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Composition and light absorption of nitroaromatic compounds in organic aerosols from laboratory biomass burning

Mingjie Xie[1,2,3,4,*], Xi Chen[4], Michael D. Hays[4], Amara L. Holder[4]

[1]Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, 219 Ningliu Road, Nanjing 210044, China
[2]State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, China
[3]Oak Ridge Institute for Science and Education (ORISE), Office of Research and Development, U.S. Environmental Protection Agency, 109 T.W. Alexander Drive, Research Triangle Pak, NC 27711, USA
[4]National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, 109 T.W. Alexander Drive, Research Triangle Pak, NC 27711, USA

*Correspondence to: Mingjie Xie

E-mail: mingjie.xie@colorado.edu; mingjie.xie@nuist.edu.cn;

Tel: +86-18851903788;

Fax: +86-25-58731051;

Mailing address: 219 Ningliu Road, Nanjing, Jiangsu, 210044, China

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ABSTRACT

This study seeks to understand the compositional details of nitroaromatic compounds (NACs) emitted during biomass burning (BB) and their contribution to light-absorbing organic carbon (OC), also termed brown carbon (BrC). Three laboratory BB experiments were conducted with two U.S. pine forest understory fuels typical of those consumed during prescribed fires. During the experiments, submicron aerosol particles were collected on filter media and subsequently extracted with methanol and examined for their optical and chemical properties. Significant correlations ($p < 0.05$) were observed between BrC absorption and elemental carbon (EC)/OC ratios for test specific data. However, the pooled experimental data indicated that the BB BrC absorption depends on more than the BB fire conditions as represented by the EC/OC ratio. Fourteen NACs were identified in the BB samples, four of which ($C_{10}H_{11}NO_4$, $C_{10}H_{11}NO_5$, $C_{11}H_{13}NO_5$ and $C_{11}H_{13}NO_6$) have not been observed previously in chamber-based secondary organic aerosols, and are expected to have methoxyphenol-type structure specific to the pyrolized biomass lignin based on mass spectral evidence, suggesting these compounds may be unique to BB aerosols. The average total contribution of NACs to organic mass (0.023 ± 0.0089 to 0.18 ± 0.067%) was 5–10 times lower than the average contribution to the overall BrC absorption at 365 nm (0.12 ± 0.047 to 2.44 ± 0.67%). The average contributions (%) of total NACs to organic mass and aqueous extracts absorption correlated significantly ($p < 0.05$) with EC/OC for both test specific and pooled experimental data. These results suggested that the formation of NACs from BB depended more on burn conditions than the bulk absorptive properties of BB BrC.

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1 Introduction

Biomass burning (BB), including residential burning for cooking, heating, and open burning, is a major source of atmospheric carbonaceous aerosol, contributing 62% and 93% of black carbon (BC) and primary organic carbon (OC) emissions, respectively (Bond et al., 2004). BC can absorb sunlight across the entire spectral range with a weak dependence on wavelength (λ) (Bond, 2001;Bond et al., 2013;Lack and Langridge, 2013), while light absorption of BB OC increases rapidly from the shorter visible region (400–550 nm) to the ultraviolet (UV) region (300–400 nm) (Kirchstetter et al., 2004;Laskin et al., 2015;Chakrabarty et al., 2016;Xie et al., 2017b). The light absorption caused by BC and OC from BB can affect the Earth's radiative balance (Ramanathan et al., 2001;Anderson et al., 2003;Bond and Bergstrom, 2006), and BC emission factors and its warming effect have been intensively investigated (Bond et al., 2004;Bond et al., 2013). However, the optical properties and chemical composition of light-absorbing OC, also termed brown carbon (BrC) from BB is less well characterized. The chromophores in BrC are expected to have high degree of unsaturation or conjugation (Chen and Bond, 2010;Lin et al., 2014;Laskin et al., 2015), but are seldom identified and used as BrC tracers in the atmosphere (Desyaterik et al., 2013;Zhang et al., 2013;Teich et al., 2016).

Polycylic aromatic hydrocarbons (PAHs) and their derivatives are typical BrC chromophores (Samburova et al., 2016;Huang et al., 2018), of which the light absorption in the UV and visible wavelength range is highly dependent on ring numbers and degree of conjugation (Samburova et al., 2016). However, PAH emissions are not source-specific, but are associated with multiple different combustion processes, including BB (Samburova et al., 2016), coal burning (Chen et al., 2005), motor vehicle emissions (Riddle et al., 2007), etc. Therefore, PAHs are not unique to BB BrC. Nitroaromatic compounds (NACs) are another class of BrC

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chromophores that have been detected in BB (Lin et al., 2016), cloud water (Desyaterik et al., 2013) and atmospheric particles (Zhang et al., 2013;Teich et al., 2017). In water extracts of atmospheric particles, NACs contribute greater than 3% of the light absorption at 365–370 nm (Zhang et al., 2013;Teich et al., 2016). Lin et al. (2017) investigated the influence of BB on BrC absorption during a nationwide bonfire festival in Israel, and found that NACs accounted for 50% – 80% of water extractable BrC absorption at $\lambda > 400$ nm. These results suggest that NACs are important BB BrC chromophores, but their composition and structures are less certain. Nitrophenols, nitrocatechols, and methyl nitrocatechols (including isomers) are commonly observed in BB aerosols (Claeys et al., 2012;Lin et al., 2016;Lin et al., 2017), and are also generated from the photo-oxidation of benzene, toluene, and *m*-creosol in the presence of NO_X (Iinuma et al., 2010;Lin et al., 2015;Xie et al., 2017a). As such, other NAC structures specific to BB are needed to represent BB BrC chromophores. Additionally, very few studies have examined the influence of burn conditions on the formation of NACs in BB emissions, although it is well known that increasing combustion temperature, or flaming dominated combustion, is associated with strong BrC absorption (Chen and Bond, 2010;Saleh et al., 2014).

The present study attempts to identify additional NAC structures in laboratory BB samples, characterize the compositional profile of NACs from BB, and investigate the relationship between their formation and fire conditions. A high-performance liquid chromatograph interfaced to a diode array detector (HPLC/DAD) and quadrupole (Q)-time-of-flight mass spectrometer (ToF-MS) was used to examine NACs in $PM_{2.5}$ (particulate matter with aerodynamic diameter $\leq$ 2.5 μm) from three BB experiments. A thermal-optical instrument determined bulk OC and elemental carbon (EC) in the PM, and a UV/Vis spectrometer was used to measure total BrC absorption in methanol extracts of BB $PM_{2.5}$. The results of this study will

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benefit the exploration of organic molecular markers for BB BrC in the atmosphere, and help explain the influence of fire conditions on the formation of BrC chromophores.

2 Methods

2.1 Laboratory open BB simulations

Laboratory simulations of open BB were conducted at the U.S. EPA [Research Triangle Park (RTP), North Carolina (NC)] Open Burn Test Facility (OBTF), a 70 m^3 enclosure, as detailed in Grandesso et al. (2011). Details of the protocols for biomass fuel collection and burn simulations were provided elsewhere (Aurell and Gullett, 2013;Aurell et al., 2015;Holder et al., 2016). Briefly, forest understory fuels were gathered from two different locations in the southeastern United States — Florida (FL) and NC. The FL forest field (Eglin Air Force Base, FL) is characteristic of a well-managed long leaf pine (*Pinus palustris*) ecosystem. The NC forest was located near the EPA campus in RTP, and it contained mainly Loblolly pine (*Pinus taeda*) with some deciduous hardwood trees leaf litter. Biomass fuel was divided by a quartering procedure (Aurell and Gullett, 2013) and burned in batches (1 kg) on an aluminum foil-coated steel pan (1 m × 1 m). Ambient air was pulled into the OBTF through a large inlet at ground level and the combustion exhaust was drawn through a roof duct near a baghouse using a high-volume blower. $PM_{2.5}$ was sampled at 10 L min^{-1} on Teflon (47 mm, Pall, Ann Arbor, Michigan, USA) and pre-heated (550 ^{o}C, 12 h) quartz filters (QF, diameter 43 mm, Pall) with a $PM_{2.5}$ impactor (SKC, Pittsburgh, Pennsylvania, USA). For the NC forest fire simulation, filter samples were collected during an initial flaming phase lasting approximately 1–3 minutes. After most of the flames were extinguished, a second set of filter samples were obtained for the smoldering emissions. Smoldering samples were collected until there was little or no visible smoke being emitted from the fuel bed, typically lasting 6–15 minutes. Two separate experiments were done

with the NC forest fuels in spring and summer, respectively, with different ambient temperatures (Table S1). Sampling of the FL forest fire simulations was done in autumn over the complete burn, not by combustion phase. Only one experiment was done for the FL forest fuels collected in fall. Background samples were obtained post-burn inside the OBTF. A summary of the sample information is provided in Table S1 of the supporting information.

2.2 Bulk carbon and light absorption measurement

Details of the bulk OC, EC and light absorption analysis methods are provided in Xie et al. (2017a,b). Briefly, the bulk OC and EC were measured using an OC-EC analyzer (Sunset Laboratories, Portland, OR) with a modified NIOSH method 5040 protocol (NIOSH, 1999). Filters were extracted in methanol (supplementary information) and the light absorption of the extracts was measured by a UV/Vis spectrometer (V660, Jasco Incorporated, Easton MD). The extraction efficiency (η, %) was calculated from the analysis of residual OC on the methanol-extracted filter. The light absorption coefficient (Abs_{λ}, Mm^{-1}), mass absorption coefficient (MAC_{λ}, $m^2\ gC^{-1}$) and solution absorption Ångström exponent ($Å_{abs}$) of methanol extractable OC were calculated to reflect the light-absorbing properties of bulk BB BrC. Details of the calculation method are provided in the supplementary information. In this work, we focus on the BrC absorption at λ = 365 and 550 nm, representing near UV and visible regions (Zhang et al., 2013;Saleh et al., 2014), respectively.

2.3 Filter extraction and HPLC/DAD-Q-ToFMS analysis

The $PM_{2.5}$ filter extraction and subsequent instrumental analysis methods used here are the same as those described in Xie et al. (2017a). Briefly, a 4–6 cm^2 piece of each filter was pre-spiked with 25 μL of 10 ng $μL^{-1}$ nitrophenol-d4 (internal standard, IS), and extracted ultrasonically in 3–5 mL of methanol twice (15 min each). After filtration and concentration, the

final volume was roughly 500 µL prior to HPLC/DAD-Q-ToFMS analysis. An Agilent 1200 series HPLC equipped with a Zorbax Eclipse Plus C18 column (2.1×100 mm, 1.8 µm particle size, Agilent Technologies) was used to separate the target NACs; the identification and quantification of NACs were determined with an Agilent 6520 Q-ToFMS. The Q-ToFMS was equipped with a multimode ion source operating in electrospray ionization (ESI) and negative (–) ion modes. All samples were analyzed in full scan mode (40–1000 Da), and then selected samples were re-examined using MS/MS mode under identical chromatographic conditions. The MS/MS spectra of target $[M–H]^-$ ions provided *m/z* data, which was used for identifying NAC structures. Table S2 provides the standard, surrogate assignments, proposed structures, and formulas of the identified NACs. The criterion for surrogate selection is provided in supplementary information. Acceptance criterion of ± 10 ppm mass accuracy was set for compound identification and quantification. The extracted ion chromatograms (EICs) and Q-ToF MS/MS spectra for identified compounds in selected BB samples are provided in Figs. S1–S2 of the supplementary information. The Q-ToF MS/MS spectra of standard or surrogate compounds used in this work are provided in Fig. S3 for comparison. The quality assurance and quality control (QA/QC) procedures applied for NACs quantification were provided in Xie et al. (2017a). Quantification was conducted using the internal standard method with 9-point calibration curves (~0.01–2 ng μL^{-1}). The compounds corresponding to each NAC formula (including isomers) were quantified individually and added together for the calculation of mass contribution (%) to organic matter (OM µg m^{-3}) in each sample. Field blank and background samples were free of contamination for NACs. Average recoveries of standard compounds ranged from 75.1 to 116%, and the method detection limit ranged from 0.70 to 17.6 pg (Table S3).

3 Results and discussion

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3.1 Light absorption of extractable OC

The average EC/OC ratio, OC extraction efficiency, MAC_{365}, MAC_{550}, and $Å_{abs}$ of all samples grouped by experiment and fire phase are shown in Table 1. Abbreviations for each sample group are also listed in the table. The optical properties and bulk composition of the FL forest samples were reported in Xie et al. (2017b). The average extraction efficiency for all groups of BB samples is greater than 95% (range 97.0 ± 1.87 to 99.5 ± 0.33%), and the light absorption exhibits strong wavelength dependence, with average $Å_{abs}$ values ranging from 5.68 ± 0.70 to 7.95 ± 0.22. For each of the two NC forest experiments, the samples collected during the flaming phase (NF1 and NF2) have significantly higher (student's *t* test, $p < 0.05$) average EC/OC ratios, MAC_{365} and MAC_{550}, and lower ($p < 0.05$) $Å_{abs}$ than those collected during the smoldering phase (NS1 and NS2). When combining the results from the two NC forest experiments, the average MAC_{365} values for NC forest 2 are significantly ($p < 0.05$) higher than NC forest 1, despite having a comparable EC/OC ratio (NF1 = 0.042 ± 0.014 and NF2 =0.049 ± 0.011, NS1 = 0.0098 ± 0.0024 and NS2 = 0.0075 ± 0.0026). Additionally, the average EC/OC ratio of FF samples is 5–30 times higher than NF and NS samples, while the average MAC_{365} and MAC_{550} values of FF samples (1.13 ± 0.15 and 0.053 ± 0.023 m^2 gC^{-1}) are comparable to NS1 samples (1.10 ± 0.11 and 0.054 ± 0.015 m^2 gC^{-1}), but lower than other NC forest samples.

High temperature pyrolysis or intense flaming conditions are known to increase the fraction of EC in the total carbonaceous aerosol emissions of BB (Hosseini et al., 2013;Eriksson et al., 2014;Martinsson et al., 2015;Nielsen et al., 2017). Several studies found that the light-absorbing properties of BB OC could be parameterized as a function of the EC/OC or BC/organic aerosol (OA) ratio, a measurement proxy for burn conditions (McMeeking et al., 2014;Saleh et al., 2014;Lu et al., 2015;Pokhrel et al., 2016), and inferred that the absorptivity of

191 BB OC depended strongly on burn conditions, not fuel type. In Xie et al. (2017b). significant
192 correlations ($p < 0.05$) between MAC_{365} of methanol extractable OC from BB and EC/OC ratios
193 were observed only for samples with identical fuel type, but not for pooled samples with
194 different fuel types, indicating that both burn conditions and fuel types can impact the light
195 absorption of BB OC. The contradiction is possibly ascribed to different approaches used in
196 characterizing the light absorption of BB OC and different test fuel types (Xie et al., 2017b).

197 In this work, the comparison of the flaming versus smoldering samples for each NC
198 experiment suggests that the light absorption of OC from BB is strongly dependent on burn
199 conditions when the fuel type and ambient conditions are similar. The difference in MAC_{365}
200 values between the two NC forest experiments might suggest that the light absorption of BB OC
201 is also dependent on ambient conditions, as the two NC forest experiments were conducted in
202 spring and summer, respectively, with distinct ambient conditions (Table S1). The comparison of
203 the FL versus NC forest experiments suggests that the fuel type can also play a role in BB OC
204 absorption. Thus, the light absorption of BB OC may be influenced by factors other than burn
205 conditions. Additionally, EC/OC ratios alone may not predict BB OC light absorption from
206 burns with varying fuel types and ambient conditions.

207 **3.2 Identification and quantification of NACs**

208 In the current work, fourteen NAC chemical formulas in BB samples were identified
209 (Table S2) using the HPLC/DAD-Q-ToFMS analysis, covering all the NACs with high
210 abundance and strong absorption in ambient and BB particles reported in previous work (Claeys
211 et al., 2012;Mohr et al., 2013;Zhang et al., 2013;Chow et al., 2016;Lin et al., 2016;Lin et al.,
212 2017). Their EICs are provided in Fig. S1. The NACs structures corresponding to each chemical
213 formula were examined using MS/MS data in Fig. S2. In Table S4, the averages and ranges of

relative mass contribution of identified NACs to OM are provided by BB experiment and burn condition. Here the OM mass was calculated as 1.7 × OC mass (Turpin et al, 2001). In addition, the average relative mass contributions of each NAC in BB samples are shown in Fig. 1.

The three BB experiments have consistent mass contribution profiles (Fig. 1), although they used different fuel types and were conducted in different seasons. The BB samples collected during flaming periods (NF1 and NF2) contain significantly higher ($p < 0.05$) average relative mass contributions from total NACs to OM ($tNAC_{OM}$%: NF1 0.18 ± 0.067%, NF2 0.16 ± 0.045%) than those collected during smoldering periods (NS1 0.055 ± 0.026%, NS2 0.023 ± 0.0089%). During the FL forest burn experiment, flaming and smoldering phases were not separated for sampling, and the average $tNAC_{OM}$% is 0.13 ± 0.059%, which is between the $tNAC_{OM}$% of the flaming and smoldering samples of the NC forest experiments. If we recalculate the average $tNAC_{OM}$% for the NC forest experiments by combining the flaming and smoldering sample data in each burn, the three BB experiments (FL forest, NC forest 1 and 2) show similar average $tNAC_{OM}$% (0.11 ± 0.017–0.13 ± 0.059%), and the average $tNAC_{OM}$% across all samples in this work is 0.12 ± 0.051% (range 0.037 to 0.21%). This value is comparable to that observed at Detling (~ 0.5%), United Kingdom during winter, when domestic wood burning is prevalent (Mohr et al., 2013). In the current work, most of the NACs were quantified using surrogates, and their contributions to OM from BB may change if authentic standards or different surrogates are used for quantification. However, the three experiments might still have consistent relative mass contribution profiles of NACs and similar average $tNAC_{OM}$%, assuming burn conditions and fuel types have minor impact on the OM/OC ratio. Therefore, unlike the light absorption of methanol extractable OC, the formation of NACs in BB seem to depend largely on burn conditions, rather than fuel types and ambient conditions.

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Among the fourteen identified NAC formulas, $C_6H_5NO_4$ and $C_9H_9NO_4$ have the highest concentrations (Fig. 1) in FL forest and NC forest flaming-phase samples, accounting for 0.029 ± 0.011 to 0.037 ± 0.011% and 0.023 ± 0.012 to 0.049 ± 0.016% of the OM, respectively (Table S4). In NC forest smoldering-phase samples, $C_6H_5NO_4$ has the highest mass contribution (NS1 0.024 ± 0.0098%, NS2 0.010 ± 0.0027%), followed by $C_7H_7NO_4$ (NS1 0.0087 ± 0.0030%, NS2 0.0043 ± 0.0010%) and $C_9H_9NO_4$ (NS1 0.0052 ± 0.0033%, NS2 0.0047 ± 0.0013%) (Table S4). The $C_6H_5NO_4$ was identified as 4-nitrocatechol by comparing its MS/MS spectrum (Fig. S2b) with that of an authentic standard (Fig. S3b). The EIC of $C_9H_9NO_4$ exhibited 3–4 isomers (Fig. S1i), while only two MS/MS spectra (Fig. S2l,m) were obtained due to the weak EIC intensity for compounds eluting at times ≥ 10 min. The fragmentation patterns of $C_9H_9NO_4$ compounds (Fig. S2l,m) are different from that of 2,5-dimethyl-4-nitrobenzoic acid (reference standards with the same formula, Fig. S3g) without the loss of CO_2, suggesting that the $C_9H_9NO_4$ compounds identified in this work lack a carboxylic acid group. Both MS/MS spectra of $C_9H_9NO_4$ reflect the loss of CNO (Fig. S2l,m), suggesting a skeleton of benzisoxazole or benzoxazole. One less likely explanation for the loss of CNO is the existence of a cyanate (–O–C≡N) or isocyanate (–N=C=O) group, which may not survive the extraction process. Authentic standards are needed to validate the structure of NAC formulas proposed here.

$C_6H_5NO_3$ (Fig. S2a) is identified as 4-nitrophenol using an authentic standard (Fig. S3a). $C_7H_7NO_4$ has at least two isomers as shown in Fig. S1c that are identified as 4-methyl-5-nitrocatechol and 3-methyl-6-nitrocatechol according to Iinuma et al. (2010) and Xie et al. (2017a). Referring to the MS/MS spectrum of 4-nitrocatechol (Fig. S3b), the $C_6H_5NO_5$ compound should have a nitrocatechol skeleton with an extra hydroxyl group on the benzene ring. Like $C_9H_9NO_4$ (Fig. S2l,m), the loss of CO_2 was not observed for the fragmentation of

260 $C_8H_7NO_4$ in the MS/MS spectra (Fig. S2f,g), and a structure with a benzoxazole skeleton was
261 proposed (Table S2). The $C_8H_9NO_4$ identified in this work should have several isomers (Fig.
262 S1f), and two representative MS/MS spectra are provided in Fig. S2h and i. The first isomer of
263 $C_8H_9NO_4$ has a dominant ion of *m/z* 137, reflecting the loss of NO and CH_3. So, the first
264 $C_8H_9NO_4$ isomer might contain a methyl nitrophenol skeleton with a methoxyl group. The
265 fragmentation pattern of the second isomer of $C_8H_9NO_4$ is similar as $C_7H_7NO_4$, and the molecule
266 is postulated as ethyl nitrocatechol. $C_7H_7NO_5$ has a similar fragmentation pattern as $C_6H_5NO_4$
267 and $C_7H_7NO_4$, and is identified as methoxyl nitrocatechol. For NC forest burns, $C_{10}H_7NO_3$ was
268 only detected in flaming-phase samples (Fig. 1). The MS/MS spectrum of $C_{10}H_7NO_3$ is subject to
269 considerable noise, although the loss of NO_2 could be identified (Fig. S2k). The $C_8H_9NO_5$
270 compound was identified as dimethoxyl nitrophenol based on its MS/MS spectrum (loss of two
271 CH_3). The MS/MS spectra of $C_{10}H_{11}NO_4$, $C_{10}H_{11}NO_5$, $C_{11}H_{13}NO_5$, and $C_{11}H_{13}NO_6$ are very
272 different from 4-nitrophenol and 4-nitrocatechol (Fig. S3a,b), with multiple losses of CH_3 groups
273 (Fig. S2o–t). Their structures are proposed in Table S2 and most of these might have at least one
274 methoxyl group; the loss of CNO might suggest a skeleton of benzisoxazole or benzoxazole.

275 In this work, some of the identified NACs, such as 4-nitrophenol, 4-nitrocatechol, and
276 methyl nitrocatechols, were commonly observed in BB emissions or BB impacted atmospheres
277 (Claeys et al., 2014;Mohr et al., 2013;Budisulistiorini et al., 2017). However, these compounds
278 can also be generated from the photo-oxidation of aromatic VOCs in the presence of NO_X
279 (Iinuma et al., 2010;Lin et al., 2015;Xie et al., 2017a). Both BB and fossil fuel combustion can
280 emit a mixture of aromatic precursors (e.g., benzene, toluene) for secondary NACs formation
281 (Martins et al., 2006;Lewis et al., 2013; George et al., 2014;Gilman et al., 2015;Hatch et al.,
282 2015;George et al., 2015). Therefore, the NACs uniquely related to BB need to be identified to

represent BB BrC. In this work, the NACs formula with molecular weight (MW) < 200 Da (from $C_6H_5NO_3$, 138 Da to $C_8H_9NO_5$, 198 Da) were all identified in secondary organic aerosol (SOA) generated from chamber reactions with NO_X (Xie et al., 2017a), although they might have different structures. The $C_{10}H_{11}NO_4$, $C_{10}H_{11}NO_5$, $C_{11}H_{13}NO_5$, and $C_{11}H_{13}NO_6$ compounds identified in this work were not observed in any previous SOA formation study, to our knowledge. Among the four formulas, $C_{10}H_{11}NO_4$ and $C_{11}H_{13}NO_5$ were detected in all samples with relative mass contributions to OM ranging from 0.0019 ± 0.0008% to 0.014 ± 0.0036% and 0.0016 ± 0.0003% to 0.012 ± 0.0060%, respectively (Table S4). These compounds may contain a methoxyphenol structure, which is a feature in polar organic compounds from BB (Schauer et al., 2001;Simpson et al., 2005;Mazzoleni et al., 2007). Before using the $C_{10}H_{11}NO_4$, $C_{10}H_{11}NO_5$, $C_{11}H_{13}NO_5$, and $C_{11}H_{13}NO_6$ compounds as source markers to represent BB BrC chromophores, additional work is warranted to understand their exact structures and lifetimes in the atmosphere. The quantification of these compounds might also be subject to high variability due to the usage of surrogates.

3.3 Contribution of NACs to Abs_{365}. For each sample extract, individual NACs contributions to Abs_{365} ($Abs_{365,NAC}$%) were calculated using their mass concentrations (ng m^{-3}) and the MAC_{365} values of individual compound standards ($MAC_{365,NAC}$), as applied in Zhang et al. (2013) and Xie et al. (2017a). Here, the $MAC_{365,NAC}$ value is OM based with a unit of m^2 g^{-1}. Each NAC formula was assigned to an authentic or surrogate standard compound to estimate the contribution to Abs_{365} of extracted OM (Table S2). The UV-Vis spectra of standard compounds and details of the method for $Abs_{365,NAC}$% calculation are provided in Xie et al. (2017a). The $MAC_{365,NAC}$ values for identified NACs formulas in this work are also obtained from Xie et al. (2017a) and shown in Table S5. Since the standard compounds used in this work have no

306 absorption at 550 nm, the identified NACs contributions to Abs_{550} were expected to be 0. The
307 average and ranges of $Abs_{365,NAC}$% in BB samples are listed in Table S6. For simplicity, the
308 average $Abs_{365,NAC}$% in the five groups of BB samples (FF, NF1 and 2, NS1 and 2) are stacked
309 in Fig. 2.

310 In general, the average contributions of total NACs to Abs_{365} ($Abs_{365,tNAC}$% 0.12 ± 0.047
311 to 2.44 ± 0.67%) are 5–10 times higher than their average $tNAC_{OM}$% (0.023 ± 0.0089 to 0.18 ±
312 0.067%) in BB samples (Tables S6 and S4), indicating that the identified NACs are strong BrC
313 chromophores. Similar to the NACs mass contributions and compositions, the samples collected
314 during flaming periods (NF1 and NF2) have significantly higher ($p < 0.05$) average $Abs_{365,tNAC}$%
315 (NF1 2.44 ± 0.67%, NF2 0.80 ± 0.23%) than those collected during smoldering periods (NS1
316 1.00 ± 0.40%, NS2 0.12 ± 0.047%). $C_6H_5NO_4$ (0.098 ± 0.034 to 0.31 ± 0.11%) and $C_9H_9NO_4$
317 (0.21 ± 0.041 to 0.79 ± 0.14%) have the highest $Abs_{365,NAC}$% in the FL forest and NC forest
318 flaming-phase samples. $C_6H_5NO_4$ has the highest $Abs_{365,NAC}$% (NS1 0.29 ± 0.095%, NS2 0.037
319 ± 0.0080%) in the NC forest smoldering-phase samples (Table S6). The average $Abs_{365,tNAC}$%
320 values here are comparable to those obtained for atmospheric particles in Germany (0.10 ± 0.06
321 to 1.13 ± 1.03%) (Teich et al., 2017) and Detling, United Kingdom (4 ± 2%) (Mohr et al., 2013),
322 but more than 10 times lower than those from chamber reactions of benzene (28.0 ± 8.86%),
323 naphthalene (20.3 ± 8.01%) and *m*-cresol (50.5 ± 15.8%) with NO_X (Xie et al., 2017a). Di
324 Lorenzo et al. (2017) studied the absorbance as a function of molecular size of organic aerosols
325 from BB, and concluded that the majority of aqueous extracts absorption (λ = 300 nm) was due
326 to compounds with MW greater than 500 Da and carbon number greater than 20. In this work,
327 less than 5% of the BrC absorption in BB aerosols at λ = 365 was ascribed to the identified
328 NACs with a MW range of 138 to 254 Da, of which the contribution at longer wavelength (λ =

550 nm) was expected to be 0. Future work is needed to identify high MW light-absorbing compounds in BB aerosols to apportion a greater fraction of BrC absorption in BB aerosols.

3.4 Regression analysis with EC/OC ratio. As mentioned earlier, burn conditions are an important factor impacting the light absorption of BB OC, and the EC/OC ratio has been used as a measurement proxy of burn conditions to parameterize light-absorbing properties of BB OC in a number of studies (McMeeking et al., 2014;Saleh et al., 2014; Lu et al., 2015; Pokhrel et al., 2016;Xie et al., 2017b). We combined the sample measurements from all three BB experiments and analyzed the correlations of bulk MAC_{365} vs. EC/OC, $tNAC_{OM}$% vs. EC/OC, and $Abs_{365,tNAC}$% vs. EC/OC (Fig. 3). For the analysis, we removed one FL forest experiment sample due to the extremely high EC/OC ratio of 0.58 (burn 3, Table S1). Generally, EC/OC ratios are < 0.4 for laboratory BB (Akagi et al., 2011;Pokhrel et al., 2016;Xie et al., 2017b), and ≤ 0.1 for field BB (Aurell et al., 2015;Xie et al., 2017b;Zhou et al., 2017). Thus, the burn condition of the FL forest burn 3 (Table S1) is unrepresentative of laboratory BB simulations or field BB.

In Fig. 3a, the bulk MAC_{365} of methanol-extracted OC correlated significantly ($p < 0.05$) with EC/OC for each BB experiment. However, grouping these sample measurements resulted in no relationship between MAC_{365} and EC/OC ratio (Fig. 3b). So besides burn conditions, BB BrC absorption might also be sensitive to fuel type and ambient conditions. Similar results were also observed for MAC_{550} vs. EC/OC and $Å_{abs}$ vs. EC/OC correlations (Fig. S4a–d). Unlike the bulk MAC_{365} and MAC_{550}, $tNAC_{OM}$% and $Abs_{365,tNAC}$% correlated ($p < 0.05$) with EC/OC for both test specific data (Fig. S4e,f) and the pooled experimental data (Fig. 3c,d), supporting that burn conditions are an important factor in determining NACs formation in BB.

4 Conclusions

The comparisons of light-absorbing properties (MAC_{365}, MAC_{550}, and $Å_{abs}$) of BB OC with EC/OC in this study support that burn conditions are not the only factor impacting BrC absorption (Xie et al., 2017b). Other factors like fuel type and ambient conditions may also play important roles in determining BrC absorption from BB. It may be impractical to predict BrC absorption solely based on EC/OC ratios in BB emissions from different fuels or over different seasons. The present study identified fourteen NAC chemical formulas in BB aerosols. The average $tNAC_{OM}$% of the FL forest, NC forest 1 and 2 (flaming and smoldering samples were combined) experiments are 0.13 ± 0.059%, 0.13 ± 0.067%, and 0.11 ± 0.017%, respectively, and the NAC composition is also similar across the three BB experiments. The average $tNAC_{OM}$% of the flaming-phase samples (NF1 0.18 ± 0.067%, NF2 0.16 ± 0.045%) is significantly higher (p < 0.05) than those of smoldering-phase samples (NS1 0.055 ± 0.026%, NS2 0.023 ± 0.0089%) in the two NC forest BB experiments. These results suggest that the formation of NACs from BB depends on burn conditions, and is less impacted by other factors like fuel type and ambient conditions. Four of the identified NAC formulas ($C_{10}H_{11}NO_4$, $C_{10}H_{11}NO_5$, $C_{11}H_{13}NO_5$ and $C_{11}H_{13}NO_6$) were not observed in previous chamber studies examining SOA formation. MS/MS spectra indicated that these compounds might contain a methoxyphenol skeleton, which is featured in polar organic compounds from BB. So, these compounds may be uniquely related to BB and used as source tracers representative of BB-specific BrC in the atmosphere. However, determinations of their exact structures and lifetimes require further study. The NACs identified here are strong BrC chromophores, as their total contributions (0.12 ± 0.047 to 2.44 ± 0.67%) to bulk Abs_{365} are 5–10 times higher than their contributions to OM mass (0.023 ± 0.0089 to 0.18 ± 0.067%). However, more light-absorbing compounds from BB with high MW need to be identified to apportion the unknown fraction (> 95%) of BrC absorption. Significant correlations

($p < 0.05$) were observed for $tNAC_{OM}$% vs. EC/OC and $Abs_{365,tNAC}$% vs. EC/OC with pooled test data, supporting that the burn conditions are an important factor for NACs formation in BB.

Competing interests

The authors declare that they have no conflict of interest.

Disclaimer

The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

Author contribution

MX and AH designed the research. MX and XC performed the experiments. AH and MH managed sample collection. MX analyzed the data and wrote the paper with significant contributions from all co-authors.

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Table 1. EC/OC ratio, OC extraction efficiency and light-absorbing properties of organic aerosols in $PM_{2.5}$ from laboratory biomass burning.

Experiment	Phase	Abbr.	Fuels	EC/OC	Extraction efficiency (%)	MAC_{365} (m^2 gC^{-1})	MAC_{550} (m^2 gC^{-1})	Åabs
FL forest[a]	No separation	FF	long leaf pine (N=9)	0.21 ± 0.16	97.0 ± 1.87	1.13 ± 0.15	0.053 ± 0.023	7.36 ± 0.59
NC forest 1	Flaming	NF1	hardwood/loblolly pine (N=3)	0.042 ± 0.014	97.7 ± 0.41	1.47 ± 0.25	0.15 ± 0.065	5.68 ± 0.70
	Smoldering	NS1	hardwood/loblolly pine (N=3)	0.0098 ± 0.0024	97.9 ± 0.22	1.00 ± 0.11	0.054 ± 0.015	6.83 ± 0.52
NC forest 2	Flaming	NF2	hardwood/loblolly pine (4)	0.049 ± 0.011	99.5 ± 0.33	4.07 ± 0.15	0.17 ± 0.0051	7.38 ± 0.069
	Smoldering	NS2	hardwood/loblolly pine (4)	0.0075 ± 0.0026	99.2 ± 0.10	3.25 ± 0.35	0.12 ± 0.033	7.95 ± 0.22

[a] Data were obtained from Xie et al. (2017b).

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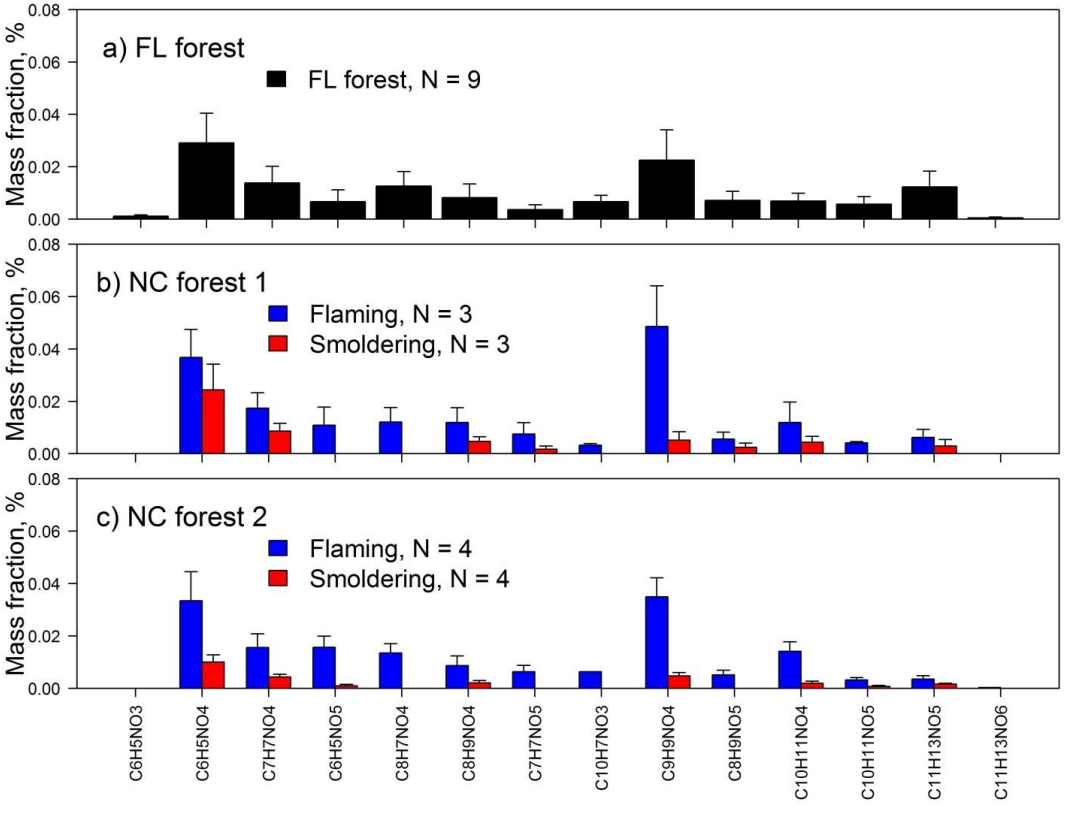

Figure 1. Relative mass contributions of identified nitroaromatic compounds in BB burning samples collected during (a) FL forest, (b) NC forest 1 and (c) NC forest 2 experiments.

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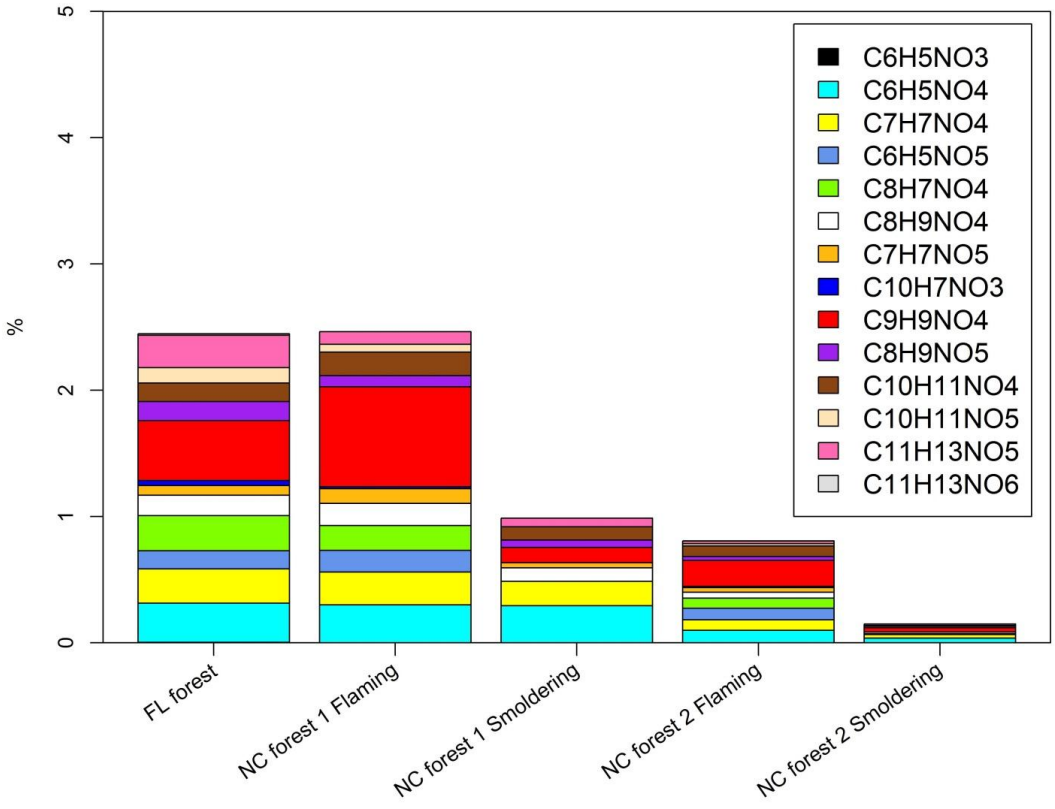

Figure 2. Average contributions (%) of nitroaromatic compounds to Abs_{365} of methanol extractable OC from laboratory biomass burning.

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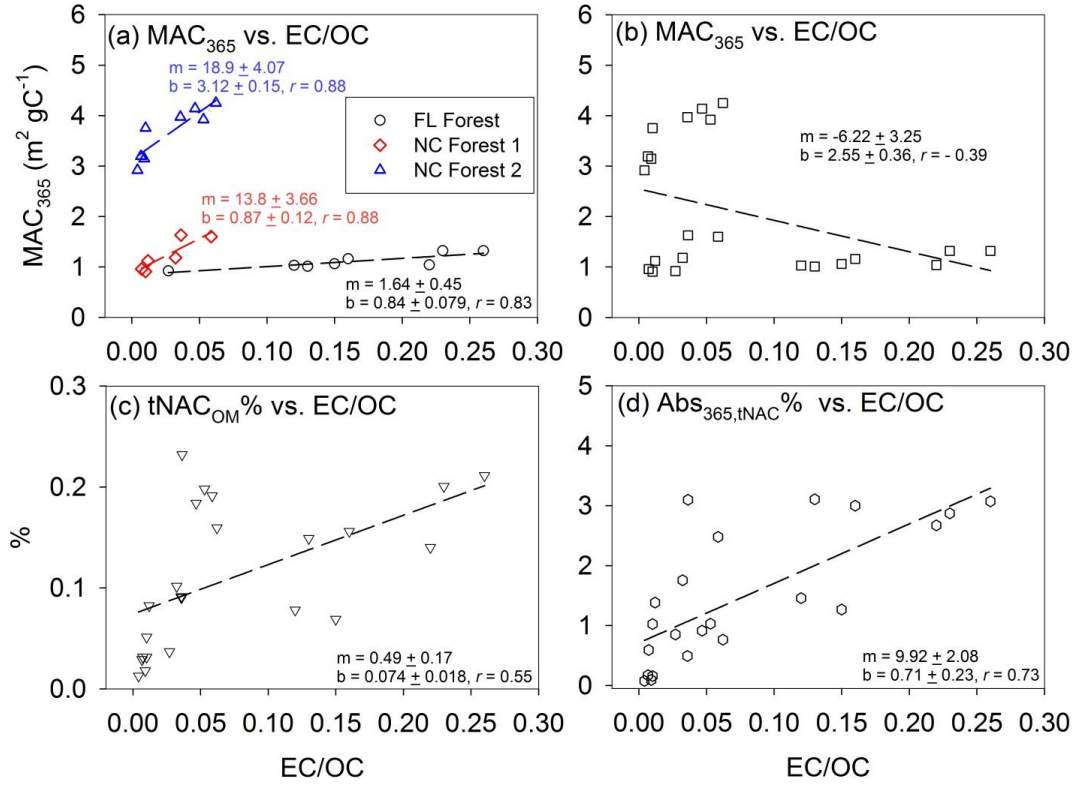

Figure 3. Linear regressions of (a) MAC_{365} vs. EC/OC with sample data of each experiment, (b) MAC_{365} vs. EC/OC, (c) $tNAC_{OM}$% vs. EC/OC and (d) $Abs_{365,tNAC}$% vs. EC/OC with pooled sample data of all the three experiments.