

Interactive comment on “Polar semi-volatile organic compounds in biomass burning emissions and their chemical transformations during aging in an oxidation flow reactor” by Deep Sengupta et al.

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Reviewer 2. This study quantified a number of compounds produced by burning six different fuels, most of them peat, and examined the effect of aging of the biomass burning smoke by reactions with OH (and to some extent ozone) in an oxidation flow reactor (OFR). The authors report emission factors (EFs) for all the compounds as well as the change in the effective EFs after OFR.

AC: We thank the reviewer 2 for the constructive review of our paper. First we re-

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sponded to major comments and then we addressed specific comments. All corrections were highlighted in the manuscript.

Reviewer 2: Major comments 1. The reported dataset is comprehensive but it is not very clear to the reader what one can do with these data. While the decrease in the EFs can likely be modeled with known OH rate constants, the increasing EFs are hard to interpret without knowing whether additional products came from gas-ozone chemistry or from heterogeneous oxidation of particles by OH. There are some hints of this discussion in the paper, for example, on line 554. It would be good to expand this discussion.

AC: We acknowledge the reviewer's concern regarding interpretation of the reported EFs for the aged samples. For example, for some fuels (Malaysian and Malaysian agricultural peat) hexanoic acid levels (EFs) were higher after the OFR-oxidation, while for Pskov peat there was an obvious decrease after the OFR (Figure 4c, Page 33). The formation of hexanoic acid after the OFR can be explained by the oxidation of alkanes in fresh BB emissions. However, to confirm this theory, more analyses with a simplified set of compounds are needed. Considering the fact that we analyzed only 84 specific polar compounds in a very complex BB mixture, it is difficult to interpret the formation of different products without speculation. We also acknowledge that the oxidation on the filters during the sampling can affect chemistry of the collected BB aerosols. However, considering high concentration of OH radicals and residence time of BB emissions in the OFR (Bhattarai et al, 2018), we believe that OH radical reactions in the gas-phase prevails over the gas-phase ozone chemistry and heterogeneous oxidation in the particulate-phase inside the OFR chamber. This discussion is presented on Page 36 and we also added one more sentence that highlights this issue (Page 10, line 246-247)

Reviewer 2: Major comments 2. I always find it surprising how small the mass fraction of quantified compounds is despite clearly sophisticated analytical chemistry methods. Would it be possible to discuss what the rest of the compounds could be? Are there

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giant peaks in the GC data that are not reported because of the lack of standards?

AC: We appreciate the reviewer's concern about quantifying only a small fraction of the total organic aerosol mass. In earlier studies, semivolatile organic compounds from biomass burning emissions were analyzed semi-quantitatively through both on-line (Fortenberry et al., 2018) and offline (Jen et al., 2019) sample collection techniques. Those studies also tried to establish mass balance closure of different compound classes but only with identified fraction of organic aerosol mass. However, no attempt was made to compare the identified compounds to the total organic mass. In our work, we performed full quantification of 84 compounds and we found those compounds account only for 5-7% of total organic aerosol mass.

Yes, the reviewer suggestion regarding other unknown species that can be present in the extracts (unidentified peaks on GCMS chromatograms) is absolutely right. We do observe some high-intensity peaks on full-scan GC-MS chromatograms of our samples. For example, NIST library search indicates that one of those peaks is ribose type sugars. Currently we are working on identification of these unknown species. Further results on this ongoing work will be presented in our forthcoming publication.

Specific comments:

1. Lines 126-133, 144-154: These sentences belong to either introduction or discussion. In the experimental section, it is better to focus on the specifics of the fuels used (such as water content, carbon content, etc.), not on the general importance of peatland ecosystems and eucalyptus forests

AC: In the Introduction section we added the paragraph on the importance of peat fuels per reviewer suggestion (Pages 3-4, lines 71-79), however we think it is still better to keep some description of fuels in the Experimental section too.

2. Line 165: it would probably help to know which molecule comes from which company.

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AC: The company names were added (Page 8, lines 194-195) and highlighted in the reviewed manuscript.

3. Line 215: I do not think it is a sufficient argument. Reactions with OH are limited to a short time the mixture spends in OFR. In contrast, residual ozone comes out from OFR and has a chance to react with compounds on filter for the duration of sampling. Therefore, secondary oxidation of BB compounds on filter by ozone is quite possible and can only be ruled out if the residual ozone is low. The authors discuss these effects later in the paper on line 760.

AC: Please see our response on the major comment 1.

4. lines 61-72: This study uses peat as the main BB fuel. Be more specific about the importance of peat burning and why there needs to be a global emphasis on peat burning emissions.

AC: We agree and we emphasized the importance of analyzed fuels in the reviewed manuscript (Pages 3-4, lines 71-79).

5. Line 287: MW should be 124.14 g/mol

AC: Typo with the error removed (Page 14, line 328)

6. Line 360: missing right parenthesis

AC: Parenthesis was added (Page 17, line 399)

7. Line 492: replace)(with a semicolon

AC: The problem with the reference was fixed (Page 24, lines 529-530).

8. Lines 568, 660: you already used LMW on line 448, it would be better to define it there, or not use this abbreviation at all, as it is used only a few times.

AC: Thank you for the suggestion. We corrected the text and use "low MW" and "high MW" everywhere in the text. The "MW" abbreviation is explained on Page 1, line 29.

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9. Line 664: error in 2.4 ± 0.001 appears to be unrealistically small considering other errors reported in this paper.

AC: The reviewer is right. This error can not be that small and was due to a typo. This typo was corrected (Page 32, line 701).

10. Figure 4c: two panels have only one number on the X-axis, and ticks are too small making it hard to estimate the values from the figure (the tick comments applies to all similar figure).

AC: Ticks were fixed for Figures 4a, 4b, 4c (Pages 29, 31, and 33).

11. Figure 5: the text (on line 736) suggests that similar figures exists for other fuel types, however, they are not presented in the supporting information section

AC: The figures (Fig. S3 and Fig. S4) were added to the SM.

References:

Fortenberry, C.F., Walker, M.J., Zhang, Y., Mitroo, D., Brune, W.H., Williams, B.J., 2018. Bulk and molecular-level characterization of laboratory-aged biomass burning organic aerosol from oak leaf and heartwood fuels. *Atmos. Chem. Phys.* 18, 2199–2224. doi:10.5194/acp-18-2199-2018

Jen, C.N., Hatch, L.E., Selimovic, V., Yokelson, R.J., Weber, R., Fernandez, A.E., Kreisberg, N.M., Barsanti, K.C., Goldstein, A.H., 2019. Speciated and total emission factors of particulate organics from burning western US wildland fuels and their dependence on combustion efficiency. *Atmos. Chem. Phys.* 19, 1013–1026. doi:10.5194/acp-19-1013-2019

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