

# Molecular Chemistry of Atmospheric Brown Carbon Inferred from a Nationwide Biomass Burning Event

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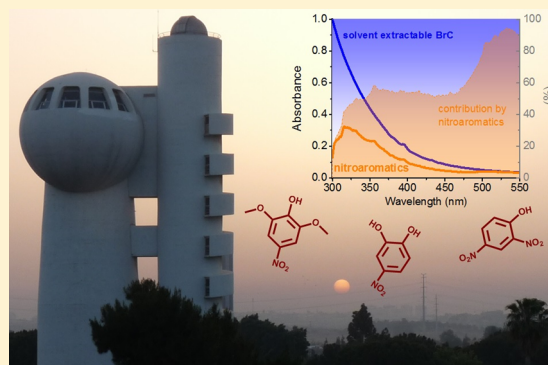
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## Supporting Information

**ABSTRACT:** Lag Ba'Omer, a nationwide bonfire festival in Israel, was chosen as a case study to investigate the influence of a major biomass burning event on the light absorption properties of atmospheric brown carbon (BrC). The chemical composition and optical properties of BrC chromophores were investigated using a high performance liquid chromatography (HPLC) platform coupled to photo diode array (PDA) and high resolution mass spectrometry (HRMS) detectors. Substantial increase of BrC light absorption coefficient was observed during the night-long biomass burning event. Most chromophores observed during the event were attributed to nitroaromatic compounds (NAC), comprising 28 elemental formulas of at least 63 structural isomers. The NAC, in combination, accounted for 50–80% of the total visible light absorption (>400 nm) by solvent extractable BrC. The results highlight that NAC, in particular nitrophenols, are important light absorption contributors of biomass burning organic aerosol (BBOA), suggesting that night time chemistry of  $\bullet\text{NO}_3$  and  $\text{N}_2\text{O}_5$  with particles may play a significant role in atmospheric transformations of BrC. Nitrophenols and related compounds were especially important chromophores of BBOA. The absorption spectra of the BrC chromophores are influenced by the extraction solvent and solution pH, implying that the aerosol acidity is an important factor controlling the light absorption properties of BrC.



## INTRODUCTION

Atmospheric brown carbon (BrC) is an important component of aerosol particles that affects climate forcing through direct interactions with incoming solar and emitted terrestrial radiation.<sup>1–5</sup> BrC is a highly complex and very dynamic mixture of organic compounds similar to atmospheric humic-like substances, with poorly understood properties and aging mechanisms. BrC can be generated from a variety of primary emissions and secondary formation processes.<sup>6,7</sup> Light absorption by BrC has a characteristic wavelength dependence increasing from the visible to the ultraviolet ranges. Furthermore, its optical properties may change as a result of various atmospheric processes such as oxidation,<sup>8,9</sup> solar irradiation,<sup>10,11</sup> changes in temperature,<sup>12</sup> and relative humidity.<sup>13–15</sup> These factors make the chemical composition and concentration of BrC highly variable across sources and locations,<sup>6,7</sup> which in turn results in substantial uncertainties in predicting and mitigating their climate effects.<sup>2,16,17</sup> Because light absorption spectra of organic compounds strongly depend on their molecular structures, identification of atmospheric

chromophores is essential for understanding sources and dynamic optical properties of BrC in the atmosphere.<sup>6,18</sup>

Emissions from biomass burning (BB) caused by wild and prescribed forest fires, burning of crop residues, and domestic heating/cooking have been recognized as the most important source of “primary BrC” worldwide.<sup>19–24</sup> Substantial absorption of light by BrC has been reported in regions with high BB activity,<sup>25</sup> and showed good correlation with organic tracers of BB.<sup>26</sup> In particular, it has been reported that BB was the dominant source of atmospheric BrC in the rural areas of southeastern United States.<sup>27</sup> Numerous studies have been conducted to assess the contribution of BB emissions to atmospheric BrC. Some of them reported measurements of optical properties of either aerosol ensembles<sup>23,28</sup> or aerosol solvent extracts.<sup>21,29</sup> Additional studies investigated the chemical speciation of BrC and evaluated their contributions

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to total aerosol light absorption.<sup>30–35</sup> Nevertheless, our knowledge of chemical identity of BrC chromophores, their specific light-absorbing properties, and atmospheric stability, is still limited.

Recently, we investigated the molecular composition of freshly emitted biomass burning organic aerosols (BBOA) collected during burns of selected biomass fuels.<sup>36</sup> We demonstrated that BrC in fresh BBOA contains numerous chromophores with diverse chemical structures, polarity, and volatility. After emission into the atmosphere, BBOA undergo dilution, coagulation, and chemical processing on the time scales of seconds to days.<sup>37</sup> These processes affect the overall optical properties of BBOA during its lifetime in the atmosphere.<sup>36–38</sup> Thus, evaluating the atmospheric impacts of BrC originating from BB requires not only an adequate description of its light absorption properties and molecular composition at the emission source, but also understanding atmospheric mechanisms resulting in its physical and chemical transformations.

In this study, we investigate the chemical composition and light absorption properties of atmospheric BrC collected during a nationwide bonfire festival which took place on the night of May 6, 2015 in Israel. In this national holiday, people heap wood piles and ignite thousands of bonfires in cities and towns throughout the entire country. This single-night festival starts in the evening, with the most bonfires occurring at night, and ends next morning before sunrise.<sup>39</sup> Samples of ambient aerosol were collected before, during and after the festival for offline analysis using high-performance liquid chromatography (HPLC) coupled with UV–vis detection and electrospray ionization mass spectrometry (ESI–MS) of eluting species. The BBOA samples collected in this study had already mixed with urban atmosphere before they arrived to the sampling site. Therefore, they are considered as slightly aged in comparison with the fresh BBOA emissions. These samples provided a unique opportunity to examine the influence of individual BrC chromophores and their atmospheric evolution on the optical properties of BrC in local atmosphere. We determine the chemical composition of BrC chromophores and discuss chemical processes and atmospheric parameters affecting the overall light absorption by BrC.

## ■ EXPERIMENTAL SECTION

Aerosol sampling and in situ measurements were performed between May third and eighth, 2015. The aerosol samples were collected on preweighed 8" × 10" mixed cellulose ester filters (type 41, Whatman band, GE healthcare, Buckinghamshire, U.K.) using a PM<sub>2.5</sub> high volume air sampler (HiVol 3000, Ecotech, Victoria, Australia). The sampler was installed on the roof of a four-story building of the Department of Earth and Planetary Sciences at the Weizmann Institute of Science in Rehovot (31°53' N, 34° 48' E) that is located in a suburban to urban, semiarid area.<sup>40</sup>

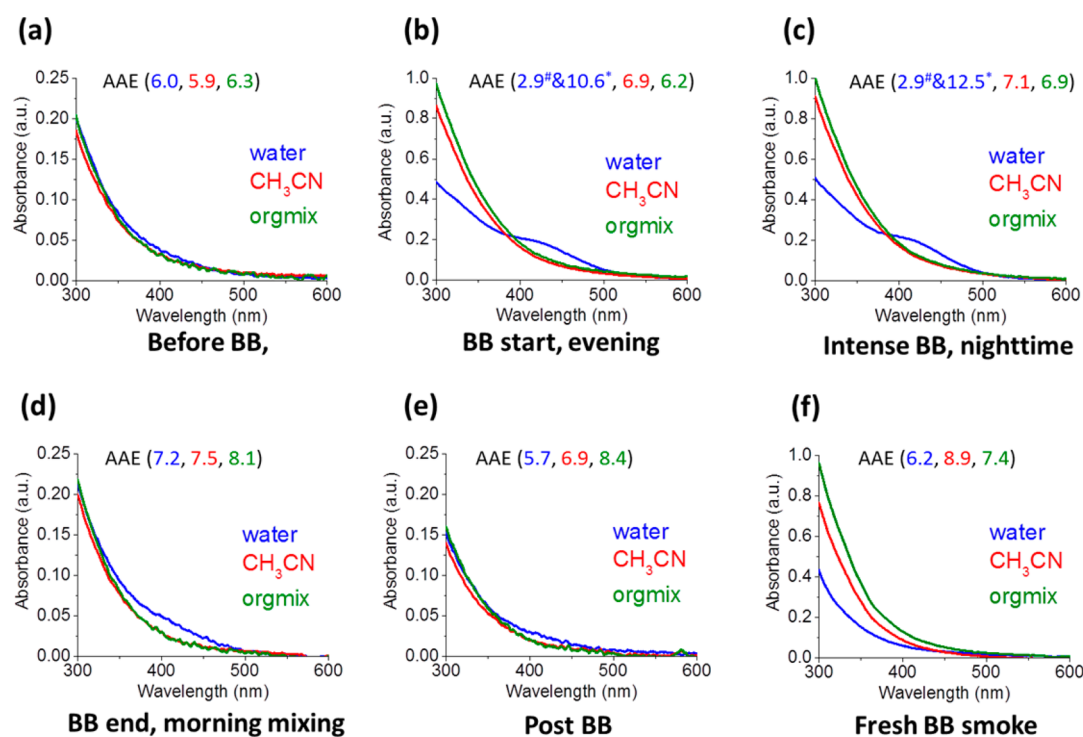
A suite of in situ measurement techniques was employed to monitor the aerosol optical and physical parameters such as wavelength dependent scattering, absorption, extinction coefficients, and size-resolved particle number concentrations. These measurements were used to explore time- and spectral-dependent optical properties of atmospheric aerosols and determine the effective broadband complex refractive index (RI) of ambient aerosol. Detailed description of aerosol sampling and characterization performed during this time period is presented elsewhere.<sup>40</sup> Here, we use a subset of those

results relevant to our data on the molecular identity of major BrC chromophores, which have never been reported before.

A custom built multipass photoacoustic spectrometer (PAS)<sup>40,41</sup> was employed to continuously monitor the absorption coefficient at 404 nm,  $\alpha_{\text{abs}}(404 \text{ nm})$ , as an indicator of BBOA's influence on the ambient atmosphere, and distinguish the periods of before, during and after the bonfire event. Seven PM<sub>2.5</sub> filter samples were collected during the observation period (Table S1 of the Supporting Information, SI). Portions of the aerosol-loaded filters (1/16 area) were extracted with 5 mL of solvent in an ultrasonic bath for 40 min. Three different solvents were used: (1) ultrapure water, (2) acetonitrile, and (3) a mixture of three organic solvents with broad polarity index hereafter referred to as "orgmix" (acetonitrile: dichloromethane: hexane = 2:2:1, v/v). The extracts were filtered using syringe filters with 0.45  $\mu\text{m}$  PTFE membrane to remove insoluble fractions. The bulk UV–vis absorption spectra of the resulting BrC solutions were acquired using a UV–vis spectrometer (USB 2000+, Ocean Optics) over a 250–900 nm wavelength range.

BrC water extracts were analyzed using a HPLC/PDA/HRMS platform.<sup>42,43</sup> The platform consists of a Surveyor Plus system (including a quaternary LC pump, an auto sampler and a PDA detector), a standard IonMAX electrospray ionization (ESI) source, and a high resolution LTQ-Orbitrap mass spectrometer (all modules are from Thermo Electron, Inc.). The separation was performed on a reverse-phase column (Luna C18, 2 × 150 mm<sup>2</sup>, 5  $\mu\text{m}$  particles, 100 Å pores, Phenomenex, Inc.). The binary solvent included: (A) water with 0.05% v/v formic acid and (B) ultrapure grade acetonitrile with 0.05% v/v formic acid. Gradient elution was performed by the A+B mixture at a flow rate of 200  $\mu\text{L}/\text{min}$ : 0–3 min hold at 10% of B, 3–43 min linear gradient to 90% B, 43–50 min hold at 90% B, 50–51 min return back to 10% of B, and 51–70 min hold at 10% of B to recondition the column for the next sample. The pH of this mixed solution was between 3 and 4 during the gradient period, measured with pH test strips (SIGMA P4661, 0.0–6.0 pH, resolution: 0.5 pH unit). UV–vis absorption was measured using the PDA detector over the wavelength range of 200 to 700 nm. The ESI settings were as follows: 4.0 kV spray potential, 35 units of sheath gas flow, 10 units of auxiliary gas flow, and 8 units of sweep gas flow. ESI/HRMS data were acquired in both positive and negative modes. Positive ESI mode preferentially ionizes oxygenated aliphatic compounds and nitrogen bases; while negative ESI mode favors detection of compounds with acidic protons (e.g., nitro-phenols and carboxylic acids).<sup>36,42,44</sup> With the purpose of investigating the pH-dependent light absorption properties of BrC chromophores, the same  $\sim 100 \mu\text{L}$  amount of extracted aerosol samples (filter IDs f4 and f5) were also analyzed with a different column (Kinetex Biphenyl, 2 × 150 mm, 100 Å pores, 5  $\mu\text{m}$  particles, Phenomenex, Inc.) under neutral mobile phase conditions (pH  $\approx 7$ , confirmed with pH test strips SIGMA P3536, 6.0–7.7 pH, resolution: 0.3 pH unit). In this case, solvents A (water) and B (acetonitrile) did not contain formic acid but the LC gradient and ESI instrument settings were the same as those in experiments using the C18 column.

Xcalibur (Thermo Scientific) software was used to acquire raw data. The HPLC/PDA/HRMS data were processed with an open source software toolbox, MZmine 2 (<http://mzmine.github.io/>), to perform peak deconvolution and chromatogram construction.<sup>45</sup> Analysis and assignments of MS peaks were performed using a suite of Microsoft Excel macros developed in



**Figure 1.** UV–vis spectra of bulk BrC solutions extracted with different solvents for (a)–(e) five samples collected at different periods of the field campaign (f2, f4, f5, f6, and f7, as noted in Table S1) and (f) fresh BB smoke particles collected from burning of ponderosa pine during the FIREX campaign (<https://www.esrl.noaa.gov/csd/projects/firex/>). The AAE values were calculated by a linear regression fit to  $\log(\text{abs})$  vs  $\log(\lambda)$  in the wavelength range of 300–600 nm. The colors denote AAE values and spectra obtained with different solvents. \*AAE calculated for the 300–450 nm range; \*AAE calculated for the 450–600 nm range.

our group that enable background subtraction, first and second-order mass defect analysis and grouping of homologous peaks.<sup>46</sup> Elemental formulas of one representative peak from each group were assigned using MIDAS molecular formula calculator (<http://magnet.fsu.edu/~midas/http://magnet.fsu.edu/~midas/>). Formula assignments were performed using the following constraints:  $C \leq 100$ ,  $H \leq 200$ ,  $N \leq 3$ ,  $O \leq 50$ ,  $S \leq 1$ , and  $Na \leq 1$ . The double-bond equivalent (DBE)<sup>47</sup> values of the neutral formulas were calculated using the equation:  $\text{DBE} = c - h/2 + n/2 + 1$ . The aromaticity index (AI)<sup>48,49</sup> was calculated using the equation  $\text{AI} = [1 + c - o - s - 0.5h]/(c - o - n - s)$ , where  $c$ ,  $h$ ,  $o$ ,  $n$ , and  $s$  correspond to the number of carbon, hydrogen, oxygen, nitrogen, and sulfur atoms in the neutral formula, respectively.

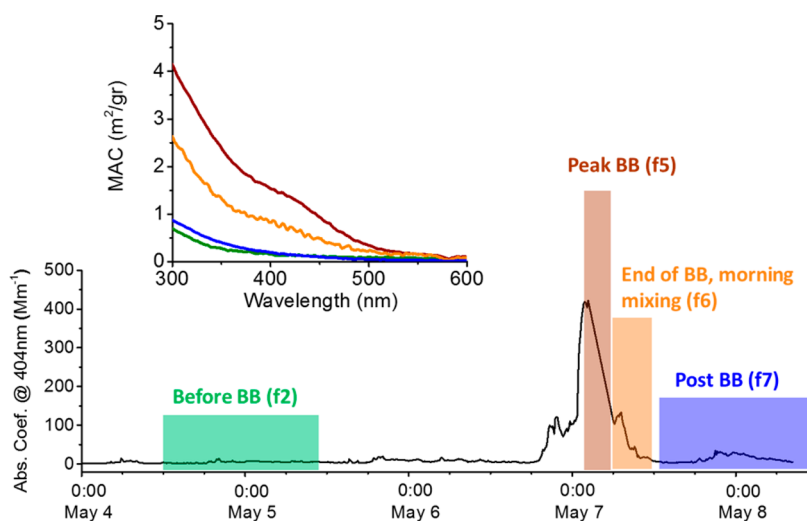
## RESULTS AND DISCUSSION

Quantitative understanding of the light absorption properties of BrC in the atmosphere relies on identification and quantification of BrC chromophores. The HPLC/PDA/HRMS approach employed in this study is well-suited for this task. However, the results of this analysis may be affected by the effect of solvent composition, we compared bulk solution properties of BrC extracted using different solvents. Figure 1 shows comparison of the UV–vis spectra of BrC extracted with water, acetonitrile, and orgmix. The Absorption Ångström exponent (AAE) was calculated by a linear regression fit to  $\log(\text{abs})$  vs  $\log(\lambda)$  in the wavelength range of 300–600 nm. For all the samples examined in this study, light absorption of BrC drops off with increasing wavelength, with AAE ranging from 2.9 to 12.5. For ambient aerosol samples collected in this study, similar extraction efficiency was observed using acetonitrile and

orgmix (Figure 1a–e), while fractions extracted with water varied between different samples.

In samples before the BB event (filters f1, f2, and f3), very similar UV–vis spectra were measured for BrC extracted with water, acetonitrile, and orgmix (Figure 1a). However, in the BB-affected aerosol samples, BrC extracted with water exhibited very different light absorption features compared to that extracted with acetonitrile and orgmix (Figure 1b,c). At shorter wavelength (<380 nm), the organic extract showed higher light absorption than water extract. In contrast, at longer wavelength (>380 nm), higher light absorption was observed for the water extracts. We also observed that in the UV–vis spectra of water extracts, the wavelength dependent absorption decreases more slowly and has a characteristic absorption band in the 380–500 nm range, suggesting contribution from molecular-specific chromophores associated with BB emissions. This absorption band is most prominent for the night time samples and starts to disappear in the morning sample, after the BB event (Figure 1d). Later in the day, as BB emissions are further diluted by ambient air, the UV–vis spectra of aerosol samples change gradually back to the same spectra as those observed for the background aerosol before the event. This trend indicates that solvent-extracted BrC compounds in the background atmosphere of this study are mostly highly oxidized water-soluble organic compounds. In contrast, BrC in fresh BB smoke particles contains a diverse mixture of compounds with different polarity.<sup>36</sup> As a result, the amount of BrC light absorption detected in the solvent extracts follows the trend of orgmix > acetonitrile > water. In that sample, a significant portion of light absorption can be attributed to nonpolar or intermediate polarity compounds, consistent with findings of a previous study on BrC materials from wood combustion.<sup>21</sup>



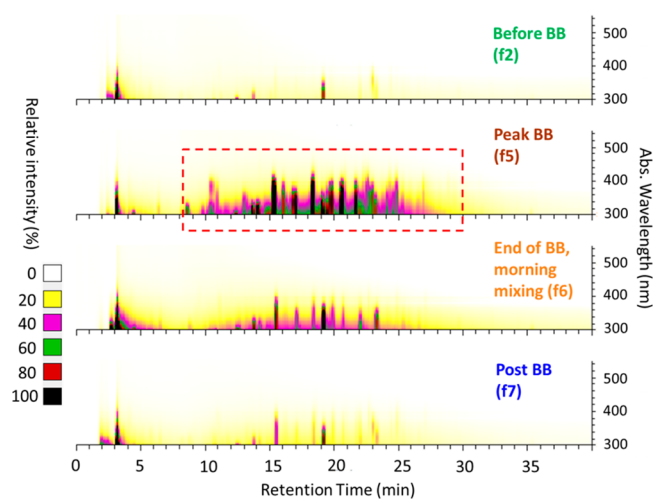


**Figure 2.** Ambient aerosol absorption coefficient measured at 404 nm wavelength with PAS.<sup>40</sup> The colored shaded regions indicate the periods when four aerosol samples (f2, f5, f6, and f7, as listed in Table S1) were collected on filter substrates for chemical analysis. The inset shows the wavelength dependent mass absorption coefficient (MAC) of water extractable BrC contents<sup>40</sup> corresponding to these four representative samples collected before biomass burning (BB) event (f2, green), during the BB event (f5, brown), next morning after the BB event ended (f6, orange), and a day after the BB event (f7, blue).

Figure 2 displays time dependence of the aerosol absorption coefficient,  $\alpha_{\text{abs}}(404 \text{ nm})$ , which increased considerably at night during the bonfire festival. Although in situ measurement of organic speciation was unavailable for this study, a distinct increase of organic aerosol mass and the BB marker fragments ( $m/z = 60$ , measured with a time-of-flight Aerodyne aerosol mass spectrometer) had been observed in a previous case study on the Lag BaOmer day in 2009.<sup>39</sup> In the morning after the festival, the value of  $\alpha_{\text{abs}}(404 \text{ nm})$  decreased due to dilution and mixing processes, as well as photolysis and other transformation reactions in the atmosphere.<sup>51</sup> Meanwhile, the concentration of the SOA tracer fragment,  $m/z = 44$ , was observed to increase during the day following the burning.<sup>39</sup> These results clearly indicate the influence of BB on light absorption by ambient aerosol, as well as the fast chemical evolution of BB plume in ambient air. Although all seven samples were analyzed in this study, only four of them (f2—before BB, f5—dominated by BB smoke particles, f6—at the end of the BB event, and f7—post BB period) were selected for further discussion.

Figure 3 shows the HPLC-PDA chromatograms of these four samples. Many more individual chromophores were detected in the sample collected during the nighttime BB event than in the samples collected before and after the event. These chromophores are at least partially responsible for the elevated light absorption observed in the bulk UV–vis spectra. BrC chromophores were identified using an approach described in our previous studies.<sup>36</sup> Briefly, this approach identifies mass spectral features with LC elution times that coincide with light absorption in the near-UV and visible wavelength ranges detected using PDA. The elemental formulas are subsequently assigned using a procedure described in the Experimental Section.<sup>31,36,42,43</sup>

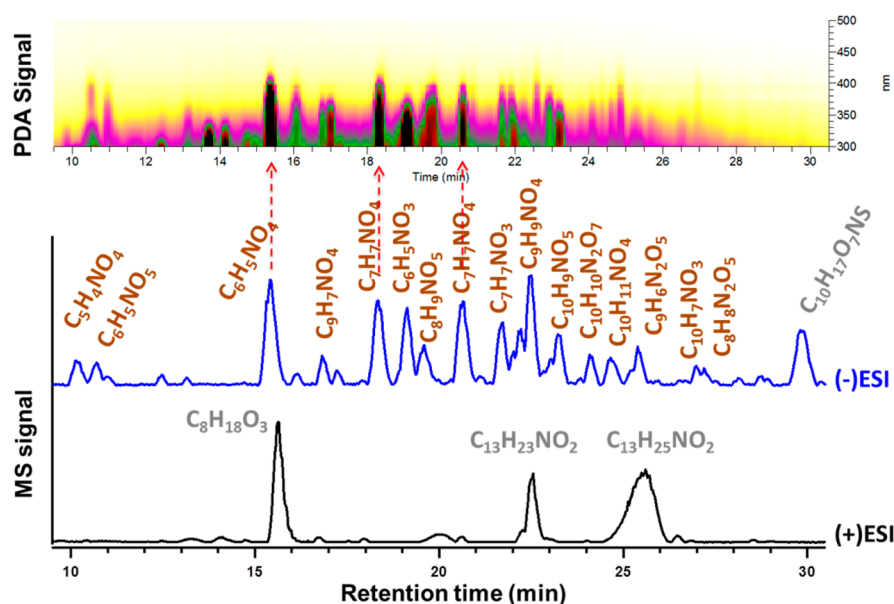
Figure 4 shows HPLC-PDA-HRMS chromatograms of the f5 sample (water extract) collected at the peak of the festival. Major peaks detected in the positive ESI-HRMS chromatogram correspond to compounds with low degree of unsaturation ( $\text{DBE} \leq 3$ ). They are unlikely BrC chromophores due to the lack of poly conjugated  $\pi$  bonds. In addition, elution time of these peaks did not coincide with elution times of



**Figure 3.** HPLC-PDA chromatograms of BrC samples collected at different periods of the field campaign. To facilitate visual comparison, the PDA signals are scaled with respect to the sampled air volume to facilitate visual comparison.

chromophores obtained using PDA detector. In contrast, elution profiles of peaks observed in the negative ESI-HRMS chromatogram correspond well with the absorption features seen in the PDA chromatogram. Table S2 summarizes the list of identified molecular species for which their time-resolved negative mode MS features correlate well with that of the PDA light absorption signals. For clarity, we report all detected compounds as neutral species, unless stated otherwise. A majority of these compounds contain one or two nitrogen atoms and at least three oxygen atoms. These species have high degrees of unsaturation with  $\text{AI} > 0.5$  and are observed only in negative mode spectra, indicating that they are likely nitroaromatic compounds, such as nitrophenols and nitroaromatic acids.

For example, the UV–vis spectrum of a chromophore,  $\text{C}_6\text{H}_5\text{NO}_3$ , eluted at  $\text{RT} = 19.08 \text{ min}$  is characterized by a single absorption maximum ( $\lambda_{\text{max}}$ ) around 318 nm, which matches the

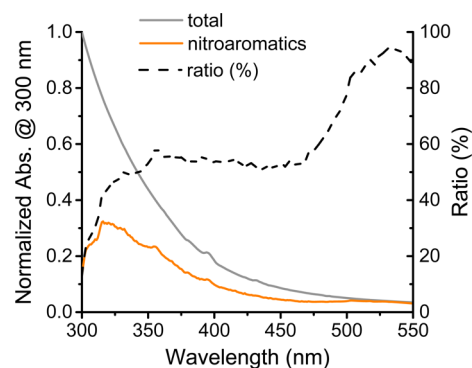


**Figure 4.** HPLC/PDA/HRMS chromatograms of BrC water extract from a sample (f5) collected during the biomass burning event. The lower panel shows the base peak chromatograms acquired in the (–) ESI mode (blue) and (+) ESI mode (black). Molecular formulas in brown color denote representative BrC chromophores with retention times (RT) corresponding to the light absorption peaks detected on the PDA detector. Formulas in gray color denote compounds detected with high ion abundance but unlikely BrC chromophores due to their degree of unsaturation ( $\text{DBE}/\text{C} \leq 0.3$ ).

UV–vis spectrum of 4-nitrophenol (4NP).<sup>52</sup> Similarly,  $\text{C}_6\text{H}_5\text{NO}_4$  eluted at  $\text{RT} = 15.35$  min exhibits a  $\lambda_{\text{max}}$  at  $\sim 345$  nm and a shoulder at  $\sim 309$  nm, resembling the literature reported spectrum of 4-nitrocatechol (4NC),<sup>53</sup> which has been identified in aromatic SOA produced under high  $\text{NO}_x$  conditions<sup>43</sup> and in rural ambient aerosol affected by wood burning.<sup>54</sup>  $\text{C}_6\text{H}_5\text{NO}_5$  ( $\text{RT} = 10.96$  min) could be a nitrobenzenetriol produced through further oxidation of 4NC<sup>55</sup> or directly emitted from wood burning.<sup>36</sup> These compounds eluted as single species with their characteristic RTs in the HPLC–HRMS chromatograms (Table S2), suggesting no other isomers and confirming their molecular identity. It is interesting to point out that many of the known primary and secondary sources of BrC yield either comparable or even higher amount of 2-nitrophenol (2NP) than 4NP in the atmosphere.<sup>51</sup> It is also reported that the degradation rates of 4NP upon photolysis or reactions with atmospheric radicals are either similar or faster than those of 2NP under typical atmospheric conditions in both gas and aqueous phases.<sup>51,56</sup> Therefore, the prevalence of 4NP in BrC aerosols is likely a result of gas-particle partitioning, consistent with its lower vapor pressure and higher Henry's law constant in comparison with 2NP.<sup>57</sup> This observation suggests that volatility and polarity of organic compounds, which determine their partitioning between phases, are important parameters influencing light absorption properties of atmospheric BrC.

Many nitroaromatic species were detected as multiple structural isomers sharing the same elemental formula. For example, three isomers of  $\text{C}_7\text{H}_7\text{NO}_4$  were detected as prominent PDA features at  $\text{RT} = 18.26$ ,  $19.53$ , and  $20.58$  min. The latter was confirmed to be 4-nitroguaiacol by comparison with a standard, and the other two have UV–vis features resembling spectra of two isomeric methyl nitrocatechols.<sup>30</sup> Likewise,  $\text{C}_7\text{H}_5\text{NO}_5$  eluted at  $16.11$  and  $22.10$  min may represent two isomers of carboxynitrophenol.<sup>35,58</sup> Overall, there were 29 elemental formulas identified as nitroaromatic

compounds (NAC), which are all featured as a  $\text{DBE}/\text{C}$  ratio greater than 0.6 and contain at least one nitrogen and three oxygen in each formula. They are composed of at least 63 structural isomers eluted at different times (Table S2). The absorbance of these chromophores was added together to evaluate the contribution of nitroaromatic species to the overall absorption by water-soluble species. We note that the water extract is diluted by the LC solvent, so direct comparison between the bulk absorption spectra measured with UV–vis spectroscopy and the summed spectra of chromophores measured with HPLC–PDA method is impractical. Therefore, to facilitate comparison, the overall light absorption was determined by injecting the water extract through the HPLC–PDA platform with  $\text{pH} \approx 3$  solvent, but bypassing the column.<sup>36</sup> Figure 5 shows the result of this comparison with the PDA signals of other wavelengths (nm) normalized by that observed at 300 nm. It is shown that the contributions from NAC account for 20% at 300 nm, over 50% at 350–475 nm, and up to 80% over 500 nm. Of note, the detection of



**Figure 5.** Total light absorption from water extract (gray solid), absorption from identified nitroaromatics (orange solid), and the ratio of identified/total absorption (black dash) vs wavelength.

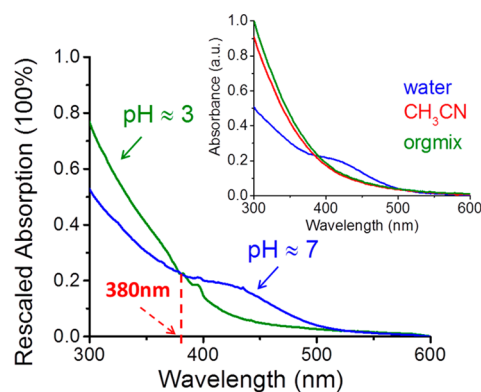
chromophores is incomplete due to the presence of numerous weak chromophores that could not be separated from this complex mixture. Furthermore, some chromophores may be missing due to the incomplete elution from the HPLC column. Thus, our result provides an upper bound estimate of the contribution of nitroaromatics to BrC absorption in the area of study. It has been reported that BB emissions contain abundant aromatic compounds such as alkylphenols, methoxyphenols, and substituted benzoic acids, from pyrolysis of lignin and other vegetation.<sup>59,60</sup> These aromatic compounds are further transformed to nitroaromatics through reactions with reactive nitrogen species either formed in the fire plumes<sup>61,62</sup> or pre-existing in gas- and aqueous phases.<sup>51</sup> Nitroaromatic species have been previously reported as abundant BrC chromophores in organic aerosols collected during the burning season of the Amazon Rainforest,<sup>30</sup> and in cloudwater samples impacted by agricultural biomass burning in eastern China.<sup>31</sup> The latter study demonstrated that the sum of 16 identified nitroaromatic species accounted for ~55% of overall absorption by water-soluble organics at 370 nm.<sup>31</sup> Another study quantified the concentration of five nitrophenols at a downwind location of London, U.K., and estimated their contribution to 370 nm light absorption by BrC. The values ranged between 1% and 29%, exhibiting significant diurnal variations.<sup>33</sup>

It is noted that none of the BrC chromophores observed in the HPLC-PDA chromatograms have characteristic absorption bands above 450 nm apparent in the spectra of water-soluble BrC samples (Figure 1b,c, and insert of Figure 2). This can be attributed to the pH dependent absorptivity of water-soluble BrC chromophores. The nitroaromatic chromophores detected in this study are acidic in nature and exist either in neutral or deprotonated form in aqueous solution, depending on their  $pK_a$  and the pH of the solution. Neutral and deprotonated forms of the same species may have different UV-vis absorption spectra. For example, the absorption maxima of nitrophenols shift toward longer wavelengths (red shift) when they are deprotonated.<sup>43,52,53</sup> Meanwhile, the UV-vis spectra of benzoic acid and its derivatives without nitro-substitution usually exhibit blue shift when deprotonated.<sup>63</sup>

The results shown in Figures 3 and 4 were obtained on the C18 column using an acidic mobile phase with  $pH \approx 3$ . At this pH, the ionized fraction of phenols and carboxylic acids is very low, making it possible to achieve both good retention and separation of major BrC chromophores present as neutral species.<sup>36,43</sup> The C18 column is not suitable for separating ionized compounds present in solvent extracts under neutral or basic conditions.<sup>42</sup> To investigate the effect of solvent pH on the measured BrC absorptivity, we conducted an additional separation experiment on a biphenyl column using mobile phase at  $pH \approx 7$ . The biphenyl structure of the column's stationary phase provides additional retention capability to some aromatic compounds via  $\pi$ - $\pi$  interactions and steric recognition interactions,<sup>42</sup> which helps retain some ionized forms of nitroaromatic compounds at higher pH. As shown in Figure S1, the HPLC-PDA chromatogram obtained under  $pH \approx 7$  is different from the one obtained under  $pH \approx 3$ , revealing a number of chromophores with absorption maximum above 400 nm (Figure S1b). In addition, a substantial fraction of BrC chromophores present in an ionic form eluted at the beginning of the chromatogram. Although it is impossible to separate the individual ionic chromophores under the experimental conditions of  $pH \approx 7$ , their absorption bands above 400 nm are clearly seen at  $RT = 3$ –5 min.

Figure S2 shows an example of the pH dependent absorptivity of BrC chromophores separated at  $pH \approx 3$  and  $pH \approx 7$ . The red shift of their absorption maxima from 300 to 400 nm to 400–500 nm at  $pH \approx 7$  can be attributed to conversion of neutral chromophores into their anionic form. The results provide additional information that confirms the chemical identity of selected BrC chromophores. For instance, in the experiment using C18 column, the  $C_8H_9NO_5$  chromophore exhibits  $\lambda_{max}$  of 345 nm at  $pH \approx 3$  ( $RT = 19.79$  min, Table S2). On the basis of the elemental composition and assuming its structural similarity with other identified chromophores, its molecular structure was assigned to 4-nitrosyringol. In the absence of a 4-nitrosyringol standard or a published UV-vis spectrum of its neutral form, molecular identity of this chromophore remains uncertain. However, another species with the same elemental formula is well separated ( $RT = 22.51$  min) in the chromatogram obtained at  $pH \approx 7$ , and its UV-vis spectrum matches that of the literature report for deprotonated 4-nitrosyringol ( $\lambda_{max} \approx 465$  nm),<sup>64</sup> supporting the assignment of this chromophore.

PDA chromatograms acquired at two pH conditions were integrated from  $RT = 0$  to 40 min to obtain integrated UV-vis spectra of water extractable BrC under both acidic and neutral conditions. Figure 6 shows that the total UV-vis spectrum



**Figure 6.** UV-vis spectra of water extractable BrC collected during the biomass burning event and measured with the PDA detector at different pH conditions. The inset shows the UV-vis spectra of BrC extracted with different solvents from the same sample (panel c of Figure 1). The vertical dashed line with red color indicates the wavelength of 380 nm.

recorded at  $pH \approx 7$  is very similar to that measured for the bulk water-extracted sample (Figure 1c), featuring a characteristic band at 380–500 nm. Under acidic conditions ( $pH \approx 3$ ), this absorption band disappears, and light absorption in the UV range increases. This spectrum is similar to the spectra of BrC extracted in acetonitrile or orgmix, indicating that these BrC chromophores are mainly neutral species that do not dissociate in pure organic solvents. Thus, for the aerosol samples collected during the BB event (Figure 1b,c), differences in light absorption properties between the water and organic extracts of BrC materials can be partly attributed to differences in relative abundances of neutral and ionic nitroaromatic chromophores. The results shown in Figure 6 further confirm that nitroaromatic species are major BrC chromophores produced during the bonfire event. Furthermore, our results indicate that aerosol acidity plays an important role in determining light absorption properties of BrC. This conclusion



is consistent with a recent study of Teich et al.,<sup>34</sup> which introduced acidity-based calculation of the mass absorption coefficient (MAC). Presently, the MAC values are commonly derived from the measured absorption spectra of BrC solutions extracted with either water or organic solvents, without considering the effect of aerosol acidity.<sup>65,66</sup>

Our results also suggest that the effect of aerosol acidity on BrC light absorption vanishes at wavelength of  $\sim 380$  nm which is probably close to an isosbestic point of the absorption spectra for the major BrC chromophores. The effect is more significant at other wavelengths. This conclusion can be also extended to BrC formed in SOA from photo-oxidation of aromatic VOCs where nitroaromatic species are also major BrC chromophores,<sup>43,67</sup> but may differ for other BrC systems such the ones produced through imine-based chemistry.<sup>15,68</sup>

Molecular characteristics of BrC chromophores detected in this study are somewhat different from the chromophores found in fresh wood burning emissions.<sup>36</sup> Although a number of the nitroaromatic species were also present in fresh BBOA, a majority of the chromophores observed by Lin et al. were aromatic compounds containing multiple hydroxyl/methoxy and aldehyde/ketone groups but no nitro groups,<sup>36</sup> which are consistent with thermally decomposed fragments of lignin.<sup>60</sup> The results of this study suggest that nitroaromatic species are dominant BrC chromophores in the atmospherically aged BB emissions at least in urban environments. During this night-long BB event, NO<sub>2</sub> and O<sub>3</sub> concentrations were measured in the range of 20–40 ppb and 5–40 ppb, respectively.<sup>40</sup> As high as 90% of RH was observed through midnight to next morning.<sup>40</sup> Such conditions may favor the formation of nitrate radical ( $\bullet\text{NO}_3$ ) and N<sub>2</sub>O<sub>5</sub>, leading to the nitration of aromatic compounds in both gas and particle phases.<sup>51</sup> It was reported that the gas-phase oxidation of aromatic hydrocarbon by  $\bullet\text{NO}_3$  is fairly slow under such conditions.<sup>69,70</sup> However, the gas-phase reactions of  $\bullet\text{NO}_3$  with phenolic compounds take place at least 4 orders of magnitude faster,<sup>70</sup> and are even much faster in the aqueous phase.<sup>71</sup> Such reactions substantially decrease the volatility of aromatic compounds and promote SOA formation.<sup>72</sup> It also shifts the peak of light absorption toward longer wavelengths, making BBOA more “brown”.<sup>73</sup> Aging of BBOA in the atmosphere occurs mainly by oxidation reactions, which also cause degradation of larger molecules.<sup>74</sup> Thus, our results suggest that chemical aging of smoke particles in the presence of urban atmospheric oxidants make the chemical composition of BBOA less diverse and exhibit certain structural similarity (i.e., nitration on the aromatic ring) among individual BrC chromophores. Additional studies are needed to better understand physical and chemical transformations of BBOA in the atmosphere.

The results presented here demonstrate that, under certain conditions, light absorption by nitroaromatic chromophores can dominate the overall light absorption of BrC. Furthermore, pH dependent equilibrium between neutral and ionized forms of nitroaromatic species may play an important role in controlling their effect on BrC absorption, particularly in the visible range ( $>400$  nm). Ambient aerosols in urban areas are typically acidic (pH  $< 4.0$ ).<sup>75,76</sup> It is reasonable to assume that at pH  $< 4.0$  most of the nitroaromatic chromophores in aerosols are in their neutral form. Thus, UV–vis spectra obtained under acidic conditions (pH  $\approx 3$ ) are more atmospherically relevant, while measurements of BrC absorption in water extracts likely underestimate light absorption in the near UV range and overestimate light absorption in the

visible range (e.g., Figure 6). Because UV–vis spectra measured in organic solvents are similar to those obtained in water under acidic conditions, extraction of aerosol samples into organic solvents may be a preferred approach for measuring BrC light absorption in ambient samples from acidic environments. Since brown carbon chromophores are various organic compounds, their LC extraction using a mixture of organic solvents with different polarities has higher extraction efficiency than using pure water in most of the cases, particularly for source samples.<sup>21</sup>

Cloud or fog droplets are usually less acidic than aerosol particles due to their higher liquid water content,<sup>77,78</sup> which favors dissociation of nitroaromatic species into their ionized forms, thus red-shifting their absorption spectra. Moreover, some aerosols produced from natural processes, such as mineral dust or sea salt particles, contain significant fraction of alkaline components.<sup>79,80</sup> These aerosols have great capacity to buffer aerosol acidity so that light absorption properties of nitroaromatic chromophores may be significantly modified after partitioning into such particles. For example, it was recently reported that a substantial fraction of nitrophenols adsorbed on surfaces of mineral or marine aerosols are deprotonated, causing the UV–vis absorption cross section to red-shift as far out as 650 nm.<sup>81</sup> This further indicates that the aerosol microenvironment (e.g., pH, phase state, or matrix effect) is an important factor that can affect BrC absorption. Molecular level chemical characterization of BrC chromophores is therefore essential to better understand those processes and the underlying mechanisms. Since BB and mineral dust are two important sources of the light absorbing aerosols in the atmosphere and extensive research have been done separately on their climate relevant properties, future work is warranted to investigate the combined effects due to the interactions between inorganic and organic components.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b02276.

Table S1. List of the PM2.5 filter samples collected with a high volume air sampler. Table S2. List of identified BrC chromophores. Figure S1. (a) HPLC-PDA chromatogram obtained with a C18 column at pH  $\approx 3$ . Figure S2. UV–Vis spectra of several BrC chromophores measured with HPLC-PDA analysis at different pH conditions. Additional references. (PDF)

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### Notes

The authors declare no competing financial interest.

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