On the Use of Brown Carbon Spectra as a Tool to Understand Their Broader Composition and Characteristics: A Case Study from Crop-residue Burning Samples

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ABSTRACT: This study proposes a novel approach to the use of brown carbon (BrC) absorption spectra as a tool to understand their broader composition and characteristics. The ratios of absorption coefficient ($b_{abs}$) spectra over a wavelength range (310–600 nm) for water-soluble and methanol-soluble BrC were used to quantify the relative contribution of water-soluble and water-insoluble chromophores to total BrC. The same ratios for the samples collected during the day versus night were used to assess the diurnal variability in BrC composition and concentrations. Ratios of $b_{abs}$ at different wavelengths with respect to that at 365 nm were used to understand whether BrC is predominantly composed of one type of chromophore, that is, humic-like substances, or different chromophores (e.g., nitroaromatic compounds) with the understanding that different chromophores absorb predominantly at different wavelengths. As a case study, day/night pairs of PM$_{2.5}$ samples collected from Patiala (30.33°N, 76.4°E) during paddy residue burning were used, and results are discussed. A majority of BrC from paddy residue burning were found to be water-insoluble, and the fraction of water-soluble BrC to total BrC showed a decreasing trend with increasing wavelength. During the burning period, night-time water-soluble nitrogenous organic species were found to be more absorbing than daytime water-soluble nitrogenous species. The proposed method will be very useful for BrC studies over the globe.

1. INTRODUCTION
Carbonaceous aerosol consists of organic matter (OM) and black carbon (BC). BC is known to exert a strong warming effect on global and regional climate. Some assessments suggest that the positive radiative forcing by BC is second only to carbon dioxide. Recent studies found that certain types of organic carbon (OC), termed “brown carbon (BrC),” also absorb radiation efficiently in near-ultraviolet (UV) and visible regions and contribute ≈35% to direct radiative forcing by carbonaceous aerosol. BrC is a light-absorbing part of OC and characterized by an absorption spectrum that smoothly increases from the visible to UV wavelengths. Sources of BrC in the atmosphere are a variety of primary emissions and secondary formation processes. The primary sources of BrC are incomplete combustion of fossil fuels (related to traffic), industrial processes, domestic heating, and biomass burning (BB). Further, several laboratory chamber experiments and ambient measurements showed the formation of secondary BrC chromophores through various mechanisms such as photo-oxidation of aromatic volatile organic compounds (VOCs), ozonolysis of terpenes, and subsequent aging in the presence of ammonium ions and humidity. Emissions from BB are shown to be a large source of primary BrC as well as precursors of secondary BrC on regional and global scales. Atmospheric humic-like substances (HULIS), major primary BrC, are an important fraction in organic aerosol.

A BrC consists of a variety of organic compounds with different absorbing characteristics. It is very difficult to identify individual BrC species and their optical properties, and therefore, they are often presented as the absorption coefficient at a certain wavelength. Furthermore, optical properties of BrC are reported to change with various atmospheric processes such as oxidation, solar irradiation, and changes in temperature and relative humidity. These factors result in highly variable composition and concentration of BrC in time and space, which in turn results in substantial uncertainties in predicting their climate effects.

This paper mainly focuses on the use of BrC spectra of water-soluble and methanol-soluble OC as a tool to understand their broader composition and optical characteristics as well as to assess the relative contribution of water-soluble and water-insoluble BrC to total BrC.

2. MATERIALS AND METHODS
As a case study for the proposed approach, particulate matter smaller than 2.5 μm aerodynamic diameter (PM$_{2.5}$) samples were used. The sampling site was located on the terrace of the Department of Physics, Punjabi University, Patiala (30.33°N, 76.4°E, 250 m above mean sea level), a semi-urban city
surrounded by agricultural area within a few kilometers. Patiala is situated in the northwestern part of the Indo-Gangetic Plain. Day/night (10 h integration time) pairs of ambient PM$_{2.5}$ samples ($n = 69$) were collected every day before ($n = 21$), during ($n = 36$), and after ($n = 8$) a large-scale paddy residue burning from October to November 2014. The samples were collected on precombusted (at 450 °C for 10–12 h) Tissuquartz filters (PALLFLLEX, 25 × 20 cm$^2$) using a high-volume air sampler (Thermo-Anderson, HVS) with the flow rate of ∼1.13 m$^3$ min$^{-1}$. Soon after their collection, the filters were wrapped in aluminum foils, sealed in plastic ziplock bags, and stored in a deep freezer (−19 °C) until the time of analysis. Further, a wide variety of chemical species were analyzed in these filters. They included water-soluble OC (WSOC) and water-soluble organic nitrogen (WSON = water-soluble total nitrogen−inorganic nitrogen (IN), where IN is the sum of NH$_4^+$−N and NO$_3^−$−N), and were analyzed using a TOC−TN analyzer (Shimadzu, model-TOC−LCPH with AS−L autosampler). Elemental carbon (EC) and OC were analyzed with the EC−OC analyzer (Sunset Inc.), and inorganic cations (NH$_4^+$, Na$^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$) and anions (Cl$^−$, NO$_3^−$, and SO$_4^{2−}$) were analyzed using ion chromatography (Dionex, ICS-5000). A detailed description of analytical procedures is given elsewhere.

3. RESULTS

The PM$_{2.5}$ concentration ranged from ∼90 to 500 µg m$^{-3}$ during the study period with the average values of 154 ± 57, 271 ± 122, and 156 ± 18 µg m$^{-3}$ during pre-burning ($T_1$: 11th–22nd October, $n = 25$), burning ($T_2$: 23rd October to 10th November, $n = 36$), and post-burning ($T_3$: 12th–15th November, $n = 8$) periods, respectively, reflecting the effect of BB on ambient PM$_{2.5}$ concentrations. For the total daytime PM$_{2.5}$ samples, the contributions of OM (2.1 times the measured concentration of OC, Rajput and Sarin, 2014) were 36, 46, and 46%; water-soluble inorganic species (WSIS = sum of NH$_4^+$ + Na$^+$ + K$^+$ + Mg$^{2+}$ + Ca$^{2+}$ + Cl$^−$ + NO$_3^−$ + SO$_4^{2−}$) were 14, 41, and 15%; and EC were 5, 3, and 5% during $T_1$, $T_2$, and $T_3$, respectively. Similarly, for nighttime samples, the contributions of OM were 46, 63, and 46%; WSIS were 11, 13, and 18%; and EC were 5, 3, and 5% during $T_1$, $T_2$, and $T_3$, respectively. The observation suggests that OM was dominating in all the three periods, and nighttime OM concentrations were always higher than those observed during the daytime. Similar observations were reported by Rastogi et al. (2014) from the same sampling site. Highest OM concentrations (OM ≈ 63%) were observed in nighttime samples collected during $T_3$ period, and they were slightly higher compared to the previously reported value (OM ≈ 56%).

3.1. Proposed Concept of Using BrC Spectra to Assess Their Composition and Characteristics. BrC species may consist of a variety of organic chromophores with variable concentrations and different absorbing characteristics. The absorption coefficient ($b_{abs}$) spectra of water extracts or methanol extracts of aerosol represent the bulk optical property of water-soluble or methanol-soluble (assumed to be total) BrC, respectively, as a function of wavelength. If the BrC composition is uniform from sample to sample, then the ratio of $b_{abs}$ spectra for different samples shall be uniform (constant) as a function of wavelength. The magnitude of this constant would suggest the relative abundance of BrC chromophores in different samples. However, if the BrC composition is not uniform from sample to sample, then one would expect variable ratio at different wavelengths depending on the change in composition and concentrations of different chromophores. It is known that different types of chromophores absorb strongly at different wavelengths, for example, HULIS-type BrC (usually primary BrC) absorbs strongly at around 365 nm, whereas nitroaromatic-type BrC (usually secondary BrC) absorbs strongly at a relatively higher wavelength (>400 nm). The wavelengths at which non-uniformity in $b_{abs}$ spectra ratio is observed would indicate the change in the type of BrC in a given sample. It is relevant to state here that the proposed method is not the replacement of doing molecular speciation of BrC, but it shall be very useful in understanding the possible dominant BrC species present in a given sample.

Further, the same concept can be applied to water extracts and methanol extracts of the same sample. One can calculate the ratio of $b_{abs}$ at different wavelengths for water extract to that for methanol extract and use it to quantify the relative contribution of water-soluble and water-insoluble chromophores to total BrC as a function of wavelength in a given sample presuming that methanol-soluble BrC represents total BrC, which is a valid assumption as per literature.
concepts are used in the subsequent sections on the samples collected from Patiala as a case study.

3.2. BrC Composition and Characteristics through \( b_{abs} \) Spectra. Figure 1 shows a comparison of the \( b_{abs} \) spectra for BrC extracted with water (\( b_{abs_{\text{Water}}} \)) and methanol (\( b_{abs_{\text{Methanol}}} \)). They exhibit very different light absorption properties during the \( T_2 \) period compared to those observed during the \( T_1 \) and \( T_3 \) periods. The variability in the night/day (N/D) ratio of \( b_{abs_{\text{Water}}} \) spectra during the \( T_2 \) period was large compared to those observed during the \( T_1 \) and \( T_3 \) periods (Figure 2a−c). The observation during \( T_2 \) suggests that BB emits a variety of BrC chromophores with the highest concentrations of chromophores absorbing in 310−400 nm range. Magnitudes of N/D ratio were always >1, with highest values during \( T_2 \) (1.8−3) followed by \( T_3 \) (1.3−1.5) and \( T_1 \) (1−1.3) over 310−600 nm range, reflecting the changes in composition and concentrations of BrC chromophores which absorb at different wavelengths. Here, the absolute magnitude reflects the N/D change in chromophore concentrations, and the variability in magnitude indicates the N/D change in composition, as conceptualized in Section 3.1. During \( T_3 \) and \( T_1 \), a slightly lower N/D ratio with mild but noticeable variability in 450−600 nm range is suggestive of the presence of daytime secondary BrC in water extracts. The \( b_{abs_{\text{Water}}} \) showed a sharp increase in absorption at 310−400 nm range during the nights of \( T_2 \) period, which is likely due to HULIS from BB.\textsuperscript{15,28,30} In the same set of samples, a low absorption at >500 nm was also noticed, which was not observed during the \( T_1 \) and \( T_3 \) periods. Similar spectra were observed by Xie et al.\textsuperscript{33} for the laboratory-generated secondary BrC formed by the reaction between benzene and \( m \)-cresol under high NO\textsubscript{x} conditions.\textsuperscript{33} Further, a spectral enhancement was observed in 410−490 nm range of \( b_{abs_{\text{Water}}} \) during the \( T_2 \) period (as reflected in N/D ratio, Figure 1b). This observation suggests that the observed spectral band was likely associated with the presence of a variety of absorbing nitrogenous organic species, which were likely generated through secondary organic aerosol (SOA) in the presence of NO\textsubscript{x}.\textsuperscript{33} High NO\textsubscript{x} was also observed in this study during the \( T_2 \) period (figure not shown). This inference is attested by a significant correlation (\( r^2 = 0.55 \)) between WSON/WSOC ratio and absorption coefficient measured at 450 nm for water extracts (\( b_{abs_{450_{\text{Water}}}} \)) in the samples collected during nighttime of \( T_2 \) period (Figure 2b). Higher WSON/WSOC is an indicative of a larger fraction of water-soluble nitrogenous organic species in the total water-soluble organic species. Further, absorbing properties of nitrogenous organic species in samples collected during daytime and nighttime were likely different, as for similar WSON/WSOC ratios, the \( b_{abs_{450_{\text{Water}}}} \) values were very different (Figure 2a,b). Daytime WSON/WSOC ratios were also poorly correlated with \( b_{abs_{450_{\text{Water}}}} \) (Figure 2a). Satish et al.\textsuperscript{22} also documented that absorbing nitrogenous species are

![Figure 1.](image1.png) \( b_{abs} \) spectra during day and night and their N/D ratio for water-soluble BrC during (a) pre-burning (\( T_1 \)), (b) during burning (\( T_2 \)), and (c) during post-burning (\( T_3 \)) periods, and for methanol-soluble BrC during (d) pre-burning (\( T_1 \)), (e) during burning (\( T_2 \)), and (f) during post-burning (\( T_3 \)) periods. Note that y-axis range is different for the figures (a−c) and (d−f).

![Figure 2.](image2.png) Linear relationship between WSON to WSOC ratio and absorption coefficient at 450 nm for water extracts (\( b_{abs_{450_{\text{Water}}}} \)) in (a) daytime samples and (b) nighttime samples. Higher nighttime WSON/WSOC ratios were associated with higher \( b_{abs_{450_{\text{Water}}}} \), suggesting that nighttime nitrogenous compounds were more absorbing.
volatile and/or photosensitive, and therefore, their abundance reduces during daytime.

A recent study by Cheng et al.36 suggested that majority (~85%) of organic compounds in the ambient PM could be methanol-soluble. In the present study, the average WSOC/OC ratio is about 0.60, that is, ~40% of OC is water-insoluble. Figure 1d–f shows the \( b_{\text{abs}} \) spectra and their N/D ratio for methanol extracts during \( T_1 \), \( T_2 \), and \( T_3 \), respectively. The \( b_{\text{abs, Methanol}} \) values were much higher than the \( b_{\text{abs, Water}} \) values, suggesting that water-insoluble BrC species are relatively more absorbing during all the three periods. During \( T_2 \), both \( b_{\text{abs, Water}} \) and \( b_{\text{abs, Methanol}} \) show higher values in shorter-wavelength range (310–400 nm); however, \( b_{\text{abs, Methanol}} \) showed the higher value in the visible region too (Figure 1e). This observation suggests that \( b_{\text{abs, Methanol}} \) contains a significant fraction of water-insoluble chromophores which can absorb radiation in the visible region. This can be ascribed to differences in solubility of the chromophores in water and methanol.16,27,38,39 Some studies suggest that the molecules comprising more aromatic rings (i.e., a higher degree of conjugation) have higher absorption that extends to longer wavelengths.39 Further, Zhang et al. (2013)37 had documented BrC chemical speciation, which showed that larger molecular weight polycyclic aromatic hydrocarbons (PAHs) absorbed more toward the visible range and have lower solubility in water. Sun et al.35 suggested two kinds of OC: a water-soluble organic mixture with some UV-visible absorption and a water-insoluble OC with higher absorption.16,36 Further, quinoid compounds are strong candidates for such absorption.35 This type of absorption spectra was present in the nights of the \( T_3 \) period; however, it disappeared in day samples (Figure 1b,e). This could be due to various reasons such as the evaporation of higher-volatility compounds (e.g., nitrophenols), photobleaching, and so forth. A similar observation is reported in Lin et al.,40 which suggests that the decrease in absorbance does not follow a single exponential decay because different chromophores decompose at different rates.39 It is important to state here that these statements are postulations from the measured absorption spectra of water-soluble and methanol-soluble extracts and reported maximum absorption by different chromophores at different wavelengths in literature. To make firm conclusions, more work such as comparison of the actually measured molecular speciation with absorbance spectra is needed.

In general, the absorption in the visible range is more important to the energy balance than the absorption in the UV range as nearly 40% of solar energy is found at wavelengths between 400 and 600 nm. UV absorption affects photolysis, but wavelengths below 400 nm provide only about 4% to solar energy.35

3.3. Relative Contribution of Water-Soluble and Water-Insoluble Fraction to Total BrC. To investigate the contribution of water-soluble and water-insoluble fraction to total BrC during different periods, the ratio of \( b_{\text{abs}} \) (water/methanol) was calculated (Figure 3). The \( b_{\text{abs, Methanol}} \) represents total BrC, and \( b_{\text{abs, Water}} \) denotes water-soluble BrC, and their difference reflects water-insoluble BrC. This approach helps in assessing the fraction of water-soluble BrC in the total BrC. It was observed that on average (integrated over 310–600 nm), the water-soluble BrC contributes ~33, 27, and 26% in daytime samples, whereas 26, 19, and 23% in nighttime samples to total BrC in the samples collected during \( T_1 \), \( T_2 \), and \( T_3 \) periods, respectively. Observations clearly suggest that contributions of water-soluble BrC were more in daytime samples compared to that in nighttime samples, and its fraction was minimum during \( T_3 \), maximum during \( T_2 \), and in-between during \( T_1 \). These observations also suggest that water-insoluble BrC dominates total BrC over the study regions during the study period. However, this water-soluble fraction of BrC was not uniform at all wavelengths. It decreases with increasing wavelength and goes to as low as ~10% at 600 nm.

Further, % water-insoluble BrC in both day-and-night samples was also estimated using the eq 2.

\[
\% \text{ Water-insoluble BrC} = \frac{b_{\text{abs, Methanol}} - b_{\text{abs, Water}}}{b_{\text{abs, Methanol}}} \times 100
\]

The \( b_{\text{abs}} \) (water/methanol) ratios for shorter (310–400 nm) and longer-wavelength region (400–600 nm) were averaged. At the shorter-wavelength region, water-insoluble fractions during the day (59, 67, and 67%) and night (67, 72, and 70%) samples were significant in \( T_1 \), \( T_2 \), and \( T_3 \) periods, respectively. Similarly, at the longer-wavelength region, water-insoluble fractions during the day (72, 77, and 79%) and night (79, 86, and 81%) were dominant in \( T_1 \), \( T_2 \), and \( T_3 \) periods, respectively. During \( T_2 \) period, night samples influenced by BB emissions showed highest fraction (~86%) of water-insoluble BrC and day/nights differences at the shorter-wavelength region were less than those observed at the longer-wavelength region (Figure 3b). Lee et al.17 reported that chemical composition and optical properties of BrC

Figure 3. \( b_{\text{abs}} \) (water/methanol) ratio versus wavelength and % of water-insoluble fraction versus wavelength during (a) pre-burning \( (T_1) \), (b) during burning \( (T_2) \), and (c) during post-burning \( (T_3) \) periods. Note that shaded area is overlapped, that is, daytime W/M (blue) was always higher than that during nighttime (red); however, the absolute value of ratio varied as a function of wavelength. Green and black lines exhibit % water-insoluble BrC fraction as a function of wavelength during day and night, respectively.
cannot be viewed as static, as they may change with time. Light-absorbing compounds (responsible for the color of BrC) can be potentially photobleached in sunlight and lose their ability to absorb visible radiation.11 Our observations suggest that BrC absorbing at higher wavelengths is predominantly water-insoluble, and they are affected by daytime atmospheric processes such as photolysis/oxidation of BrC chromophores and other transformation reactions.13,40,41

3.4. Temporal Variability in BrC Composition through Absorption Spectra. In order to understand the day-to-day variability in BrC composition through absorption spectra, the absorptions at 400, 405, 420, 450, 500, and 550 nm wavelength (representing absorption by nitroaromatics)23,37,39,41 were normalized to the absorption at 365 nm (representing absorption by HULIS compounds).15,28,30

As shown in Figure 4, the absorbance at different wavelengths normalized to that at 365 nm, and 450 nm, respectively.23 These compounds could be an important fraction of BrC in the urban atmosphere. Further, the overall normalized ratios for $b_{\text{abs, Water}}$ were higher compared to those for $b_{\text{abs, Methanol}}$ further suggesting that there was always a significant insoluble fraction of BrC. However, this insoluble fraction was not uniform and showed maximum contribution during the burning period.

4. CONCLUSIONS

A novel approach has been proposed to use only $b_{\text{abs}}$ spectra of water-soluble and methanol-soluble OC as a tool to understand the broader composition and characteristics of water-soluble and water-insoluble BrC, which otherwise need copious amount of work and expensive facilities. As a case study, $b_{\text{abs}}$ spectra of PM$_{2.5}$ samples collected before ($T_1$), during ($T_2$), and after ($T_3$) a large-scale paddy residue burning over Patiala were used. Magnitudes of N/D $b_{\text{abs}}$ spectra ratios were always $>1$, with highest values during $T_2$ (1.8−3) followed by $T_3$ (1.3−1.5) and $T_1$ (1−1.3) for 310−600 nm wavelength range, reflecting the changes in composition and concentrations of BrC chromophores. BrC abundances and composition were found to be very different during $T_2$ nights, with significant contributions of chromophores absorbing in 310−400 nm range. The contribution of water-soluble BrC to total BrC decreases with wavelength, and water-insoluble BrC dominates total BrC composition during the whole study period. On average (integrated over 310−600 nm), the water-soluble BrC contributes ~33, 27, and 26% in daytime samples, whereas 26, 19, and 23% in nighttime samples to total BrC during $T_1$, $T_2$, and $T_3$ periods, respectively. Further, temporal variability in $b_{\text{abs}}$ at different wavelengths normalized to that at 365 nm in day and night samples suggests that BB likely emits nitroaromatics, which are photosensitive and/or volatile. The proposed approach shall be useful in BrC studies over different regions.

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Notes

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