Light absorption properties of brown carbon (BrC) in autumn and winter in Beijing: Composition, formation and contribution of nitrated aromatic compounds

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HIGHLIGHTS

- Absorption characteristics of methanol-extracted BrC have been analyzed during autumn and winter of Beijing.
- Concentration and possible sources of NACs have been analyzed in autumn and winter in Beijing.
- Nitration by NO2 and nitrate has been discussed through the correlation analysis with NO2, NO3 and pH in situ.
- Contributions of NACs to the light absorption of methanol-soluble BrC were estimated.

GRAPHICAL ABSTRACT

ABSTRACT

Nitro-aromatic compounds (NACs) are an important part of brown carbon because of their strong light absorbing properties in the visible and near ultraviolet regions. In this study, the concentration and formation mechanism of eight NACs, as well as their relative contribution to the light absorption of methanol-extracted BrC, were determined from fine particle samples collected in Beijing using ultra-high performance liquid chromatography coupled with high resolution mass spectrometry and ultraviolet-visible light spectrophotometry. The average concentrations of the eight NACs were 20.27 ± 12.40 ng m⁻³ and 74.17 ± 50.66 ng m⁻³ in autumn and winter, respectively. Among the detected NACs, 4-nitrophenol (4NP) and 4-nitrocatechol (4NC) were the most abundant compounds. The correlation analysis showed that the NACs other than 2,4-dinitrophenol (2,4-DNP) are strongly intercorrelated. Significant correlations among nitro catechols (NCs), nitro salicylic acids (NSAs) and NO3 support their proposed origin from secondary formation in the presence of OH + NO2 (daytime process) or NO3 + NO2 (nighttime process). Significant correlations among nitrate, sulfate and NSAs were also found, indicating that the nitration of salicylic acid by nitric acid and sulfuric acid was another possible mechanism formation of NSAs. The methanol-extracts in winter had much higher light absorption than those in autumn.
1. Introduction

Brown carbon (BrC) is a kind of organic material that can strongly absorb solar radiation in the visible and near ultraviolet optical regions (between 200–550 nm) (Bahadur et al., 2012). This kind of material has the characteristic to scatter and absorb light, and most BrC compounds are yellowish or brown (Andreae and Gelencser, 2006). Studies have shown that BrC has an important impact on regional radiation forcing and regional climatic conditions (Bahadur et al., 2012; Healy et al., 2015; Liu et al., 2014). The latest model study showed that the contribution of BrC to global radiation forcing is approximately 27%–70% of that of black carbon (Lin et al., 2014). The IPCC (Intergovernmental Panel on Climate Change, IPCC) first took the climate effect of brown carbon as the object of focus in its fifth assessment report (IPCC, 2013). However, quantitative estimates of the warming effect of BrC are still uncertain (Jo et al., 2016; Saleh et al., 2015).

BrC is a highly complex and dynamically mixed organic matter because of its complex primary sources and secondary formation processes. The primary sources include the incomplete combustion of coal and biofuel (Van et al., 2017; Zheng et al., 2013). Secondary formation processes mainly include gas phase reactions, liquid phase reactions and aerosol aging (Desyaterik et al., 2013; Laskin et al., 2015; Saleh et al., 2013; Smith et al., 2014; Updyke et al., 2012).

Nitro-aromatic compounds (NACs) are classes of nitro derivated phenols, including nitrophenols, nitrocatechols, nitrosalicylic acids (NSAs) and nitroguaic acids (NGAs), and are an important species of BrC. Primary emissions are main source of NACs including automobile traffic emissions (Morville et al., 2004; Tremp et al., 1993), herbicide and insecticide use (Harrison et al., 2005), coal combustion (Lüttke et al., 1997) and biomass burning (Inumaa et al., 2010a; Wang et al., 2017). NACs can also be formed in-situ by secondary chemistry (Pereira et al., 2015; Xie et al., 2017), including nitration of aromatic compounds, which can occur in both the aqueous and gas phases (Harrison et al., 2005a). In addition, NACs have strong cytotoxicity, mutagenicity and carcinogenicity (Inumaa et al., 2010b), which have multiple deleterious health effects. It is necessary to study the NACs of their light absorption, composition and formation in the atmosphere. In addition, previous studies showed that NACs can increase the absorption intensity, possibly increasing the atmospheric warming potential of the BrC via the direct or indirect effects, and the warming impact of BrC will strongly depended on the aging processes of NACs in the atmospheric (Hems and Abbott, 2018; Zhao et al., 2015).

In the past decade, the air quality of Beijing, China has been improved significantly, but severe haze pollution still frequently occurs in autumn and winter due to enhanced emissions from the heating of houses. In the present study, PM2.5 samples from Beijing during autumn and winter were collected, and the NACs and light absorption properties of atmospheric BrC in the samples were investigated by using high-performance liquid chromatography (HPLC) coupled with ultraviolet-visible (UV–vis) detection and electrospay ionization mass spectrometry (ESI MS) of the extracted species. Furthermore, the contributions of the identified NACs to the light absorption of BrC were estimated. These study results can provide a comprehensive understanding about the light-absorbing characteristics of BrC at bulk chemical and molecular levels, benefiting regional climate model simulations that use optical properties.

2. Experimental details

2.1. Sample collection

PM2.5 samples were collected from September 2017 to February 2018 on the rooftop of a three-story building in Capital Normal University (39 58 N, 116 22 E). A total of 47 PM2.5 samples were obtained. A Median volume sampler (TH-150C; Tianhong Corporation, China) was used with the flow rates were set to 100 L min \(^{-1}\). Quartz fiber filters (Φ 90 mm, Pall Life Sciences, USA) were used to collect PM2.5 samples. Before sampling, the quartz fiber filters were pre-baked at 500 °C for about 4 h. PM2.5 samples were continued to collect from 08:00 to 07:30 of the next day, with the total volume of 143.3 m\(^3\) of each sample. Gaseous pollutants (NO\(_2\), SO\(_2\), CO, O\(_3\)) and meteorological parameters, including air temperature (°C), relative humidity (%), wind velocity (UV, m s\(^{-1}\)) and wind direction, were measured simultaneously using automated observation instruments.

2.2. Sample extraction and analysis

An internal standard (0.04 mL of 2, 4, 6-trinitrophenol) was added onto quarter of each filter. Then the filter were put into a glass vessel and ultrasonically extracted for 10 min with about 10 mL of methanol (HPLC grade, >99.8%) and again for 10 min with about 10 mL of acetonitrile (HPLC grade, >99.8%). The extract was combined and filtered into a pear-shaped glass flask and rotary evaporated to ~0.1 mL. Approximately 3–5 mL of methanol was used to replace the solvent and rotary evaporated to ~0.1 mL, then the extraction was transferred into a solvent-rinsed 1.5 mL amber vial and blown dry under N\(_2\) flow. The final extract sample was concentrated to 400 μL and filtered using syringe filters with a 0.22 μm PTFE membrane for high-performance liquid chromatography/diode array detector-quadrupole-time-of-flight mass spectrometer (HPLC/DAD-Q-TOFMS) and UV/Vis spectrometer (UV- 2550, Shimadzu) analysis.

The identification and quantification of target NACs were conducted with a UPLC (Acquity H Class, Waters) coupled to a UV/vis DAD followed by a Q-TOFMS (Xevo G2-XX-ToF). The Q-TOFMS used a multimode source operating in electrospay ionization (ESI) and negative ion (\(\text{---}\)) modes. Details of the UPLC/DAD-Q-TOF MS instrument parameters and methods were provided in the Supporting Information. The best conditions of the instruments, detectable limits, precision, and rate of recovery and so on were selected and researched. The recoveries were in the range between 81.2% and 115.6% (Table S1).

2.3. Light absorption analysis

100 mL of methanol extraction (description in 2.2 sample extraction and analysis) was diluted into 500 μL and analyzed with a UV-vis spectrometer. The light absorption coefficient of methanol-soluble organic carbon (Abs\(_S\), Mm\(^{-1}\)) at wavelength \(\lambda\) can be calculated as (Xie et al., 2017):

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\text{Abs}_S = A_{700} \frac{V_i}{V_o} \frac{L}{\ln 10}
\]  

(1)

Where \(A_{700}\) is the absorbance value measured by the UV–vis spectrometer. \(A_{700}\) is the systematic baseline drift. \(V_i\) (m\(^3\)) is the volume of methanol which is in agreement with the trend of NACs but contrary to the trends of PM\(_{2.5}\), water soluble ions, organic carbon and elemental carbon. The average absorption Ångström exponents (AAEs) during autumn and winter were 4.62 and 5.55, respectively, suggesting that secondary transformation were the main sources of BrC. The light absorption of NACs accounted for 1.17% and 3.18% of the total methanol-soluble BrC light absorption at \(\lambda\) 365 nm in autumn and winter, respectively, while their masses only accounted for 0.16% and 0.44% of the OC, respectively, demonstrating that although NACs are not the major contributor to BrC, but they are strong BrC chromophores, and their influence on solar radiation should be included in future modeling work.
used for extraction, $L$ is the optical path length of the quartz cuvette (0.01 m) for the UV–vis spectrometer, and $V_e$ (m$^3$) is the volume of the sampled air. The absorption coefficient at $\lambda$ 365 nm was chosen as the parameter to characterize the BrC content in this study to avoid interference of light absorption of non-brown carbon substances in liquid phase extraction.

The mass absorption efficiency (MAE, m$^2$ g$^{-1}$) of BrC in the extraction liquid was calculated by using the following formula:

$$\text{MAE}_{\lambda} = \frac{Abs_{\lambda}}{M}$$  \hspace{1cm} (2)

Where MAE$_{\lambda}$ is the mass absorption efficiency of brown carbon at a certain wavelength, and M (µg m$^{-3}$) is the concentration of organic carbon in the extraction solution. It was supposed that 100% of the brown carbon was extracted by methanol.

The spectral dependence of light absorption from different chromophores in solution can be described by absorption Ångstrom exponent (AAE). AAE was calculated through the linear regression of log (Abs) vs. log ($\lambda$) in the wavelength range of 300–550 nm.

$$Abs_{\lambda} = K \lambda^{AAE}$$  \hspace{1cm} (3)

Where $Abs_\lambda$ is the light absorbance at wavelength $\lambda$, and $k$ is a scaling constant.

2.4. Elemental carbon (EC), organic carbon (OC) and water soluble organic carbon (WSOC) measurements

OC and EC were measured with a Thermal/Optical Carbon Analyzer (DRI Model 2001, USA). Details of the procedure were offered in our previous study (Li et al., 2019). WSOC was obtained by a total organic carbon (TOC) analyzer (Shimadzu TOC-L CPN, Japan). Details of the procedure were provided in the Supporting Information.

The organic matter (OM) was estimated as 1.6 times the OC, which was based on a previous study conducted in urban China (Xing et al., 2013).

Secondary organic carbon (SOC) was estimated using the following equation:

$$\text{SOC} = \text{OC}_{\text{total}} - \text{OC}_{\text{primary}}$$  \hspace{1cm} (4)

Where $\text{OC}_{\text{total}}$ was the SOC and represents the difference between the measured OC and the primary OC. $\text{OC}_{\text{primary}}$ was the primary OC mass concentration and is obtained as follows:

$$\text{OC}_{\text{primary}} = a \times b \times \text{EC}$$  \hspace{1cm} (5)

Where $a$ is the calculated slope, and $b$ is the calculated intercept. The lowest 20% of the OC/EC ratios were applied to calculate by using a least-squares regression (Li et al., 2012).

2.5. Water soluble inorganic ions and in-situ pH

The inorganic ions in PM$_{2.5}$, including chloride, sulfate, nitrate, ammonium, sodium, potassium, calcium and magnesium, were analyzed using an ion chromatography (Li et al., 2017). The particle in-situ pH was calculated using the ISORROPIA-II model with forward mode (Hennigan et al., 2015).

3. Results and discussions

3.1. Absorption characteristics of methanol-extracted BrC

3.1.1. Light absorption coefficient (Abs.)

The $Abs_\lambda$ values of the methanol extracts were investigated at wavelengths of 300 nm, 330 nm, 365 nm, 400 nm, 450 nm, 500 nm and 550 nm (Fig. 1). It was found that the methanol-extracted BrC in winter had much higher light absorption than those in autumn from 300 to 400 nm, which was in accord with many other observed results (Chen et al., 2018; Du et al., 2014; Hecobian et al., 2010; Kim et al., 2016). Higher light absorption in winter was likely due to more primary emissions and the enhanced secondary formation of light absorbing substance. The concentrations of PM$_{2.5}$ and secondary inorganic ions (SO$_2^-$, NO$_3^-$ and NH$_4^+$) were higher in autumn than in winter (Table S2), which indicated that the atmospheric boundary layer height was not the direct cause for the higher $Abs_\lambda$ values.

Average $Abs_\lambda$ at 365 nm of BrC were 8.19 ± 4.46 Mm$^{-1}$ for autumn and 12.48 ± 9.43 Mm$^{-1}$ for winter. Compared with other regions, the absolute $Abs_{365}$ values in Beijing in this study were similar with previous results in Beijing (2011: 6.9 M m$^{-1}$, and 14 ± 5.2 M m$^{-1}$ in 2013) (Cheng et al., 2016; Yan et al., 2015), but slightly lower than that in Xi’an (winter: 46 ± 20 M m$^{-1}$) (Huang et al., 2018), Indo-Gangetic Plain, India (winter: 40 ± 18 M m$^{-1}$) (Srinivas et al., 2016), and were considerably higher than that in Guangzhou, China (winter: 3.6 ± 1.3 M m$^{-1}$) (Chen et al., 2018).

Biomass burning (BB) is a dominant emission source of primary and secondary BrCs (Chakrabarty et al., 2010, 2016; Chow et al., 2016). The relationships between $Abs_{365}$ and chemical components, including SOC and WSOC (Fig. 2(a)), EC and POC (Fig. 2(b)), and K and Cl (Fig. 2(c)), which are possibly emitted during the biomass burning process (Huang et al., 2013), were analyzed. In this study, $Abs_\lambda$ at 365 nm was selected because the light absorption in this wavelength was not interfered by that of inorganics (Hecobian et al., 2010). Fig. 2 indicates that the correlations with SOC and WSOC were stronger than those with EC and POC. These results suggested that secondarily formed methanol-soluble BrC species were more abundant than primary species. Considerable positive correlations were found between $Abs_{365}$ and K and between $Abs_{365}$ and Cl, indicating that biomass burning was a major source of BrC.

3.1.2. Absorption Ångstrom exponent (AAE)

The wavelength dependence of light absorption from methanol soluble organic carbon (MSOC) was investigated by the AAE (Cheng et al., 2017). Studies have shown that the light absorption characteristics of BrC are closely related to its sources (Liu et al., 2015; Yan et al., 2018). The optical parameters of BrC are different according to the sources and compositions. Previous studies have found that the AAE value for BrC originating from fossil fuel combustion is close to 1 (Bond, 2001; Kirchstetter et al., 2004) and that from incomplete biomass burning ranges from 1 to 3 (Martinsson et al., 2015). After transforming to secondary BrC, the AAE value can increase from 3 to 7. In this study, the average AAE values during autumn and winter were 4.62 (range...
2.60–6.35) and 5.55 (range 3.19–6.88), respectively (Table S4), indicating secondary transformation played a more prominent role, supporting the findings in 3.1.1.

3.1.3. Mass absorption efficiency (MAE)

The mass absorption efficiency (MAE), with a unit of m² g⁻¹, is a key parameter that describes the light absorbing ability of different chromophores and varies according to the source of the chromophores. In this study, the average MAE values at 365 nm during autumn and winter were 0.60 m² g⁻¹ and 1.21 m² g⁻¹, respectively (Table S4). The MAE values from our study were lower than the value from other studies, such as 1.45 ± 0.26 m² g⁻¹ in Beijing in winter (Cheng et al., 2016), 2.2 m² g⁻¹ in Xianghe, China, and ~1.6 m² g⁻¹ in Los Angeles (Zhang et al., 2013). Lower MAE values may indicate a weaker light absorbing ability in Beijing. However, it should be noted that in this study, the methanol extract (Abs365) was normalized by OC rather than WSOC, and thus the MAE (Abs365/methanol) value was probably underestimated in this study. Assuming a MSOC to OC ratio of 0.85 (Cheng et al., 2016), the corrected MAE (Abs365/methanol) value should be 0.71 m² g⁻¹ in autumn and 1.42 m² g⁻¹ in winter, similar to the results from Cheng et al. for Beijing in winter (Cheng et al., 2016).

3.2. Concentration, composition and possible formation of NACs

Fig. 3 presents an overview and a comparison of the NACs in autumn and winter. Among the detected NAC species, 4-nitrophenol (4NP) and 4-nitrocatechol (4NC) were the most abundant compounds, accounting for 33% and 22% of the NACs in autumn and 22% and 24% of the NACs in winter, consistent with a previous study in Beijing (Wang et al., 2019). The concentrations of 5-nitrosalicylic acid (5NSA) and 3-nitrosalicylic acid (3NSA) were found in levels similar to 3-methyl-4-nitrophenol (3M4NP), 4-nitroguaiacol (4NGA) and 4-methyl-5-nitrocatechol (4MSNC) in winter but clearly higher than the three compounds in autumn. 2,4-Dinitrophenol (2,4-DNP) was the lowest species for all sampling campaigns. For all the detected NACs, the concentration appeared higher in winter than in autumn.

The total concentration of detected NACs was noticeably higher in winter than in autumn, which was contrary to the trends of other components, such as secondary inorganic ions (NH₄, NO₃ and SO₄²⁻), and water soluble carbon (WSOC), indicating the origin or formation of NACs was different from the above components. The nitration process of benzene, phenol and its derivatives was the most important pathway of the secondary formation of NACs and can occur both in the liquid and gas phases (Harrison et al., 2005). The oxidation mechanism of phenol in the gas phase is initiated by OH radicals and continues with the participation of NOₓ in the daytime (Olariu et al., 2002; Xu and Wang, 2013). In the nighttime, the reaction prefers to originate by NOₓ radicals (Bolzacchini et al., 2001b). Thus, the high concentrations of 4NP and 4NC in winter can be attributed to the higher NOₓ and the emissions of some precursors in Beijing.

3.3. Possible formation mechanism and sources

3.3.1. Influence of temperature

The results of the correlation analysis among the NACs species demonstrate that there is an evident relationship among the NACs detected in this study, with correlation coefficients (R) ranging from 0.48 to 0.95, except for 2,4-DNP, which might be associated with higher measurement uncertainties because of its very low atmospheric concentrations (Table S3). The high correlations among the NACs strongly suggested similar sources or formation processes for those compounds. Further analysis indicated that the correlations within each subgroup, i.e., nitratated catechols (NCS) and nitratated phenols (NPs), were even stronger than those between the subgroups.

Some studies have indicated that this feature might be attributable to the semivolatile characteristics of NACs, which lead to a temperature-dependent partitioning between the gas and particle phases. The correlations between each subgroup and the temperature were conducted.
3.4. Contributions of NACs to the light absorption of methanol-soluble BrC

In this section, the contribution of NACs to the methanol-extracted BrC light absorption are discussed. Fig. 8 shows the relative contribution of NACs to Abs, at the spectral range of 300–500 nm in autumn and winter. In general, higher contributions of NACs to the light absorption of methanol-extracted BrC were mainly found in wavelengths shorter than 400 nm. Moreover, it can be seen that the maximum values differ for individual compounds. For example, the maximum values of 4NP were found to lie at approximately 330 nm, while the maximum values for 4NC, 4MSNC and 4NGA were in the wavelength of 350 nm. The mean contributions of NACs to the methanol-soluble BrC light absorption at λ = 365 nm were 0.28%–3.44%, with an average of 1.17%, in autumn and 1.03%–6.49%, with an average of 3.18%, in winter. 4NC and 4NP contributed the most to light absorption at λ = 365 nm, accounting for 0.65% and 0.31%, respectively, of the absorption in autumn and 1.17% and 0.60%, respectively, of the absorption in winter. In contrast, the relative mass contributions of NACs to the OC concentrations were only 0.16% in autumn and 0.44% in winter (see Table S2). The above results showed that NACs are strong BrC chromophores, and even small amounts NACs can impact the light absorption properties of particles.

4. Conclusion

In the present study, the concentration levels, sources and contributions of eight NACs to the light absorption of methanol-extracted BrC were determined in Beijing. It was found that the total concentrations of the eight detected NACs were noticeably higher in winter than in autumn, similar to the trend of methanol-soluble BrC light absorption. Among the NACs, 4NP and 4NC were the most abundant compounds, accounting for 33% and 22% of the NACs in autumn and 22% and 24% of the NACs in winter, respectively. The AAE values imply that secondary transformation were the main sources of BrC in Beijing.

Further research found that methanol-soluble BrC was abundant in secondarily formed species via the gas and liquid phases. First, correlation analysis indicated that NO₂ played important roles in the processes probably related to the chemical composition of PM2.5. Similar results were also found in other studies. Kitanovski et al. (2012) reported that nitrate strongly correlated with NSAs (R² = 0.87) in samples from Ljubljana, Slovenia. A possible mechanism of salicylic acid nitration is shown in Fig. 8. In an acid condition of nitrate and sulfate, NO₂, a powerful electrophile, will be generated, and then NO₂ can react with salicylic acid to form NSAs. To verify this reaction mechanism, the relationship between NSAs and in-situ pH was also investigated (Fig. 6(c)), and NSAs were strongly negatively correlated with in-situ pH, which indicated that the nitration of salicylic acid by means of a nitric acid and sulfuric acid system was a possible formation channel (Fig. 7). This conclusion needs more simulation experiments for verification.

3.3.2. Mechanism of nitration by NO₂ and nitrate

Many studies have shown that NO₂ plays important roles in the formation of NACs (Chow et al., 2016; Harrison et al., 2005b). For example, NO₂ can be formed either in the presence of OH – NO₂ (daytime process) or in the presence of NO₃ – NO₂ (nighttime process) (Atkinson et al., 1992; Bolzschneider et al., 2001a). To further investigate the impacts of NO₂ on the secondary formation of NACs, we plotted the correlation of NO₂ with three classes of nitrated compounds. As shown in Fig. S, the concentrations of nitrated salicylic acids and nitrated catechols exponentially increased with NO₂ (P < 0.01). In contrast, there was a weak correlation between NO₂ and nitrated phenols. These correlations indicate that the NACs could have possibly formed via a gas-phase reaction.

Nitrated salicylic acids (NSAs) also showed strong correlations with nitrate and sulfate (Fig. 6(a) and b), suggesting that the formation
secondary formation of NSAs and NCs, while NPs were more susceptible to temperature because of their higher volatility. NSAs also showed strong correlations with the nitrate, sulfate and pH of PM$_{2.5}$, indicating that the nitration of salicylic acid by means of a nitric acid and sulfuric acid system was a possible formation channel of NSAs in the aqueous phase.

NACs shared only 0.16% and 0.44% of organic carbon but contributed 1.17% and 3.18% of methanol-soluble BrC light absorption at $\lambda$ 365 nm in autumn and winter. The results indicated that NACs were not the major contributor to BrC in this study and the major BrC contributors are mainly from secondary chemistry which will be discussed in a future study. However, it’s worth mentioning that NACs are strong BrC chromophores, and very small amounts of these compounds can have disproportionately high extinction affection. In future studies, more attention should be paid to the concentration, light absorption, and primary and secondary sources of these compounds.

**Author contributions section**

Xingru Li, GeHui Wang and Yuesi Wang conceived and designed the study. Yang Yang and Shuiqiao Liu performed the experiments. Qing Zhao collected the samples. Xingru Li wrote the paper. GeHui Wang and Yuesi Wang reviewed and edited the manuscript. All authors read and approved the manuscript.
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


