11–6/11	18/11–20/11	27/12–31/12
	N=8	*N*=4	*N*=6	*N*=10
$PM_{2.5}$	107 ± 29	115 ± 48	113 ± 37	108 ± 35
Temperature, ℃	13 ± 1.6	8.8 ± 4.2	1.8 ± 2.6	1.8 ± 3.8
Relative humidity, %	79 ± 10	55 ± 26	29 ± 10	36 ± 22
SO_2	1.4 ± 0.1	1.9 ± 1.1	5.0 ± 1.0	4.0 ± 1.2
NO	27 ± 19	27 ± 15	51 ± 42	47 ± 31
NO_2	30 ± 6.7	33 ± 14	40 ± 12	37 ± 8.1
SIA [a]	62 ± 20	58 ± 22	23 ± 9.9	39 ± 30
NO_3^-	39 ± 13	38 ± 15	12 ± 5.2	18 ± 14
SOC [b]	1.9 ± 1.3	2.3 ± 1.8	7.0 ± 2.8	3.9 ± 2.5
NACs (ng m^{-3})	17 ± 8.3	41 ± 36	131 ± 85	55 ± 27
OPAHs (ng m^{-3})	21 ± 7.6	62 ± 85	127 ± 53	74 ± 23

[a] SIA: secondary inorganic aerosols (the sum of sulfate, nitrate, and ammonium).
[b] SOC: secondary organic carbon ($[SOC]=[OC]-[EC]\times([OC]/[EC])_{pri}$). $([OC]/[EC])_{pri}$ was estimated from the fitting of the minimum [OC]/[EC] ratio, assuming that the primary source dominated the period with minimal secondary formation. In this work, $([OC]/[EC])_{pri}$ was estimated from the fitting of the lowest 15% [OC]/[EC] ratios during the whole sampling period.

4 Conclusions

The current study determined the concentrations of $PM_{2.5}$-bound nine NACs and eight OPAHs in autumn and winter in Beijing urban areas. The OPAHs and NACs concentrations were much higher during heating than before heating. These species have a distinct diurnal variation, with higher concentrations at night compared to day. 4-Nitrophenol, 4-nitrocatechol, and 1-Naphthaldehyde were the most abundantly existing species in the whole campaign.

The primary sources of NACs and OPAHs were biomass combustion and automobile emissions, with the secondary generation of BrC being the predominant

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contributor across the entire sampling period. Our results underscore the significant role of secondary generation in producing BrC, particularly its heightened contribution during pollution events linked to heating. A comparative analysis of the chemical constitution of $PM_{2.5}$ and BrC in four different haze events also revealed that the haze in the autumn and winter was caused by SOC during heating and by nitrate prior to heating. Increased attention should be directed towards reducing the emissions of aromatic hydrocarbons and other anthropogenic volatile organic compounds (VOCs) when heating commences. This focus is crucial for effectively mitigating pollution and ensuring the preservation of human health. There is still only a limited volume of research on the molecular makeup of BrC, with this study primarily concentrating on two chromophores. As a result, further research is needed to identify more impactful chromophores at a molecular level. Additionally, a comprehensive exploration of the secondary generation pathways and key influencing factors of BrC through field observations and laboratory simulations is essential. This investigation is crucial for accurately assessing the environmental and human health impacts of BrC.

Data availability

The field observational and the lab experimental data used in this study are available from the corresponding author upon request (Hong Li via lihong@craes.org.cn).

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Author contributions

Yanqin Ren, Gehui Wang and Hong Li designed the research; Yanqin Ren, Yuanyuan Ji and Zhenhai Wu collected the samples; Yanqin Ren, Fang Bi and Hao Zhang conducted the experiments; Yanqin Ren and Gehui Wang analyzed the data, Yanqin Ren wrote the paper; Gehui Wang, Junling Li, Haijie Zhang and Hong Li contributed to the paper with useful scientific discussions and comments.

Competing interests

The authors declare that they have no conflict of interest.

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References

Alves, C., Vicente, A., CustÃ³dio, D., Cerqueira, M., Nunes, T., Pio, C., Lucarelli, F., Calzolai, G., Nava, S., and Diapouli, E.: Polycyclic aromatic hydrocarbons and their derivatives (nitro-PAHs, oxygenated PAHs, and azaarenes) in PM2.5 from Southern European cities, Sci. Total. Environ., 595, 494-504, http://dx.doi.org/10.1016/j.scitotenv.2017.03.256, 2017.

Bai, X., Wei, J., Ren, Y., Gao, R., Chai, F., Li, H., Xu, F., and Kong, Y.: Pollution characteristics and health risk assessment of Polycyclic aromatic hydrocarbons and Nitrated polycyclic aromatic

https://doi.org/10.5194/egusphere-2023-2593
Preprint. Discussion started: 3 January 2024

hydrocarbons during heating season in Beijing, JEnvS, 123, 169-182, https://doi.org/10.1016/j.jes.2022.02.047, 2023.

Cai, D., Wang, X., George, C., Cheng, T., Herrmann, H., Li, X., and Chen, J.: Formation of Secondary Nitroaromatic Compounds in Polluted Urban Environments, J. Geophys. Res.-Atmos., https://doi.org/10.1029/2021JD036167, 2022.

Cheng, X., Chen, Q., Li, Y., Huang, G., Liu, Y., Lu, S., Zheng, Y., Qiu, W., Lu, K., Qiu, X., Bianchi, F., Yan, C., Yuan, B., Shao, M., Zhe Wang, R, M., Canagaratna, Zhu, T., Wu, Y., and Zeng, L.: Secondary Production of Gaseous Nitrated Phenols in Polluted Urban Environments, Environ. Sci. Technol., 55, 4410-4419, https://doi.org/10.1021/acs.est.0c07988, 2021.

Chow, K. S., Huang, X. H. H., and Yu, J. Z.: Quantification of nitroaromatic compounds in atmospheric fine particulate matter in Hong Kong over 3 years: field measurement evidence for secondary formation derived from biomass burning emissions, Environmental Chemistry, 13, 665, https://doi.org/10.1071/EN15174, 2015.

Claeys, M., Vermeylen, R., Yasmeen, F., Gómez-González, Y., Chi, X., Maenhaut, W., Mészáros, T., and Salma, I.: Chemical characterisation of humic-like substances from urban, rural and tropical biomass burning environments using liquid chromatography with UV/vis photodiode array detection and electrospray ionisation mass spectrometry, Environmental Chemistry, 9, 273-284, http://dx.doi.org/10.1071/EN11163, 2012.

Ding, X., Zhang, Y. Q., He, Q., Yu, Q. Q., Wang, J. Q., Shen, R. Q., Song, W., Wang, Y., and Wang, X.: Significant increase of aromatics-derived secondary organic aerosol during fall to winter in China, Environ. Sci. Technol., 13, 7432-7441, http://doi.org/10.1021/acs.est.6b06408, 2017.

Du, Z., He, K., Cheng, Y., Duan, F., Ma, Y., Liu, J., Zhang, X., Zheng, M., and Weber, R.: A yearlong study of water-soluble organic carbon in Beijing II: Light absorption properties, Atmos. Environ., 89, 235-241, http://doi.org/10.1016/j.atmosenv.2014.02.022, 2014.

Fan, Xingjun, Peng, Ping'an, Song, and Jianzhong: Temporal variations of the abundance and optical properties of water soluble Humic-Like Substances (HULIS) in PM2.5 at Guangzhou, China, Atmos. Res., http://doi.org/10.1016/j.atmosres.2015.12.024, 2016.

Finewax, Zachary, de, Gouw, Joost, A., Ziemann, Paul, and J.: Identification and Quantification of 4-Nitrocatechol Formed from OH and NO3 Radical-Initiated Reactions of Catechol in Air in the Presence of NOx: Implications for Secondary Organic Aerosol Formation from Biomass Burning, Environ. Sci. Technol., http://doi.org/10.1021/acs.est.7b05864 2018.

Guo, S., Hu, M., Zamora, M. L., Peng, J., Shang, D., Zheng, J., Du, Z., Wu, Z., Shao, M., and Zeng, L.: Elucidating severe urban haze formation in China, Proc. Natl. Acad. Sci. USA., 111, 17373-17378, http://doi.org/10.1073/pnas.1419604111, 2014.

Huang, R. J., Yang, L., Cao, J., Chen, Y., Chen, Q., Li, Y., Duan, J., Zhu, C., Dai, W., Wang, K., Lin, C., Ni, H., Corbin, J. C., Wu, Y., Zhang, R., Tie, X., Hoffmann, T., O'Dowd, C., and Dusek, U.: Brown Carbon Aerosol in Urban Xi'an, Northwest China: The Composition and Light Absorption Properties, Environ. Sci. Technol., 52, 6825-6833, http://doi.org/10.1021/acs.est.8b02386, 2018.

Iinuma, Y., Boge, O., Graefe, R., and Herrmann, H.: Methyl-Nitrocatechols: Atmospheric Tracer Compounds for Biomass Burning Secondary Organic Aerosols, Environ. Sci. Technol., 44, 8453, http://doi.org/10.1021/es102938a, 2010.

Ji, Y., Zhao, J., Terazono, H., Misawa, K., and Zhang, R.: Reassessing the atmospheric oxidation

https://doi.org/10.5194/egusphere-2023-2593
Preprint. Discussion started: 3 January 2024

mechanism of toluene, Proc Natl Acad Sci U S A, 114, http://doi.org/10.1073/pnas.1705463114, 2017.

Jiang, H., Cai, J., Feng, X., Chen, Y., Wang, L., Li, J., Tang, J., Mo, Y., Zhang, X., Zhang, G., Mu, Y., and Chen, J.: Aqueous-Phase Secondary Processes and Meteorological Change Promote the Brown Carbon Formation and Transformation During Haze Events, J. Geophys. Res.-Atmos., http://doi.org/10.1029/2023JD038735, 2023.

Kahnt, A., Behrouzi, S., Vermeylen, R., Shalamzari, M. S., Vercauteren, J., Roekens, E., Claeys, M., and Maenhaut, W.: One-year study of nitro-organic compounds and their relation to wood burning in PM10 aerosol from a rural site in Belgium, Atmos. Environ., 81, 561-568, http://dx.doi.org/10.1016/j.atmosenv.2013.09.041, 2013.

Kitanovski, Z., Shahpoury, P., Samara, C., Voliotis, A., and Lammel, G.: Composition and mass size distribution of nitrated and oxygenated aromatic compounds in ambient particulate matter from southern and central Europe – implications for the origin, Atmos. Chem. Phys., 20, 2471-2487, https://doi.org/10.5194/acp-20-2471-2020, 2020.

Lammel, G., Kitanovski, Z., Kukucka, P., Novák, J., and Wietzoreck, M.: Oxygenated and nitrated polycyclic aromatic hydrocarbons (OPAHs, NPAHs) in ambient air - levels, phase partitioning, mass size distributions and inhalation bioaccessibility, Environ. Sci. Technol., 54, 2615-2625, https://dx.doi.org/10.1021/acs.est.9b06820, 2020.

Laskin, A., Laskin, J., and Nizkorodov, S. A.: Chemistry of atmospheric brown carbon, Chem. Rev., 115, 4335-4382, http://doi.org/10.1021/cr5006167, 2015.

Li, J., Wang, G., Ren, Y., Wang, J., Wu, C., Han, Y., Zhang, L., Cheng, C., and Meng, J.: Identification of chemical compositions and sources of atmospheric aerosols in Xi'an, inland China during two types of haze events, Sci. Total. Environ., 566, 230-237, http://dx.doi.org/10.1016/j.scitotenv.2016.05.057, 2016.

Li, X., Yang, Y., Liu, S., Zhao, Q., Wang, G., and Wang, Y.: Light absorption properties of brown carbon (BrC) in autumn and winter in Beijing: Composition, formation and contribution of nitrated aromatic compounds, Atmos. Environ., 223, 117289, https://doi.org/10.1016/j.atmosenv.2020.117289, 2020.

Li, X., Han, J., Hopke, P. K., Hu, J., Shu, Q., Chang, Q., and Ying, Q.: Quantifying primary and secondary humic-like substances in urban aerosol based on emission source characterization and a source-oriented air quality model, Copernicus GmbH, https://doi.org/10.5194/acp-19-2327-2019, 2019.

Li, Y., Bai, X., Ren, Y., Gao, R., Ji, Y., Wang, Y., and Li, H.: PAHs and nitro-PAHs in urban Beijing from 2017 to 2018: Characteristics, sources, transformation mechanism and risk assessment, J. Hazard. Mater., 436, 1-11, https://doi.org/10.1016/j.jhazmat.2022.129143, 2022.

Liu, J., Mo, Y., Ding, P., Li, J., Shen, C., and Zhang, G.: Dual carbon isotopes (14C and 13C) and optical properties of WSOC and HULIS-C during winter in Guangzhou, China, Sci. Total. Environ., 633, 1571-1578, https://doi.org/10.1016/j.scitotenv.2018.03.293, 2018.

Liu, X., Wang, H., Wang, F., Lv, S., Wu, C., Zhao, Y., Zhang, S., Liu, S., Xu, X., Lei, Y., and Wang, G.: Secondary Formation of Atmospheric Brown Carbon in China Haze: Implication for an Enhancing Role of Ammonia, Environ. Sci. Technol., http://doi.org/10.1021/acs.est.3c03948, 2023.

Lu, C., Wang, X., Dong, S., Zhang, J., and Wang, W.: Emissions of fine particulate nitrated phenols from various on-road vehicles in China, Environ. Res., 179, 108709,

https://doi.org/10.5194/egusphere-2023-2593
Preprint. Discussion started: 3 January 2024

https://doi.org/10.1016/j.envres.2019.108709, 2019a.

Lu, C., Wang, X., Li, R., Gu, R., Zhang, Y., Li, W., Gao, R., Chen, B., Xue, L., and Wang, W.: Emissions of fine particulate nitrated phenols from residential coal combustion in China, Atmos. Environ., 203, 10-17, https://doi.org/10.1016/j.atmosenv.2019.01.047, 2019b.

Ma, Y., Cheng, Y., Qiu, X., Cao, G., Fang, Y., Wang, J., Zhu, T., Yu, J., and Hu, D.: Sources and oxidative potential of water-soluble humic-like substances (HULISWS) in fine particulate matter (PM2.5) in Beijing, Atmos. Chem. Phys., 18, 5607–5617, https://doi.org/10.5194/acp-18-5607-2018, 2018.

Mohr, C., Lopez-Hilfiker, F. D., Zotter, P., ŧ, A. S. H. P., Xu, L., Ng, N. L., Herndon, S. C., Williams, L. R., Franklin, J. P., Zahniser, M. S., Worsnop, D. R., Knighton, W. B., Aiken, A. C., Gorkowski, K. J., Dubey, M. K., Allan, J. D., and Thornton, J. A.: Contribution of Nitrated Phenols to Wood Burning Brown Carbon Light Absorption in Detling, United Kingdom during Winter Time, Environ. Sci. Technol., 47, 6316-6324, https://doi.org/10.1021/es400683v, 2013.

Ni, H., Huang, R. J., Pieber, S. M., Corbin, J. C., and Dusek, U.: Brown Carbon in Primary and Aged Coal Combustion Emission, Environ. Sci. Technol., 55, 5701-5710, https://doi.org/10.1021/acs.est.0c08084, 2021.

Olariu, R. I., Klotz, B. R., Barnes, I., Becker, K. H., and Mocanu, R.: FT-IR study of the ring-retaining products from the reaction of OH radicals with phenol, o-, m-, and p-cresol, Atmos. Environ., 36, 3685-3697, http://doi.org/10.1016/S1352-2310(02)00202-9, 2002.

Ren, Y., Wang, G., Wei, J., Tao, J., Zhang, Z., and Li, H.: Contributions of primary emissions and secondary formation to nitrated aromatic compounds in themountain background region of Southeast China, Atmos. Chem. Phys., 23, 6835-6848, http://doi.org/10.5194/acp-23-6835-2023, 2023.

Ren, Y., Wei, J., Wang, G., Wu, Z., Ji, Y., and Li, H.: Evolution of aerosol chemistry in Beijing under strong influence of anthropogenic pollutants: Composition, sources, and secondary formation of fine particulate nitrated aromatic compounds, Environ. Res., 204, 111982, https://doi.org/10.1016/j.envres.2021.111982, 2022.

Ren, Y., Wei, J., Wu, Z., Ji, Y., Bi, F., Gao, R., Wang, X., Wang, G., and Li, H.: Chemical components and source identification of PM2.5 in non-heating season in Beijing: The influences of biomass burning and dust, Atmos. Res., 105412, https://doi.org/10.1016/j.atmosres.2020.105412, 2021.

Ren, Y., Zhou, B., Tao, J., Cao, J., Zhang, Z., Wu, C., Wang, J., Li, J., Zhang, L., Han, Y., Liu, L., Cao, C., and Wang, G.: Composition and size distribution of airborne particulate PAHs and oxygenated PAHs in two Chinese megacities, Atmos. Res., 183, 322-330, https://doi.org/10.1016/j.atmosres.2020.105412, 2017.

Renhe, Z., Qiang, L. I., and Ruonan, Z.: Meteorological conditions for the persistent severe fog and haze event over eastern China in January 2013, Science China-earth Sciences, 57, 26-35, http://doi.org/10.1007/s11430-013-4774-3, 2014.

Sato, K., Hatakeyama, S., and Imamura, T.: Secondary Organic Aerosol Formation during the Photooxidation of Toluene: NOx Dependence of Chemical Composition, J. Phys. Chem. A, 111, http://doi.org/10.1021/jp071419f, 2007.

Song, J., Li, M., and Zou, C.: Molecular Characterization of Nitrogen-Containing Compounds in Humic-like Substances Emitted from Biomass Burning and Coal Combustion, Environ. Sci. Technol., 56, 119-130, https://doi.org/10.1021/acs.est.1c04451, 2022.

https://doi.org/10.5194/egusphere-2023-2593
Preprint. Discussion started: 3 January 2024

Song, J., Zhu, M., Wei, S., Peng, P. A., and Ren, M.: Abundance and 14C-based source assessment of carbonaceous materials in PM2.5 aerosols in Guangzhou, South China, Atmos. Pollut. Res., 10, 313-320, https://doi.org/10.1016/j.apr.2018.09.003, 2018.

Sun, Y., Du, W., Fu, P., Wang, Q., Li, J., Ge, X., Zhang, Q., Zhu, C., Ren, L., and Xu, W.: Primary and secondary aerosols in Beijing in winter: sources, variations and processes, Atmos. Chem. Phys., 16, 8309-8329, http://doi.org/10.5194/acp-16-8309-2016, 2016.

Tan, J., Xiang, P., Zhou, X., Duan, J., Ma, Y., He, K., Cheng, Y., Yu, J., and Querol, X.: Chemical characterization of humic-like substances (HULIS) in PM2.5 in Lanzhou, China, Sci. Total. Environ., 573, 1481-1490, http://dx.doi.org/10.1016/j.scitotenv.2016.08.025, 2016.

Tan, T., Hu, M., Li, M., Guo, Q., Wu, Y., Fang, X., Gu, F., Wang, Y., and Wu, Z.: New insight into PM2. 5 pollution patterns in Beijing based on one-year measurement of chemical compositions, Sci. Total. Environ., 621, 734-743, https://doi.org/10.1016/j.scitotenv.2017.11.208, 2018.

Teich, M., Pinxteren, D. V., Kecorius, S., Wang, Z., Herrmann, H. J. E. S., and Technology: First Quantification of Imidazoles in Ambient Aerosol Particles: Potential Photosensitizers, Brown Carbon Constituents, and Hazardous Components, 50, 1166-1173, http://doi.org/10.1021/acs.est.5b05474 2016.

Teich, M., Van Pinxteren, D., Wang, M., Kecorius, S., Wang, Z., Müller, T., Mocnik, G., and Herrmann, H.: Contributions of nitrated aromatic compounds to the light absorption of water-soluble and particulate brown carbon in different atmospheric environments in Germany and China, Atmos. Chem. Phys., 17, 1653-1672, https://doi.org/10.5194/acp-17-1653-2017, 2017.

Wang, G., Kawamura, K., Xie, M., Hu, S., Gao, S., Cao, J., An, Z., and Wang, Z.: Size-distributions of n-alkanes, PAHs and hopanes and their sources in the urban, mountain and marine atmospheres over East Asia, Atmos. Chem. Phys., 9, 8869-8882, http://doi.org/10.5194/acp-9-8771-2009, 2009.

Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy, Z. M., Hu, M., Lin, Y., Peng, J., Guo, S., and Meng, J.: Persistent sulfate formation from London Fog to Chinese haze, Proc Natl Acad Sci U S A, 113, 13630-13635, https://doi.org/10.1073/pnas.1616540113, 2016.

Wang, H., Gao, Y., Wang, S., Wu, X., Liu, Y., Li, X., Dandan, Huang, Lou, S., Wu, Z., Guo, S., Jing, S., Li, Y., Huang, C., Tyndall, G. S., Orlando, J. J., and Zhang, X.: Atmospheric Processing of Nitrophenols and Nitrocresols From Biomass Burning Emissions, J. Geophys. Res.-Atmos., 125, http://doi.org/10.1029/2020JD033401, 2020a.

Wang, J., Wang, G., Gao, J., Wang, H., Ren, Y., Li, J., Zhou, B., Wu, C., Zhang, L., Wang, S., and Chai, F.: Concentrations and stable carbon isotope compositions of oxalic acid and related SOA in Beijing before, during, and after the 2014 APEC, Atmos. Chem. Phys., 17, 981-992, http://doi.org/doi:10.5194/acp-17-981-2017, 2017.

Wang, L., Wang, X., Gu, R., Hao, W., and Wang, W.: Observations of fine particulate nitrated phenols in four sites in northern China: concentrations, source apportionment, and secondary formation, Atmos. Chem. Phys., 1-24, https://doi.org/10.5194/acp-18-4349-2018, 2018.

Wang, Y., Hu, M., Li, X., and Xu, N.: Chemical Composition, Sources and Formation Mechanisms of Particulate Brown Carbon in the Atmosphere (in Chinese), Progress in Chemistry, 32, 627-645, http://doi.org/10.7536/PC190917, 2020b.

Wang, Y., Hu, M., Wang, Y., Zheng, J., and Yu, J. Z.: The formation of nitro-aromatic compounds under high NOx and anthropogenic VOC conditions in urban Beijing, China, Atmos. Chem. Phys., 19,

https://doi.org/10.5194/egusphere-2023-2593
Preprint. Discussion started: 3 January 2024

7649-7665, https://doi.org/10.5194/acp-19-7649-2019, 2019.

Wang, Y., Mehra, A., Krechmer, J. E., Yang, G., and Wang, L.: Oxygenated products formed from OH-initiated reactions of trimethylbenzene: Autoxidation and accretion, Atmos. Chem. Phys., 20, 9563-9579, https://doi.org/10.5194/acp-20-9563-2020, 2020c.

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, https://doi.org/10.5194/acp-20-2017-2020, 2020.

Xu, L., Duan, F., He, K., Ma, Y., Zhu, L., Zheng, Y., Huang, T., Kimoto, T., Ma, T., and Li, H.: Characteristics of the secondary water-soluble ions in a typical autumn haze in Beijing, Environ. Pollut., 227, 296-305, http://dx.doi.org/10.1016/j.envpol.2017.04.076, 2017.

Yan, J., Wang, X., Gong, P., Wang, C., and Cong, Z.: Review of brown carbon aerosols: Recent progress and perspectives, Sci. Total. Environ., 634, 1475-1485, https://doi.org/10.1016/j.scitotenv.2018.04.083, 2018.

Yi Chen, Penggang Zheng, Zhe Wang, Wei Pu, Yan Tan, Chuan Yu, Men Xia, Weihao Wang, Jia Guo, Dandan Huang, Chao Yan, Wei Nie, Zhenhao Ling, Qi Chen, Shuncheng Lee, and Wang, T.: Secondary Formation and Impacts of Gaseous Nitro-Phenolic Compounds in the Continental Outflow Observed at a Background Site in South China, Environ. Sci. Technol., 56, 6933-6943, https://doi.org/10.1021/acs.est.1c04596, 2022.

Yuan, B., Liggio, J., Wentzell, J., Li, S. M., and Stark, H.: Secondary formation of nitrated phenols: insights from observations during the Uintah Basin Winter Ozone Study (UBWOS) 2014, Atmos. Chem. Phys., 16, http://doi,org/10.5194/acp-16-2139-2016, 2016.

Zhang, Q., Shen, Z., Zhang, L., Zeng, Y., and Cao, J. J.: Investigation of Primary and Secondary Particulate Brown Carbon in Two Chinese Cities of Xi'an and Hong Kong in Wintertime, Environ. Sci. Technol., 54, 3803-3813, http://doi.org/10.1021/acs.est.9b05332, 2020.

Zhang, R., Sun, X., Huang, Y., Shi, A., Yan, J., Nie, T., Yan, X., and Li, X.: Secondary inorganic aerosols formation during haze episodes at an urban site in Beijing, China, Atmos. Environ., 177, 275-282, https://doi.org/10.1016/j.atmosenv.2017.12.031, 2018.

Zhang, W., Wang, W., Li, J., Ma, S., and Ge, M.: Light absorption properties and potential sources of brown carbon in Fenwei Plain during winter 2018–2019, JEnvS, 102, 53-63, https://doi.org/10.1016/j.jes.2020.09.007, 2021.

Zhao, M., Qiao, T., Li, Y., Tang, X., Xiu, G., and Yu, J.: Temporal variations and source apportionment of Hulis-C in PM2.5 in urban Shanghai, Sci. Total. Environ., 571, 18-26, http://doi.org/10.1016/j.scitotenv.2016.07.127, 2016.

Zhu, C. S., Qu, Y., Zhou, Y., Huang, H., and Cao, J. J.: High light absorption and radiative forcing contributions of primary brown carbon and black carbon to urban aerosol, Gondwana Res, 90, 159-164, https://doi.org/10.1016/j.gr.2020.10.016, 2021.