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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Composition and light absorption of nitroaromatic compounds in organic aerosols from laboratory biomass burning" *by* Mingjie Xie et al.

Anonymous Referee #1

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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.

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.

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.

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.

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.

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.

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

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.

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.

Specific Comments:

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

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.

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.

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

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.

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.

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.

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

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

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

Technical Corrections:

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

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

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

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

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

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

Pg 12, ln 268 is –> was

Pg 12, ln 271 are –> were

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

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