

Chapter 13

Molecular Characterization of Atmospheric Brown Carbon

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Light-absorbing organic aerosol, commonly known as brown carbon (BrC), is a significant contributor to radiative forcing of the Earth's climate and also is of potential toxicological concern. Understanding the environmental effects of BrC, its sources, formation, and aging processes requires molecular-level speciation of its chromophores and characterization of their light-absorption properties. This chapter highlights recent analytical chemistry developments and applications in the area of molecular characterization of BrC that provided first insights into the diverse composition and properties of its common chromophores. We present chemical analysis of BrC reported in a number of case studies associated with emissions from biomass burning and anthropogenic sources producing secondary organic aerosols. The results highlight major classes of organic BrC differing in structures, polarities, and volatilities. Understanding their chemical identity requires applications of multi-modal complementary separation and ionization approaches in combination with high resolution mass spectrometry. Overall, these studies allow deciphering the BrC absorbance and studying its atmospheric evolution with respect to relative contributions from different classes of chromophores such as aromatic carboxylic acids, nitro-phenols; substituted, heterocyclic, and pure polycyclic aromatic hydrocarbons. These studies also provide a glimpse into the complex atmospheric

evolution of BrC as a result of photooxidation, photolysis and different levels of acidity. Samples of BrC materials discussed in this chapter were obtained in FIREX 2016 biomass burning experiments performed at the U.S. Forest Service Fire Science Laboratory in Missoula, MT.

Introduction

A significant and highly variable fraction of anthropogenic atmospheric aerosol absorbs solar radiation resulting in reduced visibility on regional scales and also affecting global climate forcing. “Black carbon” (BC), the most efficient light-absorbing aerosol (1), is composed of highly carbonized graphitic-like particulates generated by incomplete combustion of fuels. BC absorbs solar radiation over a broad spectral range from the ultra-violet (UV) into far infra-red (IR). Effects of BC on the environment are particularly significant in the areas heavily impacted by either large-scale forest fires or combustion of fossil fuels in densely populated developing countries. In addition to BC, certain components of organic aerosol (OA) absorb efficiently in the UV/Vis range – these species are collectively called “brown carbon” (BrC) (2).

The importance of BrC absorption on regional-to-global scales has been highlighted in a number of atmospheric modeling studies (3, 4) and has been confirmed by the satellite (5) and ground (6–8) observations. In particular, regional effects of BrC over major areas of biomass burning and biofuel combustion are substantial, where BrC and BC become equivalently important light-absorbing materials in the atmosphere (3). In these regions, the BrC warming effect is comparable to cooling by non-absorbing OA (–0.1 to –0.4 W m⁻²). However, because of large variability in their chemical composition, concentrations and optical properties of specific chromophores, it is not clear to what extent the warming effect of BrC and cooling effect of OA may cancel each other (9). Inherent to their chemical complexity, the sources of BrC are not well understood; even less is known about its transformations resulting from atmospheric ageing. Most of the earlier reports (2) attributed BrC to primary organic aerosols (POA) in the emissions from biomass burning and combustion of fossil fuels. More recent studies (10, 11) indicate that secondary organic aerosol (SOA) formed from the oxidation of selected natural and anthropogenic volatile organic compounds (VOC) also may contribute to BrC.

Even small fractions of strong chromophores may determine the overall absorption of light by the BrC material (12). Because of the low concentrations of light-absorbing molecules in complex organic mixtures present in the aerosol, identification of BrC chromophores is a challenging task. The identification and structural characterization of BrC chromophores require applications of highly sensitive molecular characterization approaches capable of detecting both strongly and weakly absorbing species in complex organic mixtures (10). This chapter provides a brief summary of the most recent advances in the molecular-level studies of BrC materials conducted in our groups.

Separation and Analysis of BrC Chromophores

A non-targeted detection of a priori unknown light absorbing components (chromophores) within complex environmental mixtures is the major challenge in the chemical characterization of BrC. To address this challenge experimentally, we use a multi-stage analytical platform that combines high performance liquid chromatography (HPLC), photodiode array (PDA) spectrophotometry, and high-resolution mass spectrometry (HRMS) assisted with soft ionization methods (13–19). The ultimate success of the entire method critically depends on the performance at each of its stages. First, the extent of HPLC separation is crucial to the subsequent analysis of BrC chromophores eluting from the column. Besides the natural variability in the chromophores' composition between different BrC samples, HPLC separation is affected by many factors, such as stationary phase and operation temperature of the column, pH of the analyte mixture, flow rate, chemical composition of the mobile phase, and other parameters. Selection of the best performing chromatographic column and development of robust separation protocols were addressed in our initial studies employing laboratory generated proxies of BrC. In these studies, BrC materials were produced through: 1) reactions of methylglyoxal (MG) and ammonium sulfate (AS) (13) and 2) OH/NO_x-induced photo-oxidation of toluene (14). We conducted systematic studies to evaluate performance of several HPLC columns for separation of BrC chromophores. We confirmed that the reverse-phase C18 column provides most practical separation of organics in complex real-world samples (15–17), where a broad range of chemically diverse BrC chromophores are typically present. However, for separation of BrC chromophores belonging to the same chemical class, columns with specially tailored stationary phases may provide a better performance. For instance, best separation of reduced nitrogen chromophores formed in the MG+AS reacting system was achieved using the SM-C18 column (13), which combines ion exchange capability with the more commonly used reverse-phase interactions.

Figure 1 illustrates the HPLC-PDA chromatogram of BrC chromophores identified in a sample of biomass burning organic aerosol (BBOA) collected from controlled burns of sagebrush biofuel during Fire Influence on Regional and Global Environments Experiment (FIREX) campaign in 2016 (20) at the U.S. Forest Service Fire Science Laboratory in Missoula, MT. The Y-axis of the plot shows wavelength of UV-vis spectra and the heatmap colors indicate absorption intensities. The chromatogram reveals abundant well-separated chromophores at retention times (RT) between 10 and 100 min (17). A substantial fraction of their light absorption lies in the visible spectral range > 390nm. The chemical composition of BrC chromophores is diverse and includes different classes of organic molecules that cannot be ionized using one common ionization mechanism. To address this limitation, their composition was investigated in four separate experiments utilizing electrospray ionization (ESI) and atmospheric pressure photoionization (APPI) sources operated in positive (+) and negative (-) modes, as illustrated in the figure legends. Elemental formulas and plausible structures of the BrC chromophores were then identified through correlative analysis of the combined HPLC-PDA and HPLC-HRMS records.

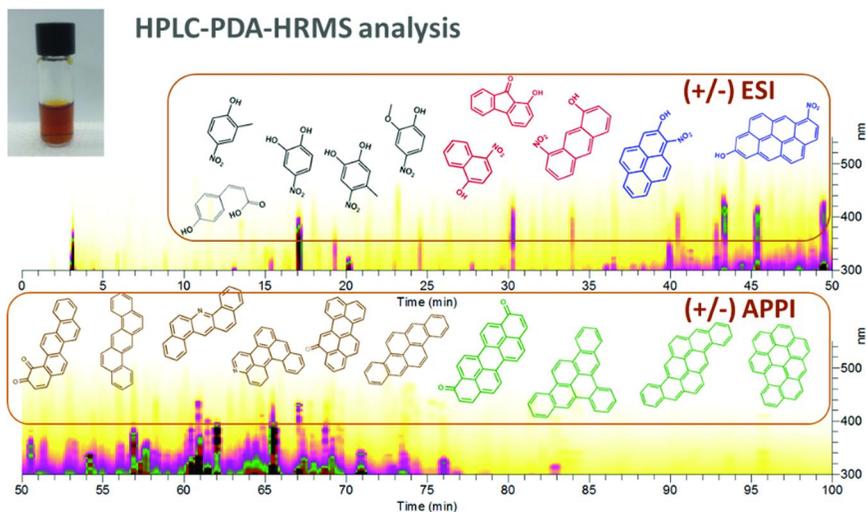


Figure 1. HPLC-PDA chromatogram of a selected BBOA sample (17). The x-axis is a retention time (RT). The y-axis and heatmap refer to the wavelength and intensity of the UV-vis absorption spectra, respectively. The molecular structures denote BrC chromophores identified in HPLC-HRMS experiments interfaced with ESI and APPI sources. Polar compounds eluted at earlier RT and are detected mostly in the ESI-HRMS experiments; non-polar compounds eluted later and are detected mostly in the APPI-HRMS experiments.

ESI-HRMS experiments are particularly sensitive to polar molecules such as carboxylic acids, nitro-organics, organo-sulfates, etc., while APPI-HRMS is the method for chemical analysis of non- and low-polarity compounds with extensive network of π -bonds such as PAH, N- and O-heterocyclic compounds. Figure 2 illustrates differences in the direct infusion mass spectra of the same BBOA sample acquired with ESI and APPI sources, each operated in positive-ion and negative-ion modes, respectively (17). Remarkably, HRMS spectra obtained using ESI+, ESI-, APPI+ and APPI- are distinctly different and only minor overlap was observed between them. These results are attributed to the differences between the ionization mechanisms. Specifically, ESI generates ions through desolvation of charged droplets, in which polar analyte molecules that possess either acidic or basic functionalities efficiently compete for charge. In contrast, APPI ionizes non-polar molecules through electron detachment or charge transfer from photo-ionized dopant ions purposely added to the sample. As illustrated by Figure 2, distinctly different classes of compounds were identified in each of the modes. It follows that repeated HRMS experiments employing different ionization modes are required for the comprehensive characterization of a broad range of organic compounds present in BBOA samples (17).

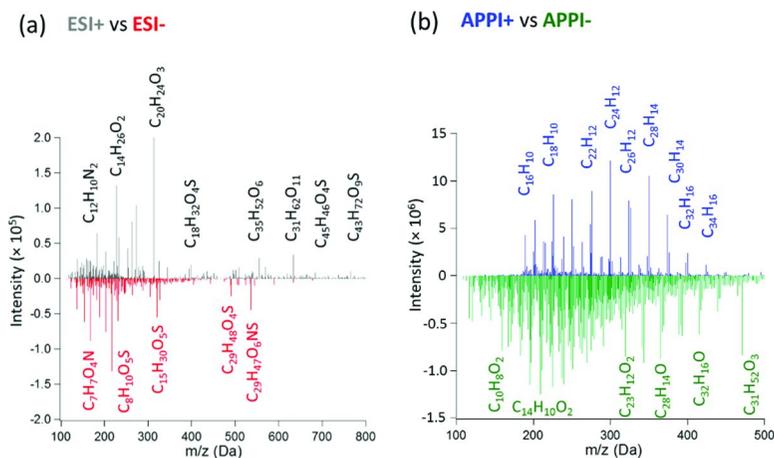


Figure 2. Mass spectra of solvent extractable BBOA compounds detected in positive and negative modes of the direct infusion ESI-HRMS (panel a) and APPI-HRMS (panel b) experiments (17). Reproduced with permission from ref. (17). Copyright 2018, ACS.

High mass resolving power and high mass accuracy are essential for assigning elemental compositions to individual BBOA components, while MSⁿ fragmentation experiments can provide additional insights into their structural characterization (21, 22). Although minimal mass resolution required for unambiguous formula assignments depends on the complexity of the BBOA analytes, we showed that good-quality assignments of the most common C_xH_yO_zN₀₋₃S₀₋₂ formulas can be routinely obtained from HRMS data recorded at 100,000 *m/Δm* mass resolving power (13, 14, 17, 19, 23–26). Furthermore, accurate mass measurements combined with calculated element-specific isotope distributions can reveal the presence of less common species, such as Mg, Al, Ca, Cr, Mn, Fe, Ni, Cu, Zn, and Ba-containing metal-organic components of BBOA (27).

Different configurations of HPLC-PDA-HRMS analytical platform were used in a number of studies where a variety of BrC chromophores were characterized in the samples of ambient BBOA (15–17, 19, 28–31) and lab-generated proxies (13, 14, 18, 32–34) of light-absorbing organic aerosol. Several classes of BrC chromophores such as alkyl-phenols, methoxy-phenols, nitro-phenols, substituted benzoic acids, imidazole- and furan-based oligomers, quinones, PAHs, nitro-PAHs, N- and O-heterocyclic compounds and others have been identified. Beyond this, it has been shown that charge transfer complexes of supramolecular aggregates contribute additionally to the overall optical properties of BrC (35).

Comparison of the BrC chromophores between different BBOA samples indicates that a large fraction of them are biofuel-specific, while certain chromophores also appear repeatedly among different samples, which may suggest their more common nature across certain types of biofuels. In nearly

all BBOA samples studied so far, we found that the total absorbance by 20-25 individual BrC chromophores accounted for 40-60% of the overall absorbance in the wavelength range of 300–500 nm. Relative contributions of the different types of BrC chromophores may be estimated by combining them into broader groups based on their chemical properties, such as similarity in molecular composition and estimated volatility, as illustrated by Figure 3. Such a grouping may provide practical input for future atmospheric process models to simulate sources, composition and transformations of BrC.

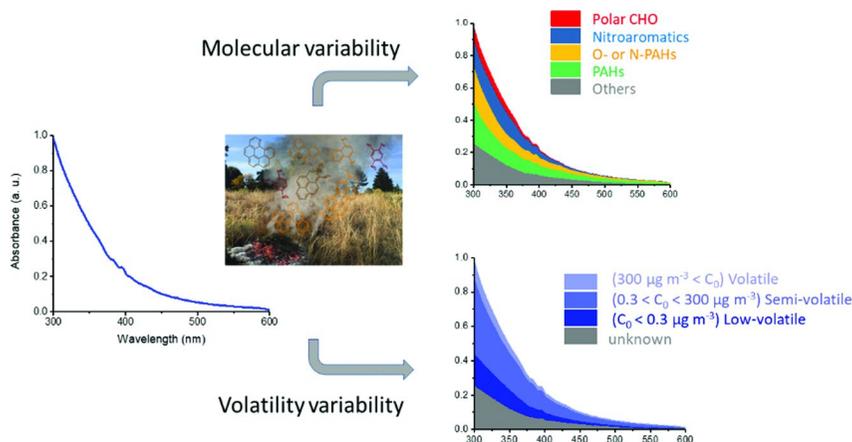


Figure 3. Relative contributions to the overall BrC absorption of a selected BBOA sample by individual chromophores grouped based on their molecular composition (upper plot) and estimated volatility (lower plot).

Processes Affecting BrC Composition and Transformations

BrC contains both water-soluble and low-solubility organic carbon, which must be considered when designing the experimental protocol for chemical analysis. The water-soluble fraction of BrC is usually below 70%, while nearly 90% of BrC can be extracted into organic solvents, such as acetonitrile and methanol (16). The water-insoluble fraction of BrC has greater absorption per unit of mass than the water-soluble fraction (36). In BBOA, the relative abundances of water-soluble and water-insoluble fractions as well as partitioning of their light-absorption properties are strongly affected by the temperature of the biomass burning processes, fuel type and its moisture content.

Light-absorption properties of water-soluble BrC are pH dependent because its chromophores exist in both neutral and ionized (protonated/deprotonated) forms and their relative abundances are defined by their pK_a and the pH of the solution. For example, UV-vis absorption by the nitro-phenol based chromophores shifts toward longer wavelengths (red shift) when they are deprotonated at neutral pH (37). Figure 4 illustrates the pH effect in the overall light absorption of the

BBOA sample with abundant presence of the nitro-aromatic chromophores (16). In contrast, chromophores containing moieties of benzoic acid and its derivatives exhibit blue shift when deprotonated (38). Therefore, although aerosol acidity plays an important role in modulating the optical properties of BrC, the combined effect of pH may not be always the same for all BrC materials.

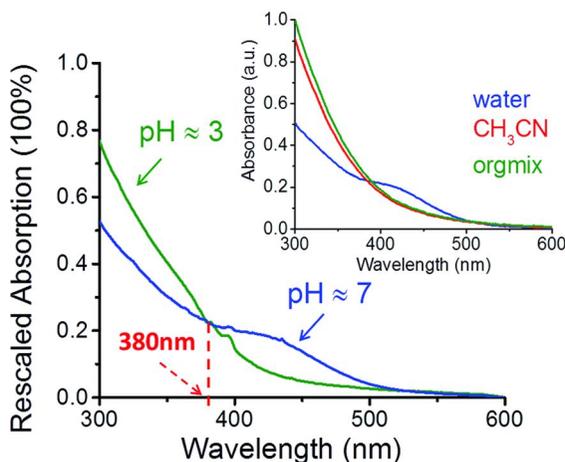


Figure 4. UV-vis spectra of water-soluble BrC fraction extracted from BBOA sample and measured at different pH conditions. The inset illustrates the UV-vis spectra of BrC extracted with water and organic solvents from the same sample (16). Reproduced with permission from ref. (16). Copyright 2016, ACS.

Heterogeneous gas-particle and condensed phase reactions of aerosols during atmospheric aging also modify the composition and light absorption of BrC chromophores. Notably, BrC components containing aromatic molecules with various oxygenated groups present in fresh BBOA (attributed to both thermal decomposition of biofuel in BBOA and to photooxidation of aromatic VOC in anthropogenic SOA) may be converted into stronger-absorbing nitro-aromatic species as a result of their reactions with various forms of nitrogen oxides (39, 40). Our studies showed that evaporation-driven (41, 42) and particle-phase condensation (18, 43, 44) reactions forming oligomer species may generate strong BrC chromophores resulting in further ‘browning’ of aged aerosol. Oxidation of nitro-aromatic compounds by OH initially makes them more light absorbing, but further oxidation destroys network of carbon-carbon double bonds in chromophores and therefore results in less absorbing BrC components (45, 46).

Direct photolysis of chromophores by solar radiation also modifies light absorption properties of BrC. We observed that photo-bleaching is the common trend, and overall BrC becomes less absorbing upon exposure to sunlight (47–49). However, photolysis rates of individual chromophores were found to be different by orders of magnitude, depending on their specific molecular composition. For

example, Figure 5 shows a fragment of HPLC-PDA chromatogram for lodge pole pine BBOA collected during the FIREX campaign. A portion of the filter sample was irradiated by 300 nm radiation from a UV light-emitting diode, while the remainder of the filter was left in the dark. Both photolyzed and unphotolyzed samples were analyzed by the HPLC-PDA-HRMS methods. The major chromophores, tentatively assigned as salicylic acid ($C_7H_6O_3$, RT=11.94 min), veratraldehyde ($C_7H_6O_3$, RT= 14.49 min), and coniferaldehyde ($C_{10}H_{10}O_3$, RT=18.45 min) diminish in abundance but remain visible in the chromatogram. Other BrC chromophores are almost completely destroyed by the prolonged exposure to 300 nm radiation. Such an analysis provides insights into which BrC chromophores are photolabile and which are photo-resistant.

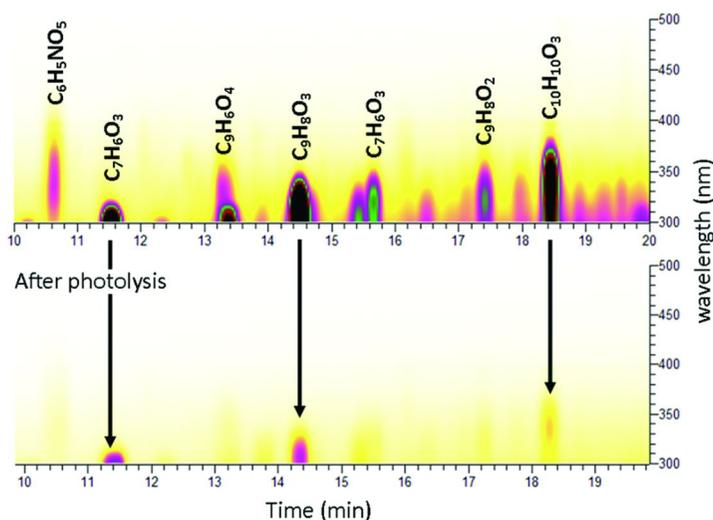


Figure 5. Upper Panel: HPLC-PDA chromatogram for lodge pole pine BBOA with tentative elemental formulas assigned for each light-absorbing compound. Lower Panel: HPLC-chromatogram for the sample after direct photolysis of the particulate matter on the filter.

We need to emphasize that photobleaching is not the only possible effect of UV irradiation on BrC. Figure 6 illustrates a more complex case where 2,4-dinitrophenol (2,4-DNP) chromophores absorbing in the UV range decompose under photolysis, but then their photolysis products undergo secondary reactions to form a new dimer product absorbing in the visible range (48). Similar observations were made for nitrophenols undergoing aqueous OH oxidation (45, 46), in which the absorption coefficient of the mixture first increased and then decreased during the oxidation process. These experiments emphasize the complicated role of photochemical aging in determining the light absorption properties of BrC samples.

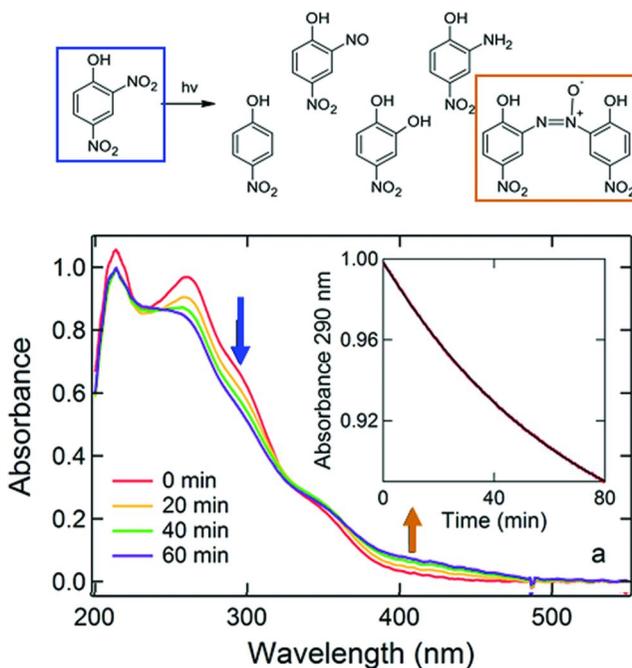


Figure 6. Upper panel: Products identified in photo-degradation of 2,4-DNP (marked by blue frame). Brown frame indicates a dimer product absorbing in the visible range. Lower panel: UV-vis absorption spectra recorded during the photo-degradation of 2,4-DNP. The blue arrow and the inset show the decay of the 290 nm peak of 2,4-DNP and the brown arrow shows buildup of the 400-450 nm absorbance attributed to the dimer product (48).

To conclude, the initial phenomenological information on the composition and transformations of BrC chromophores characteristic of BBOA and anthropogenic SOA has been formulated based on the studies highlighted above. Studies performed so far indicate that BrC chromophores have complex and diverse composition and that their molecular identity may depend on the primary source. On the other hand, several common BrC constituents also have been identified. These include nitro-aromatics, PAH, N- and O-heterocyclic compounds, and their derivatives. Several studies have examined atmospheric stability of common chromophores along with mechanisms and lifetimes of transformation under atmospherically relevant conditions. Chemical diversity of BrC chromophores and their low abundance in aerosol samples present a challenge to their successful characterization. Creative applications of multi-modal complementary mass spectrometry techniques interfaced with separation, ionization and spectroscopic platforms are essential to obtain a predictive understanding of the relationship between the chemical composition and optical properties of BrC. Because BrC is a highly dynamic system, its composition and optical properties at the emission source and later downwind may be substantially different. A general trend of the decaying BrC light absorption properties upon its atmospheric ageing has been

reported by majority of the published studies. However, certain instances of the new chromophore formation in aged BrC were also noted.

Despite all these recent research advances, the overall level of our understanding is still insufficient for predicting the properties of BrC in the atmosphere. Future studies are needed to enable practical classification of broader BrC materials for practical parameterization in the next-generation atmospheric and climate models. Although atmospheric models cannot capture the complexity of the chemical composition and optical properties of BrC in its entirety, detailed understanding of the BrC chemistry will facilitate the development of simplified model of the BrC properties and establish parameters necessary for its adequate description in atmospheric models.

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