This manuscript present a decent study on the light absorption of biomass burning organic aerosols (BBOA) from controlled laboratory burning experiment, with particular focus on the nitroaromatic compounds (NACs), which has been identified as an important light absorbers of OA recently.

1. Overall this manuscript is well written with clear logic and good English. The only problem on the organization of the content is that the authors keep so many valuable information in the SI, making it impossible to understand their major conclusions without reading the SI. I suggest to move some of them (e.g., Table S2, Figure S2-S4 with some modifications) into the main articles.

Reply:

Thanks for the reviewers comments. We re-organized the manuscript, and moved Table S2 and Fig. S2 in the original supplementary information to the main text in the revised manuscript. The method details on bulk absorption measurement and calculation, surrogate assignment for NACs quantification, and surrogate assignment for the calculation of NACs contribution to solvent extracts absorption were also moved to the main text from supplementary information (Pages 6–7, lines 135–163; pages 8–9, lines 188–194; page 17–18, lines 397–402).

2. Another major issue is the identification of NACs in section 3.2: the authors attempt to get some structural information of NACs through measuring their MS/MS spectra. However, those results should be interpreted more carefully. I don't see any references cited when they discuss the relationship of fragmentation pattern with possible molecular structures. E.g., at line 250-252, "the loss of CNO suggest the skeleton of benzisoxazole: : :: : :" similar issues can also be found at line 259-261, line 264, line 269-274. The authors may need to find some references investigating the MS/MS spectra of even-electron ions of known standard compounds with similar MS conditions (e.g., https://onlinelibrary.wiley.com/doi/pdf/10.1002/jms.1234) to make educated guess of the structures.

Reply:

In the revised manuscript, we added some references and the MS (or MS/MS) spectra of four additional standard compounds to obtain appropriate guess of NACs structures. Finally, the loss of CNO from some NACs was attributed to the existence of a phenyl cyanate structure.

Page 14–15, lines 311–331. "Both MS/MS spectra of the two $C_9H_9NO_4$ isomers reflect the loss of OCN (Fig. 1l,m), suggesting a skeleton of benzoxazole/ benzisoxazole or the existence of a cyanate (–O–C≡N) or isocyanate (–N=C=O) group. Volatile organo-isocyanate structures (e.g., CH_3NCO) were identified from anthropogenic biomass burning (Priestley et al., 2018), and benzoxazole structures have been observed in pyrolyzed charcoal smoke (Kaal et al., 2008). Giorgi et al. (2004) investigated the fragmentation of 3-methyl-1,2-benzisoxazole and 2-

methyl-1,3-benzoxazole using a CID technique under different energy frames, and found a loss of CO but not OCN for both of them. 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."

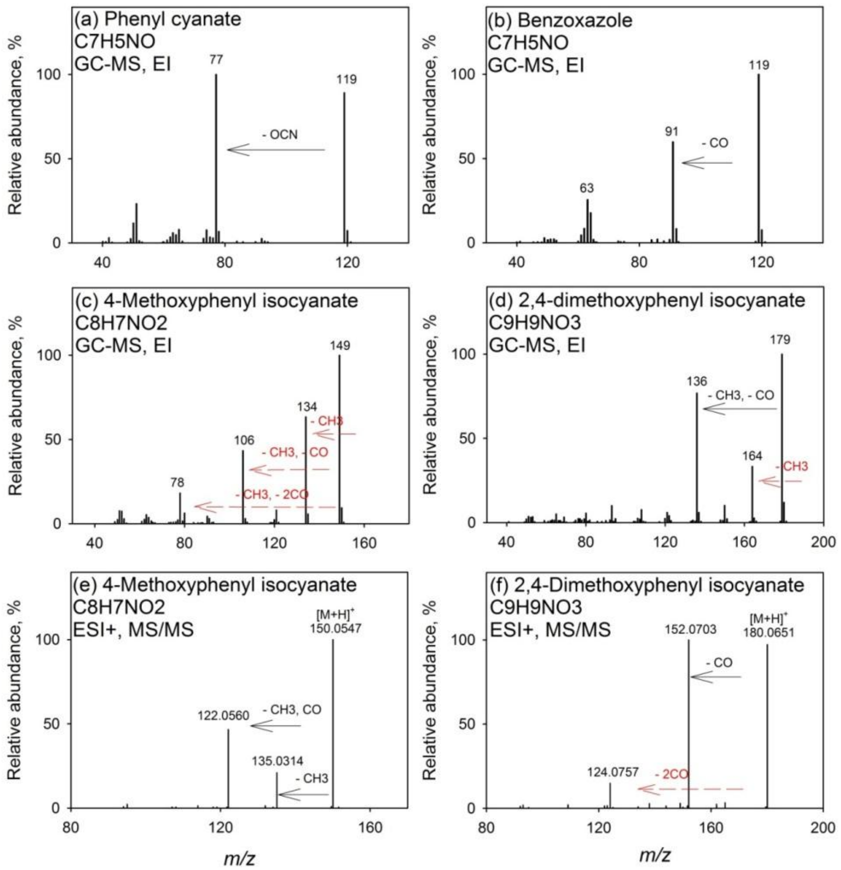

Figure S4. Mass spectra of (a) phenyl cyanate, (b) benzoxazole, (c) 4-methoxyphenyl isocyanate, and (d) 2,4-dimethoxyphenyl isocyanate with EI mode; MS/MS spectra of (e) 4-methoxyphenyl isocyanate and (f) 2,4-dimethoxyphenyl isocyanate with ESI positive ion mode.

Regarding the structure of $C_8H_7NO_4$, the original expression was changed into:

"Like $C_9H_9NO_4$ (Fig. 1l,m), the loss of OCN was observed for the fragmentation of $C_8H_7NO_4$ in the MS/MS spectra (Fig. 1f,g), and a phenyl cyanate structure was proposed (Table 2). However, the fragmentation mechanism associated with the loss of single nitrogen is unknown and warrants further study." (Page 15, 337–340)

The first isomer of $C_8H_9NO_4$ has a dominant ion of *m/z* 137, reflecting the loss of NO and CH_3. Before this, we have mentioned that the loss of CH_3 can reflect the presence of methoxy group in pages 14–15, lines 329–330. Referring to MS/MS spectrum of 4-nitrophenol (Fig. S2a), the first $C_8H_9NO_4$ isomer might contain a methyl nitrophenol skeleton with a methoxy group. Page 15, lines 341–344.

The text in lines 269–274 of the original manuscript was changed into:

"In Fig. 1n, the ion at *m/z* 167 is attributed to the loss of two CH_3 from the $[M-H]^-$ ion of $C_8H_9NO_5$, and the loss of H + CO + NO is a common feature shared by several nitrophenol-like compounds (Fig. 1b,c,e,i), so the $C_8H_9NO_5$ compound was identified as dimethoxynitrophenol. The MS/MS spectra of $C_{10}H_{11}NO_4$, $C_{10}H_{11}NO_5$, $C_{11}H_{13}NO_5$, and $C_{11}H_{13}NO_6$ were characterized by the loss of CH_3 and/or OCN (Fig. 1o–t), indicting the existence of methoxy and/or cyanate groups (Fig. S4). Although the exact structure of these NACs cannot be determined, their functional groups on the benzene ring were proposed in Table 2 from their fragmentation patterns. " (Pages 15–16, lines 349–356)

In the revised manuscript, the structures of identified NACs in this work were mostly prosed by comparing their MS/MS spectra to authentic and surrogate standard compounds.

Other problems:

1. Abstract, line 48-50: this sentence is confusing. I understand that the authors want to say that the burn conditions affect significantly on NACs formation, but slightly on the bulk absorptive properties of BB BrC. However, it reads like the author compare burn condition and bulk adsorptive properties' influence on the formation of NACs.

Reply:

Thanks for the reviewer's comment. We revised the abstract, and 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 47–52)

2. Section 2.3, HPLC/DAD-MS analysis: the authors use the same analytical method developed in their previous study and described briefly in the current manuscript. It is better to describe the HPLC elution protocols as well so that we don't need to go to another paper if someone want to try the same method or make any comparisons or evaluations about the chromatograph separation.

Reply:

Yes, we added the HPLC elution protocols in page 8, lines 172–175.

"The flow rate of the column was set at 0.2 mL min^{-1}, and the gradient separation was conducted with 0.2% acetic acid (v/v) in water (eluent A) and methanol (eluent B). The concentration of eluent B was 25% for the first 3 min, increased to 100% from 3 to 10 min, held at 100% from 10 to 32 min, and then decreased back to 25% from 32 to 37 min."

3. Line 243-244: the retention time of compound showed in Figure S2b and Figure S3b don't match, with difference ~0.3min, which is too large for a ~20-min length LC chromatogram. If they are the same compound, not only their MS/MS spectra, but also their RTs should also match with each other. Any explanation?

Reply:

Figs. S2 and S3 in the original supplementary information are now Fig.1 in the main text and Fig. S2 in the revised supplementary information, respectively.

As shown in Fig. S2 caption, the MS/MS spectra of standard compounds were obtained from the author's previous study (Xie et al., 2017) on NACs mass and absorption in simulated secondary organic aerosol (SOA). The BB samples in this work and the SOA samples in Xie et al. (2017) were not analyzed together in the same batch. Between these two studies, a few hundred of runs were performed and the properties (e.g., pressure) of guard and/or analytical HPLC columns changed, which is likely the reason for the unmatched retention time between Fig. 1b and Fig. S2b. The retention time of $C_6H_5NO_4$ (nitrocatechol) in Fig. 1b matched with the authentic standard in calibration curve solutions. To clarify that the MS/MS spectrum of 4-nitrocatechol is from a different study, we cited Xie et al. (2017) in page 8, line 186 and page 14, line 306.

References

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