We would like to thank Reviewer for the thoughtful comments and suggestions that helped us improve several aspects of our work, particularly the clarity and robustness of the revised article. Our point-by-point responses to the specific comments provided, together with the list of changed made in the revised manuscript, are provided below.

Reviewer 1 comments

General Comments:

This manuscript presents a thorough comparison of multiple NTA workflows for analysis of water-soluble brown carbon aerosol samples. This is a much-needed contribution to the field, and additionally, the best workflow was used to identify new potential precursors to aqueous SOA. My scientific comments are minor, and I have a few comments to address clarity and technical issues with the manuscript. Overall, this manuscript is worthy of publication in ACP.

Specific Comments:

Reviewer 1: It is not clear how model compounds were selected. Were these compounds chosen from studies focused on aqueous brown carbon, or on biomass burning in general? Or perhaps they were chosen because of commercial availability? Since workflow performance was assessed on the ability to correctly identify these compounds, it seems important to communicate how exactly these standards were chosen and cite references that informed the choice, if applicable.

Author's response: The model compounds were selected to best mimic the molecular composition of biomass-related, water-soluble BrC, considering the previously published data and availability of standards. Most of the model compounds are aromatics, functionalized (aromatic)acidic, phenols, or N-containing molecules previously detected in laboratory-generated and ambient BB emissions. Some model compounds are used as surrogates for similar molecules.

Changes made in the manuscript: Table S1 was added in the SI, with references justifying the use of selected standards as (model)tracers of organic compounds detected in biomass-burning emissions. This table is now referenced at the beginning of Section 2.3: "First, the workflows based on MS-FINDER, CFM-ID, Metaboanalyst, GNPS, and MZmine were tested using 59 model compounds. These molecules were selected to mimic the molecular composition of water-soluble BrC emitted by BB based on previously published results and standards availability (Tables S1 and S2), and included derivatives of cinnamic acid, nitrophenols, and polycarboxylic, furoic, and fatty acids."

Reviewer 1: I would welcome the addition of a comment from the authors about how well their combustion apparatus simulates real BB conditions, but do not feel it is absolutely necessary prior to publication. I am always a bit skeptical of these small-scale reactors in terms of their applicability to real conditions, and I am even more skeptical given this is a brand-new combustion system that has not been previously characterized. That being said, I don't think the very nice NTA work done here is invalidated by the choice of combustor.

Author's response: We agree that laboratory-scale reactors are never fully representative of the ambient conditions. At the same time, without access to large-scale installations [1, 2], or sampling ambient wildfire emissions, smaller reactors are often used to generate (proxy) BrC mixtures [3, 4]. These (small-scale setups) are generally considered capable of generating (proxy) BB emissions. A recent work also reported using liquid smoke as a surrogate for biomass burning aerosol [5].

In the presented work, we use oxygen-depleted conditions because there is little to no oxygen inside the logs or in the diffusion flame, as well as deep inside the fire [2, 3, 5, 6]. The results of chemical analyses also indicate that our approach generated representative BrC aerosols, in terms of general chemical characteristics (Fig. 6 and discussion in Section 3.2) and specific molecular markers, reported in similar samples (Fig. 9 and Tables S8 and S9).

We also agree that this new setup would benefit from a more detailed characterization, particularly analyses of size distribution, light absorption, and scattering of particles exiting the sampling assembly. However, we believe that in the context of the presented work, such analyses are not of critical importance, as mentioned by the referee.

Changes made in the manuscript: The conditions used in the combustor were better justified in Section 1: **"**Here, BrC was generated in the N_2 atmosphere in a new, custom-designed combustor. Wood pyrolysis was conducted to simulate combustion conditions during vegetation fires, as oxygen is absent inside logs and in the deeper zones of the fire [2, 3, 5, 6].**"**

Reviewer 1: I found Figure 9 to be confusing – if the unlabeled areas correspond to unidentified molecules in each group, how are the authors determining that those molecules belong to that group? The information shown in Table S4 and S5 only added to my confusion. It seems like a reference to Tables S6 and S7 here would be more appropriate.

Author's response: The compounds are assigned to specific groups based only on the elemental composition, as presented in Fig. 6 in the main text; the corresponding equations are also provided in Section S4 in the SI. Hence, it is possible to assign a given molecule to a group without any structural elucidation, as showcased in Table 1 for confidence level 4. Please note that all annotated compounds are listed in Tables S8 and S9 (formerly S4 and S5), and are sorted from confidence level 1 (confirmed

with authentic standard) to 3, listing all structural assignments, in addition to the sample structures presented in Fig. 9.

Changes made in the manuscript: The following lines were added in the caption of Figure 9: "Detected compounds were assigned to these groups based on assigned elemental formulas (confidence level 4 in Table 1) as presented in Fig. 6. Unlabeled areas correspond to unidentified molecules in each group. Only five major components from each group are shown, and all structural assignments via NTA and identification confidence levels 1 to 3 are listed in Tables S8 and S9"

Technical Corrections:

Reviewer 1: I found Table 1 to be confusing in the sense that it implies no identifications were made at the highest level of confidence (e.g. Level 1). I suggest the authors add an example in the first row, since the SI shows that the method successfully reached Level 1 for a variety of compounds.

Author's response: We agree with this comment; matching a given molecule with an authentic standard wasn't emphasized sufficiently in Table 1. The absence of a sample structure can also confuse the readers.

Changes made in the manuscript: The description of confidence level 1 in Table 1 was revised as "Confirmed with authentic standard*",* and the sample structure was added in the corresponding row.

Reviewer 1: Several times throughout the manuscript, something to the effect of "level ≥ 4" is used. The context of these sentence conflicts with the literal meaning. In other words, what I think the authors are attempting to communicate is 'a level of confidence higher than 4,' which would correspond to a level with a *numerical* value ≤ 4. This occurs at lines 279, 344, 367, and 373 (and perhaps elsewhere). While a reader familiar with the Schymanski confidence level scheme will likely understand what is being implied, I suggest these be reworded to be more clear for those less familiar with NTA.

Author's response: We agree with this comment; the use of this notation (level ≥ 4) is incorrect. **Changes made in the manuscript:** All uses of this notation **"**level ≥ 4" were removed from the text and replaced with **"**features annotated at least level 4 (elemental formula assignment)**"**, **"**confidence level 4, or higher**" "**identified at least at level 3 (Table 1)**" "**annotated at least at level 4 (Table 1)". Furthermore, the reader is now referred to Table 1 more often throughout the text.

Reviewer 1 technical comments:

All of the technical comments were revised as suggested by the Referee. Please see below for our answers to specific comments.

Commas in strange places in lines 299 and 301

Changes made in the manuscript: This sentence was revised as **"**Double-bond equivalent (DBE) values (Fig. 6C), reflecting the degree of unsaturation, ranged from 4–6 for lignin pyrolysis products, 7–8 for coumarins, and 10–12 for stilbenes and flavonoids**"**

Line 290: missing a space between the words "abundant" and "in"

Line 293: I suggest spelling out molecular weights and organic aerosols to be more clear.

Remove "identified" before the comma in line 303

Line 307: "characteristics" should be "characteristic"

Line 311: By the time I got here, I had totally forgotten what "STs" were. Consider not using an acronym all to refer to the surrogate standards.

Changes made in the manuscript: The use of the abbreviation STs was removed from the main text and the supporting information. The remaining technical corrections were revised according to the Referee's suggestions.

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