Reviewer 1

Xie et al. 2018 did laboratory burns of two fuel types, and analyzed particles using various offline methods. Most notably, they quantified nitroaromatic compounds (NACs) and their contribution to light absorption using HPLC/DAD-Q-ToFMS and authentic standards. Further characterization was done with MS/MS by comparing fragmentation patterns. The authors also examined the relationship between light absorption and mass of NACs with EC/OC ratio, a proxy for burn conditions. They determined structures for 14 nitrogen-containing chemical formulas and for many of which multiple isomers were observed. Interestingly, four of the nitrogen-containing formulas have only been observed in biomass burning applications before. However, the authors believe that these are not nitroaromatic compounds, but have benzisoxazole structures. Since these NACs are uniquely observed the authors propose that they could be good tracer compounds.

Overall assessment:

The authors have done careful analytical chemistry in regards to quantifying NACs and confirming structures. They include extraction efficiencies in Table S1, which is very useful for data interpretation. They confirmed structures to the extent possible using MS/MS and surrogate standard compounds. The mass-based contribution of NACs and their contribution to absorbance was very well done with internal standards/surrogates used for quantification. This work is an important contribution to our understanding of biomass burning emissions, and it should definitely be published. I do have some concerns and suggestions for improving the manuscript, as described below.

Reply:

We really appreciate the reviewer’s thoughtful comments, which help us to improve the manuscript. We replied to specific comments below.

General Major Comments:

1. The authors should do a little more work to characterize their proposed structures since this is a key conclusion of the paper. They propose benzoxazole structures for the some of the detected compounds based on the analysis of fragmentation patterns and observation of loss of CNO from the ions. However, Giorgi et al. (2004) showed that benzoxazole-based ions lose CO, and to some extent CH3CN, and not CNO during collision induced dissociation. This contradicts the authors’ structural assignments. I would recommend buying benzoxizole-based compounds (which are commercially available) and doing MS/MS with them to confirm the fragmentation patterns qualitatively match those observed from BB samples.

Reply:

The reviewer is right. Without enough evidence, we should not attribute the loss of OCN to the existence of benzoxazole structure. According to Giorgi et al. (2004), the MS/MS spectra of 3-methyl-1,2-benzisoxazole and 2-methyl-1,3-benzoxazole at ESI positive ion mode suggested a loss of CO, but not OCN.

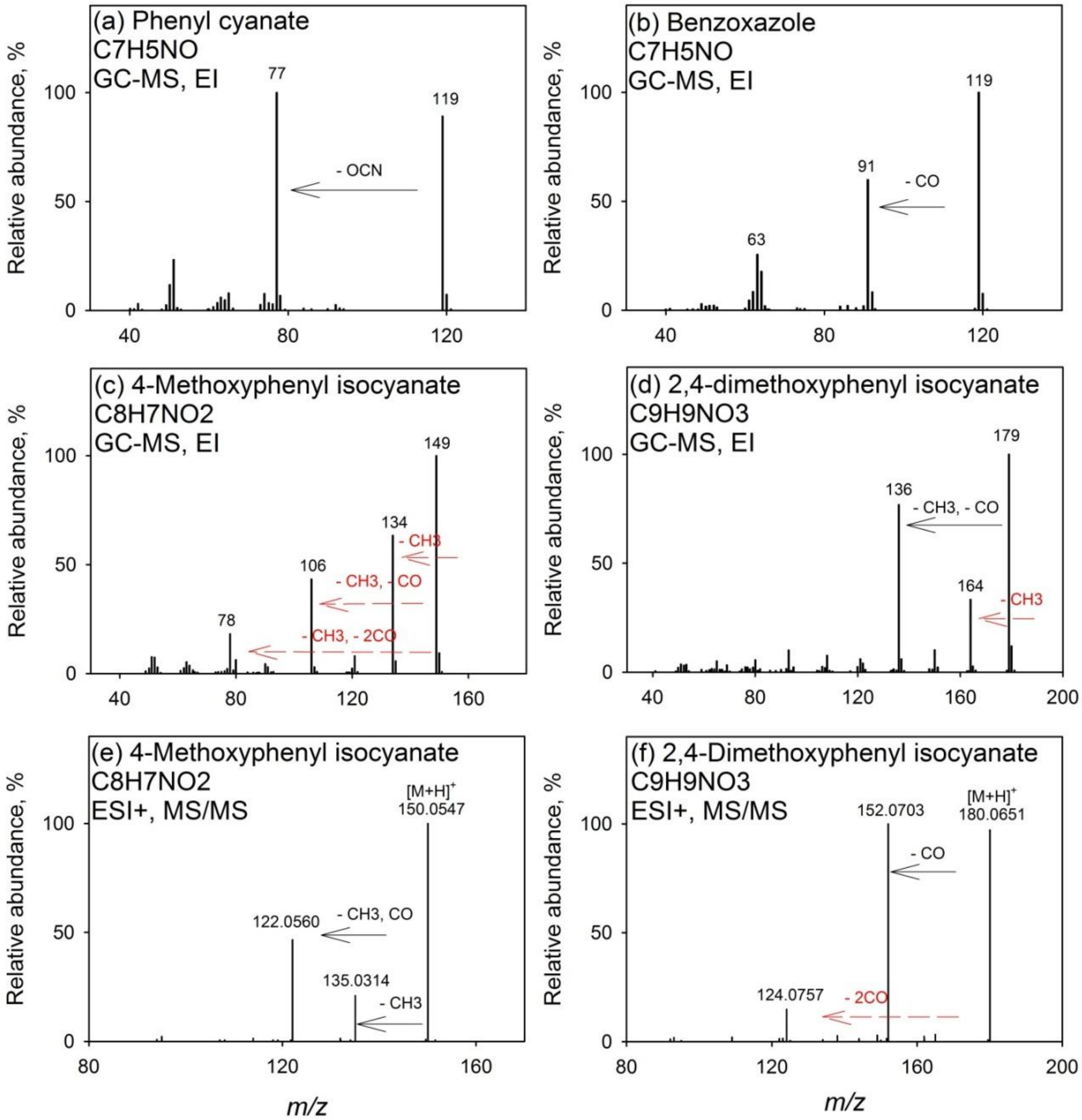


Figure S4. Mass spectra of (a) phenyl cyanate, (b) benzoxazole, (c) 4-methoxyphenyl isocyanate, and (d) 2,4-dimethoxyphenyl isocyanate with EI mode; MS/MS spectra of (e) 4-methoxyphenyl isocyanate and (f) 2,4-dimethoxyphenyl isocyanate with ESI positive ion mode.

In this work, four standard compounds, including phenyl cyanate (C_6H_5OCN), benzoxazole (C_7H_5NO), 4-methoxyphenyl isocyanate ($CH_3OC_6H_4NCO$), and 2,4-dimethoxyphenyl isocyanate [$(CH_3O)_2C_6H_3NCO$] were analyzed using a gas chromatography

(Agilent 6890) coupled to a mass spectrometer (Agilent 5975B) under electron ionization (EI, 70 ev) mode. These compounds do not have a phenol structure and cannot be detected using ESI under negative ion mode. The MS/MS spectra of 4-methoxyphenyl isocyanate and 2,4-dimethoxyphenyl isocyanate were obtained by using a modified method (ESI at positive ion mode) for NACs analysis in this work. As shown in Fig. S4a and b, the loss of OCN is observed for phenyl cyanate, but not benzoxazole. In Fig. S4c and d, the ions at *m/z* 106 and 136 can be produced from the species at *m/z* 149 and 179 through the loss of CH_3 + CO or H + NCO (43 Da). The MS/MS spectra of 4-methoxyphenyl isocyanate and 2,4-dimethoxyphenyl isocyanate (Fig. S4e,f) confirmed the loss of CH_3 + CO, and the loss of CH_3 reflected the presence of methoxy group. As such, the $C_9H_9NO_4$ compounds identified in this work is expected to contain a phenyl cyanate structure.

These results and discussions were added in the revised manuscript (Pages 14–15, Lines 311–331).

2. I would also not so easily dismiss organo-isocyanate structures as is done in the current manuscript. For example, Priestley et al. (2018) observed emissions of methyl isocyanate from biomass burning (p 7697). It is plausible that there may be aromatic isocyanates, and that they would survive extraction. On the other hand, Kaal et al. (2009) found benzoxazole in pyrolyzed charcoal smoke, so the authors can include this previous observation in the manuscript if there is evidence for the structure.

Reply:

Yes, correct. As seen in the replies to the reviewer's first comment, we analyzed four additional standard compounds with a structure that might lose OCN using GC-MS and/or LC-MS. In Fig. S4, the loss of OCN group is only observed during the fragmentation of phenyl cyanate. As such, the $C_9H_9NO_4$ compounds identified in this work is expected to contain a phenyl cyanate structure.

3. The authors claim these structures are unique to biomass burning and therefore good tracer compounds. However this requires a more comprehensive review of the chamber SOA literature. From a quick search I found that C10H11NO4 was detected in model SOA from the photooxidation of methyl chavicol, an aromatic biogenic precursor, in Pereira et al. (2015). The authors should perhaps do a more thorough job to confirm the uniqueness. Right now this statement that these are unique compounds to biomass burning is weak due to 1) uncertainty in the structures 2) incomplete review of the literature for NACs.

Reply:

Yes, $C_{10}H_{11}NO_4$ was observed as 5-methoxy-4-nitro-2-(prop-2-en-1-yl)phenol in SOA from reactions of methyl chavicol and NO_X (Pereira et al. (2015). However, the $C_{10}H_{11}NO_4$ compound observed in this work should have a different structure. Instead of discussing the uniqueness of the four compounds ($C_{10}H_{11}NO_4$, $C_{10}H_{11}NO_5$, $C_{11}H_{13}NO_5$ and $C_{11}H_{13}NO_6$) in BB NACs, we tried to shed lights on the representative functional groups of NACs from BB in the revised manuscript. Before this, we have already mentioned that that the loss of OCN group could be ascribed to the existence of a phenyl cyanate structure.

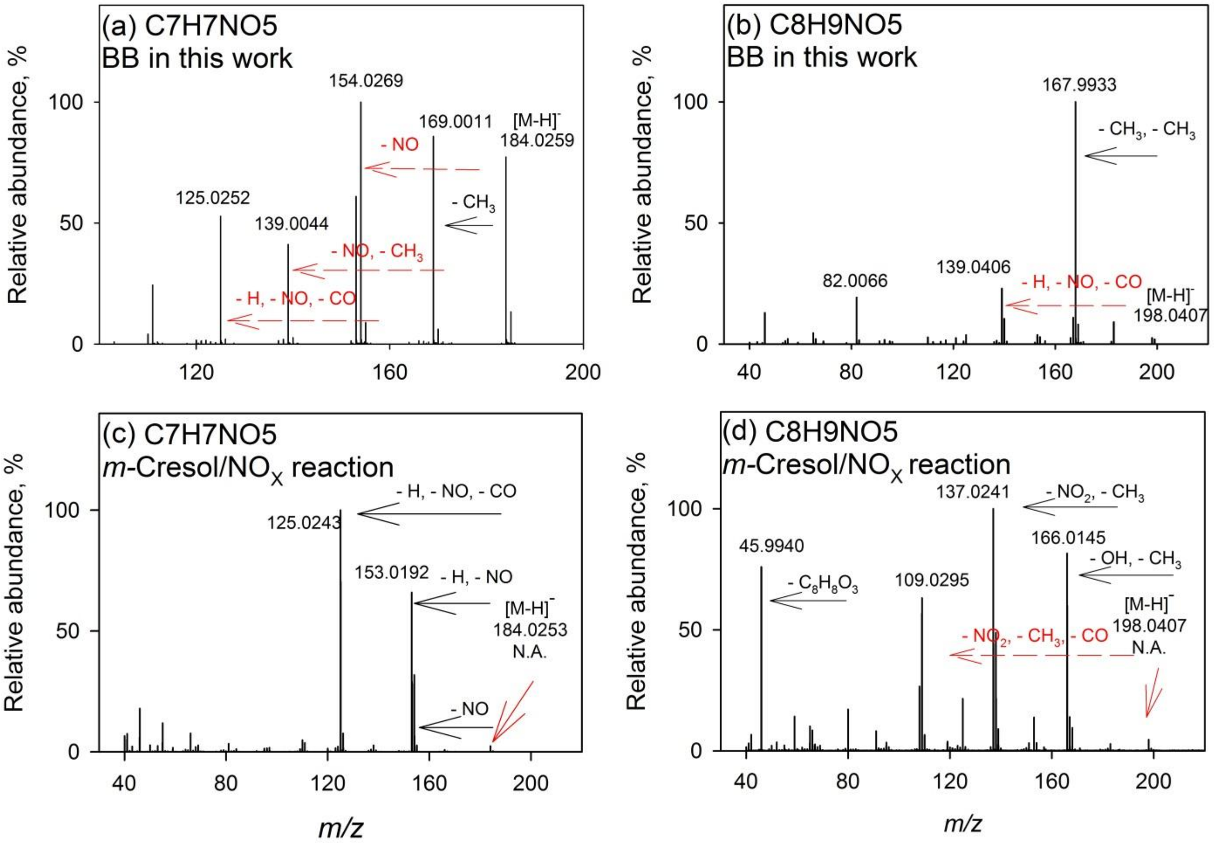


Figure S5. MS/MS spectra of (a) $C_7H_7NO_5$ and (b) $C_8H_9NO_5$ identified from BB in this work and (c, d) the same formula from photo-oxidation of *m*-cresol with NO_X.

In the revised manuscript, we stated that "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). However, the NACs from BB emissions and SOA formations with identical formulas might have different structures. For example, the MS/MS spectra of $C_7H_7NO_5$ and $C_8H_9NO_5$ from BB in this work and aromatic VOCs/NO_X reactions in Xie et al. (2017a) had distinct fragmentation patterns (Fig. S5). In Xie et al. (2017a), the $C_8H_7NO_4$ and $C_9H_9NO_4$ generated from ethylbenzene/NO_X reactions might have fragile structures and their MS/MS spectra were not available. In this work, $C_8H_7NO_4$ and $C_9H_9NO_4$ from BB emissions are more stable and are supposed to have a phenyl cyanate structure. Among the four NAC formulas with MW > 200 Da identified in this work (Table 2), $C_{10}H_{11}NO_4$ was also observed as 5-methoxy-4-nitro-2-(prop-2-en-1-yl)phenol in SOA from reactions of methyl chavicol and NO_X (Pereira et al. (2015), which cannot be assigned to the $C_{10}H_{11}NO_4$ from BB emissions in this work. Compared to the NACs in aromatic VOCs/NO_X SOA (Iinuma et al., 2010; Lin et al., 2015;Xie et al., 2017a; Pereira et al., 2015), the structures of NACs from BB in this work were characterized by methoxy and cyanate groups. The methoxyphenol structure is a feature in polar organic compounds from BB (Schauer et al., 2001;Simpson et al., 2005;Mazzoleni et al., 2007). The cyanate group was rarely reported in gas- or particle-phase pollutants from BB, which might be a missed feature of BB NACs. Vähä-Savo et al. (2015) found that cyanate could be formed during the thermal conversion (e.g., pyrolysis, gasification) of black liquor, which is the waste product from the kraft process when digesting pulpwood into paper pulp and composed by an aqueous solution of mixed biomass residues. According to Table 2 and Fig. 3, the NACs containing methoxy and/or cyanate groups are predominately generated during the flaming phase in the two NC forest experiments. Before using these compounds as source markers for BB NACs, 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." (Pages 16–17, Lines 364–390)

4. I would highly recommend transferring some of the supporting information material to the main manuscript. In particular, the method section in the supporting information should really be in the method section of the main paper. There is no page limitation in ACP, so there is no need to put important information in the SI section.

Reply:

We re-organized the manuscript. All the method details in the original supplementary information was improved and moved into the revised manuscript (Pages 6–7, lines 135–163; pages 8–9, lines 188–194; page 17–18, lines 397–402), including the bulk absorption measurement and calculation, surrogate assignment for NACs quantification, and surrogate assignment for the calculation of NACs contribution to solvent extracts absorption.

5. I would also suggest Table S2 be moved, and an example of a CID spectrum for the new structures be added. Right now it is difficult to read the manuscript without referring to the SI. While moving around the figures and tables this can be done strategically to improve the organization of the manuscript. For example, currently Figure 3a is discussed in the first paragraph of the R&D and then discussed again in the last section.

Reply:

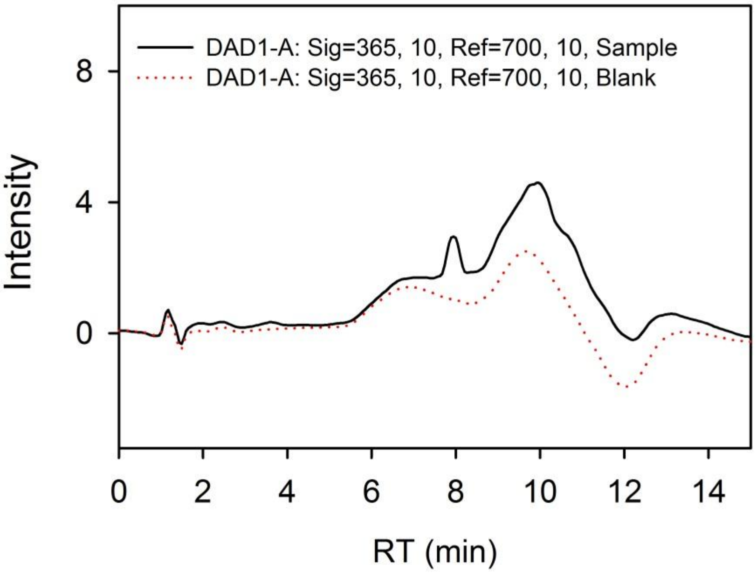
Yes, Table S2 and Fig. S1 of the original supplementary information were moved into the revised manuscript as Table 2 and Fig. 1. Fig. 3 of the original manuscript is now Fig. 2 in the revised manuscript and first appears in section 3.1, paragraph 2, and right after the discussion on the relationship between light-absorbing properties of BB OC and EC/OC ratios.

In the original manuscripts, Fig. 3a (now Fig. 2a) was not discussed in the first paragraph of section 3.1, and only Table 1 was referred to in the text.

6. It would be helpful to be able to refer to the absorption spectra for these BrC compounds. I would suggest a λ max column in Table S2 or better yet full PDA spectra. This is especially important for those four potential tracer compounds.

Reply:

In this work, a diode array detector (DAD), instead of photodiode array (PDA) spectrophotometry was interfaced with the HPLC and Q-ToFMS. The DAD measurement permits direct identification of chemical compound formulas responsible for light absorption in near UV and visible range (Xie et al., 2017). However, the DAD signals of individual NACs could not be distinguished from bulk absorption of sample extracts (shown in a plot below). This could be due to low contribution of total NACs to the mass (< 1%) and bulk absorption (< 2%) of OM.



DAD signal of a typical BB sample in this work

Moreover, the signal peaks in the HPLC/PDA or DAD chromatograms and the corresponding UV-Vis spectra are composed by a mixture of light-absorbing compounds (Lin et al., 2016), some of which are not NACs or even cannot be ionized under ESI positive or negative ion mode. As such, the λ max derived from PDA/DAD spectra cannot reflect the light-absorbing characteristics of individual NACs.

Therefore, the DAD measurements were not exhibited or used for analysis in this work, and a different method applied in Zhang et al. (2013) and Xie et al. (2017) was used to estimate the contribution of individual and total NACs to bulk absorption of extracted OM in BB emissions (Pages 17–18, lines 392–402). The UV-Vis spectra of standard compounds used for the NACs absorption calculation are provided in Fig. S6 of the revised supplementary information.

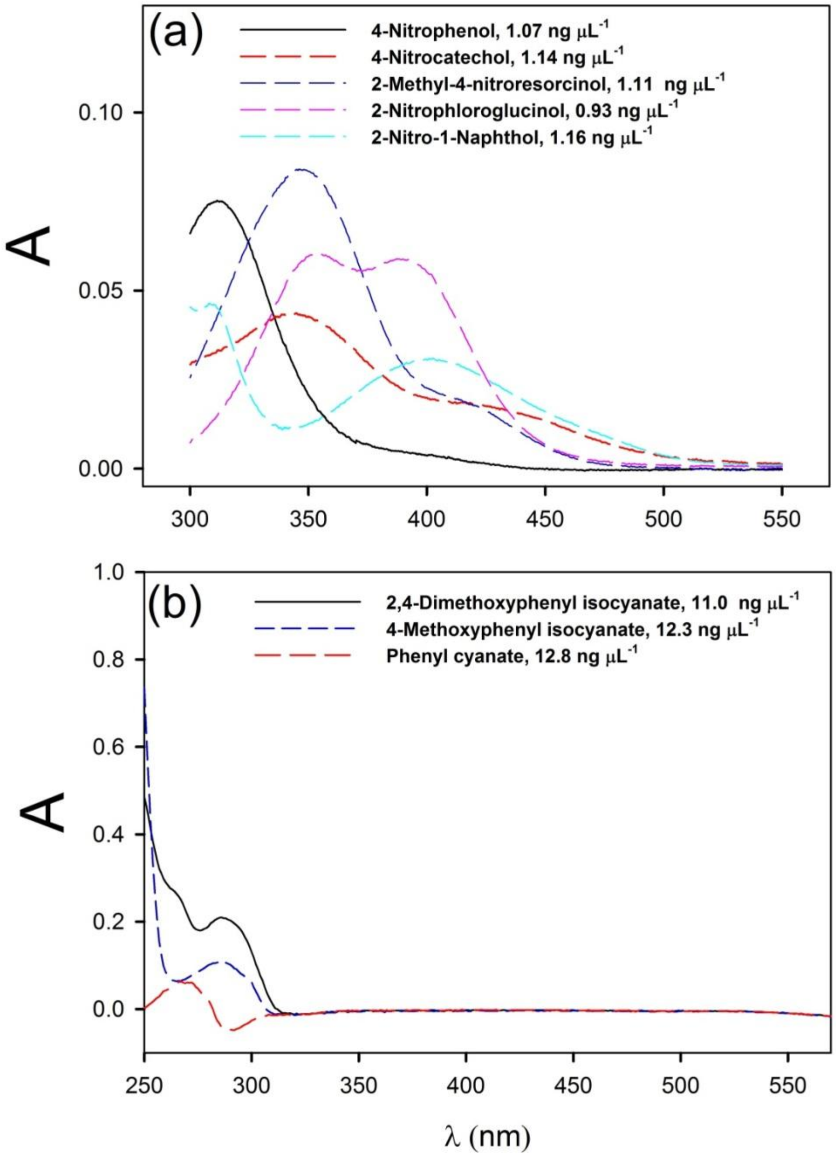


Figure S6. UV/Vis spectra of (a) 4-nitrophenol, 4-nitrocatechol, 2-methyl-4-nitroresorcinol, 2-nitrophloroglucinol, and 2-nitro-1-naphthol at ~1 ng μL^{-1} (Xie et al., 2017), and (b) 2,4-dimethoxyphenyl isocyanate, 4-methoxyphenyl isocyanate, and phenyl cyanate at ~10 ng μL^{-1}.

7. The authors call these compounds “nitroaromatic compounds”, but some of the proposed structures should not be classified as nitroaromatic compounds. They should perhaps name them N-containing aromatic compounds (also abbreviated as NAC)? If so, this should be done throughout the paper.

Reply:

Yes, thanks! The “nitroaromatic compound” was changed into “N-containing aromatic compound” (also abbreviated as NAC) throughout the manuscript.

8. The end of the introduction and conclusion should echo similar messages. The central focus of the paper is not entirely clear. At first, I thought it was to determine the viability of NACs as tracer/marker compounds for biomass burning. At the conclusion, it seems like the main point is to conclude whether fuel type or burn conditions are more important for production of NACs.

Reply:

Thanks. The central focus of this work was to identify NAC structures specifically related to BB, and quantify the contributions of NACs to BB OM and its solvent extracts abasorption. We revised the conclusion and the last paragraph of the introduction, so as to make them deliver similar information.

The last paragraph of the introduction was changed to:

“The present study attempts to characterize the compositional profile of NACs from BB, identify additional NAC structures in laboratory BB samples, and evaluate the contributions of NACs to bulk absorption of solvent extractable OC from BB. 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 ≤ 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 $PM_{2.5}$. In this work, a number of NACs formulas with structures that might be specifically related to BB were identified, and the contributions of identified NACs to bulk BrC absorption were calculated. These results shed lights on the light-absorbing characteristics of BB OC at bulk chemical and molecular levels, benefiting the understanding of BrC sources and chromophores.” (Pages 4–5, lines 94–105)

The conclusion was changed to:

“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. Other factors like fuel type or 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 were 0.13 ± 0.059%, 0.13 ± 0.067%, and 0.11 ± 0.017% by weight, respectively, and the NAC composition was also similar across the three BB experiments. Most of the NACs formulas identified in this work were also observed in simulated SOA generated from chamber reactions of aromatic VOCs with NO_X, but the same NAC formula from BB and SOA could not be assigned to the identical compound. In this work, the structures of NACs from BB were characterized by methoxy and cyanate groups, which were predominately generated during the flaming phase and might be an important feature for BB NACs. More work is warranted to understand their exact structures and lifetimes. The average $tNAC_{OM}\%$ and $Abs_{365,tNAC}\%$ of the flaming-phase samples were significantly higher ($p < 0.05$) than those of smoldering-phase samples in the two NC forest BB experiments. Unlike the bulk MAC_{365} and MAC_{550}, $tNAC_{OM}\%$ and $Abs_{365,tNAC}\%$ correlated ($p < 0.05$) with EC/OC for both individual burns and pooled experimental data, suggesting that burn conditions are an important factor in determining NACs formation in BB. Except the compounds with cyanate groups, the NACs identified in this work are likely strong BrC chromophores, as the average contributions of total NACs to bulk Abs_{365} (0.0.087 ± 0.024 to 1.22 ± 0.54%) are 3–10 times higher than their average mass contributions to OM (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 (> 98%) of BrC absorption." (Pages 19–20, lines 440–464)

Specific Comments:

Comment 1

Pg 4, ln 79-81 It would help if the authors discussed the discrepancy between the reported result (2-18%) and Lin et al. (2017) (50-80%) in the results and discussion section.

Reply:

We added some discussions on the results from Lin et al. (2017) in page 19, lines 423–431.

"Lin et al. (2016, 2017) investigated the light absorption of solvent extractable OC from BB using a combination of HPLC, photodiode array (PDA) spectrophotometry, and high resolution mass spectrometry (HRMS), and attributed a large portion (up to or greater than 50%) of the solvent extracts absorption to a limited number of NACs, of which the MW are mostly lower than 500 Da. However, the signal peaks in the HPLC/PDA chromatograms and the corresponding UV-Vis spectra are likely composed by a mixture of light-absorbing compounds, some of which are not NACs or even cannot be ionized under ESI positive or negative ion mode. These might lead to an overestimation of NACs contribution to solvent extracts absorption."

Since the results from Lin et al. (2016, 2017) might overestimate the contributions of NACs to solvent extracts of BB OM, we removed the reference in the introduction.

Comment 2

Pg 5, ln 99-100 This is a weak statement. It would be more appropriate to include a 1-2 sentence summary of the main conclusions of the paper.

Reply:

As we replied to the reviewer's 8th general comment, the last paragraph of the introduction was revised. We added a brief summary of the main conclusions and the broad implications of this work in the end.

We stated that "In this work, a number of NACs formulas with structures that might be specifically related to BB were identified, and the contributions of identified NACs to bulk BrC absorption were calculated. These results shed lights on the light-absorbing characteristics of BB OC at bulk chemical and molecular levels, benefiting the understanding of BrC sources and chromophores." (Page 5, lines 101–105)

Comment 3

Pg 7, ln 165 I suggest moving the sentence on average recoveries of standard compounds to Pg 6, ln 144. It would make more sense there.

Reply:

We re-organized the method section, and moved the method details in the supplementary information to the main text of the manuscript. The field blank and recovery analysis belong to the quality assurance/quality control (QA/QC) of the quantification, and should appear after the method details for NACs quantification. As such, we did not move the description about recoveries of standard compounds.

Comment 4

Pg 8, ln 178-181 Please consider referencing Fig 3a in the first paragraph. It is much easier to read through with visuals.

Reply:

Fig. 3 of the original manuscript is now Fig. 2 in the revised manuscript and first appears in section 3.1, paragraph 2, and right after the discussion on the relationship between light-absorbing properties of BB OC and EC/OC ratios with previous studies (Page 11, line 240).

In the first paragraph, we mainly compared the light-absorbing properties of OC across the three BB experiments using Table 1. The information presented in Fig. 2 is more related to the second paragraph in section 3.1.

Comment 5

Pg 10, ln 230-232 The sentence about quantification with surrogates should be mentioned earlier in the text and in a more systematic way. It is a strength of the paper so it should be better highlighted.

Reply:

Yes, we mentioned the use of surrogates with detail in the method section in the revised manuscript (Page 8–9, lines 188–194).

"Due to the lack of authentic standards, most of the NACs in BB samples were quantified using surrogates in this work. In general, the surrogate compound with similar molecular weight (MW) and/or structure was selected for the mass quantification of each identified NAC. Since the standard compound with hydroxyphenyl cyanate structure is not commercially available, $C_8H_7NO_4$ and $C_9H_9NO_4$ were quantified as 2-methyl-5-nitrobenzoic acid ($C_8H_7NO_4$) and 2,5-dimethyl-4-nitrobenzoic acid ($C_9H_9NO_4$), respectively; all the identified NACs with MW > 200 Da were quantified as 2-nitrophloroglucinol ($C_6H_5NO_5$)."

Comment 6

Pg 13, ln 302 Can the authors use nitroaromatic compounds as internal standards to quantify the compounds with benzisoxazole structures? The readers will not really know how these compounds absorb. This could be clarified with including the PDA spectra, as suggested above, and comparing these spectra to the surrogate's spectrum.

Reply:

As we replied to the reviewer's 1st general comments, the identified NACs with a loss of OCN group in the MS/MS spectra were expected to have a phenyl cyanate structure, but not benzoxazole or benzisoxazole structures. According the UV-Vis spectra of 2,4-dimethoxyphenyl isocyanate, 4-methoxyphenyl isocyanate, and phenyl cyanate (Fig. S6b), the contributions of those NACs with cyanate groups to the absorption of bulk solvent extracts were likely to be 0.

As we replied to the reviewer's 6th general comments, the signal peaks in the HPLC/PDA or DAD chromatograms and the corresponding UV-Vis spectra are composed by a mixture of light-absorbing compounds (Lin et al., 2016), some of which are not NACs or even cannot be ionized under ESI positive or negative ion mode. As such, the PDA/DAD spectra cannot reflect the light-absorbing characteristics of individual NACs. Fig. S6 provides the UV-Vis spectra of authentic and surrogate standard compounds, which are used to drive the mass absorption coefficients (MAC) of individual NACs in Xie et al. (2017) and this work (NACs with cyanate groups are expected to have a MAC value of 0).

In the revised manuscript, the calculation of NACs contribution to solvent extracts absorption was introduced with more details in pages 17–18, lines 392–402.

"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 2). Except the NACs with a phenyl cyanate structure, the standard compounds used for the NACs absorption calculation and mass quantification were the same (Table 2), and their UV-Vis spectra were obtained from Xie et al. (2017a) and shown in Fig. S6a. The UV-Vis spectra of three standard compounds with cyanate or isocyate groups are given in Fig. S6b, and none of them has absorption in the range from 350 to 550 nm. As such, the NACs with cyanate groups identified in this work were supposed to have no contribution to bulk Abs_{365}."

Comment 7

Pg 13 Are the identified nitrogen-containing species that are called potentially tracer compounds in this study primarily flaming or smoldering? It was not clear to me based on the writing.

Reply:

As we replied to the reviewer's 3rd general comments, instead of discussing the uniqueness of the four compounds ($C_{10}H_{11}NO_4$, $C_{10}H_{11}NO_5$, $C_{11}H_{13}NO_5$ and $C_{11}H_{13}NO_6$) in BB NACs, we tried to shed lights on the representative functional groups of NACs from BB in the revised manuscript (Page 16–17, lines 364–390). We found that the NACs from BB might be featured by methoxy and cyanate groups. According to Table 2 and Fig. 3 in the revised manuscript, the NACs containing methoxy and/or cyanate groups are predominately generated during the flaming phase of BB experiments.

In the revised manuscript, we mentioned these in section 3.2, page 17, lines 375–385, “Compared to the NACs in aromatic VOCs/NO_X SOA (Iinuma et al., 2010; Lin et al., 2015;Xie et al., 2017a; Pereira et al., 2015), the structures of NACs from BB in this work were characterized by methoxy and cyanate groups. The methoxyphenol structure is a feature in polar organic compounds from BB (Schauer et al., 2001;Simpson et al., 2005;Mazzoleni et al., 2007). The cyanate group was rarely reported in gas- or particle-phase pollutants from BB, which might be a missed feature of BB NACs. Vähä-Savo et al. (2015) found that cyanate could be formed during the thermal conversion (e.g., pyrolysis, gasification) of black liquor, which is the waste product from the kraft process when digesting pulpwood into paper pulp and composed by an aqueous solution of mixed biomass residues. According to Table 2 and Fig. 3, the NACs containing methoxy and/or cyanate groups are predominately generated during the flaming phase in the two NC forest experiments.”

and section 4 (Conclusions), page 20, lines 451–453,

“In this work, the structures of NACs from BB were characterized by methoxy and cyanate groups, which were predominately generated during the flaming phase and might be an important feature for BB NACs.”

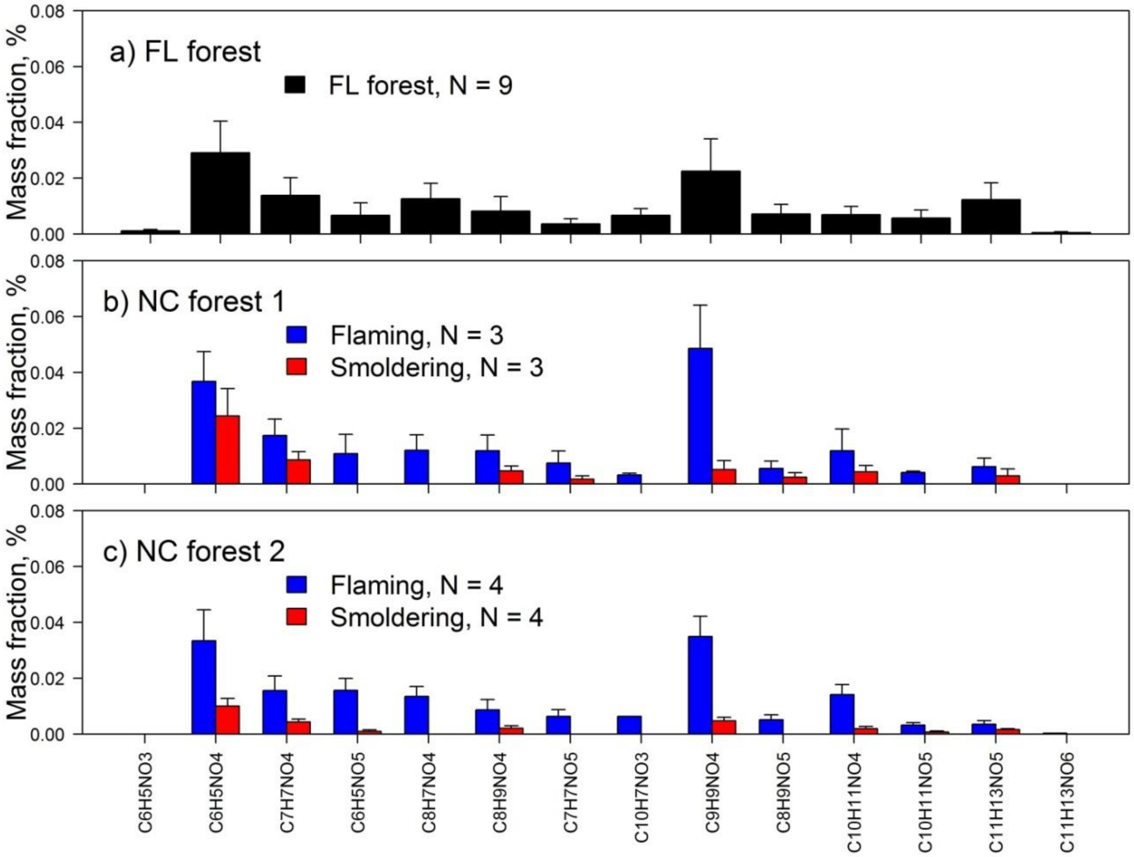


Figure 3. Relative mass contributions of identified N-containing aromatic compounds in BB samples collected during (a) FL forest, (b) NC forest 1 and (c) NC forest 2 experiments.

Comment 8

Pg 15 Do burn conditions affect substituents, i.e., the number of OH groups? A brief discussion of this would be useful.

Reply:

Yes. According to our replies to the reviewer's previous comments, the identified NACs from BB are featured by methoxy and cyanate groups, which are predominately generated during the flaming phase of the BB experiment. We discussed this in pages 16–17, lines 364–387 and mentioned this in the conclusions (page 20, lines 451–453)

Section 3.4 in the original manuscript was divided and added into previous sections in the revised manuscript separately. Pages 10–11, lines 231–244; page 13, lines 294–298; page 18, lines 415–417.

Comment 9

Pg 15, ln 344 It would be helpful to mention here light-absorbing compounds formed at low EC/OC, i.e., tar balls

Reply:

Yes. As section 3.4 was divided and added into previous sections, we mentioned the formation of light-absorbing compounds at low EC/OC (e.g., tar balls) with a reference (Chakrabarty et al., 2010) in page 11, lines 243–244.

Comment 10

Figure 3c. I would color code by fuel like in a). Also, there is not a strong correlation. Please remove the trend line.

Reply:

Fig. 3 in the original manuscript is now Fig. 2 in the revised manuscript. Individual burns data have already been colored by fuel in Fig. S3e of the supplementary information and Fig. 2c here presents the results for pooled experimental data. The correlation in Fig. 2c is not strong but significant ($p < 0.05$). So we kept the trend line in Fig. 2c, and did not color code by fuel in Fig. 2c.

Technical Corrections:

1. Pg 2 ln 38 I would I would change “test-specific data” to “individual fires”. I think it is less confusing.

Reply:

The “test-specific data” was changed into “individual burns data” throughout the manuscript.

2. Pg 2, ln 48-50 The last sentence of the abstract is unclear to me. Please consider revising.

Reply:

The expression was changed into: “The contributions of identified NACs to organic matter (OM) and BrC absorption were significantly higher in flaming-phase samples than those in smoldering-phase samples, and correlated with EC/OC ratio (p < 0.05) for both individual burns and pooled experimental data, indicating that the formation of NACs from BB largely depends on burn conditions.” (Page 2, lines 47–51)

3. Pg 3, ln 55-56 Specify OC emissions are specifically OC particle emissions

Reply:

Thanks, we added “particle” in page 3, line 60.

4. Pg 3, ln 59 Revise wording of “shorter visible region”. Should be near UV, instead of just UV (300-400 nm)

Reply:

The original expression was changed into “while light absorption of BB OC increases rapidly from the purple-green region (400–550 nm) to near ultraviolet (UV) region (300–400 nm).” (Page 3, lines 62–64)

5. Pg 4, ln 84 Cite Iinuma 2010. It is a critical reference here.

Reply:

Thanks, added as suggested in page 4, line 86.

6. Pg 7, ln 161 Include exactly which internal standards are used.

Reply:

We have already mentioned the compound name and amount of internal standard in page 6, line 143 in the original manuscript, now in page 8, line 167.

7. Pg 12, ln 268 is –> was

Reply:

Thanks, revised as suggested. Page 15, line 347.

8. Pg 12, ln 271 are –> were

Reply:

Thanks, revised as suggested. Page 16, line 353.

9. Pg 16, ln 358 Include that these are average tNACOM% by weight

Reply:

Thanks, revised as suggested. Page 20, line 447.

References:

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