RESPONSES TO REVIEWER #1 (ACP-2019-1179)
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This paper uses a flow tube reactor to simulate the atmospheric oxidation potential of organic molecular markers emitted from burning peat and eucalyptus. The peat fires smoldered while the eucalyptus ones flamed. The semi-volatile organic markers were measured off-line using GC-MS or IC-PAD. The study was able to identify the reaction potential and the formation of semi-volatile organic markers that are common to chemical mass balance models and source apportionment studies.

The study topic is good for ACP. The results are timely because oxidation flow reactors (OFRs) are coming into vogue, and we need to better understand the results that OFRs produce and the potential air quality implications. With that, the study data have value and should be published. However, this particular study also has some serious limitations that need to be better addressed.

AC: We thank the reviewer for the detailed and constructive review of our manuscript. Below, we first respond to general comments and then we address specific comments. All corrections were highlighted in the marked manuscript (Sengupta_manuscript_ACPD2019_review_marked_Final).

General comments:

For one, the paper organization makes it seem like there are two separate studies, an emissions study and an OFR study.

AC: We recognize the reviewer's concern and agree that the study does consist of two main parts (discussion of fresh and aged BB emissions). Due to the complexity of the data (EFs: fresh vs. aged, gas vs. particulate phase emissions from six different fuels) we prefer to preserve the current structure of the manuscript. Initially, we intended to present our results for fresh and aged emissions together. However, in order to increase coherency in narration we described the fresh emissions and corresponding changes after OFR oxidation separately.

The emissions part of the paper is substantially less useful because all of the semivolatile markers were observed in past studies and reported about repeatedly. Additionally, the discussion on emissions lacks information about howthese peat burning results are different than other forms of vegetation burning and what that may or may not mean for emissions reactivity. More critical thinking is warranted to help emphasize how the peat burning emissions are going to impact the SOA compared with other biomass fuels. Otherwise, it does not belong at the forefront of the paper currently. The best approach may be to emphasize the emissions work less and get to the OFR results sooner.

AC: We agree with the reviewer that some of the semivolatile markers described in this study have been already presented in other studies (Mazzoleni et al., 2007; Yatavelli et al., 2017). On the other hand, we are convinced that our research provides new and very important data on fresh emissions from globally important biomass fuels, which have not been characterized extensively before. We added the importance of the emissions from analyzed fuels in the "Introduction" section (**Pages 3-4, lines 71-79**). The goal of this study was not to identify new BB organic compounds in fresh and aged emissions. Our research was mainly focused on analysis of organic compounds (with well-developed methods) and compare them between fresh and aged BB emissions from different fuels. In addition to polar organic compounds we also analyzed PAHs, alkanes, cycloalkanes, etc. Moreover, our next goal is to identify and quantify new BB compounds. These data will be presented in our forthcoming papers. We agree with the reviewer that it would be better if the OFR results appear sooner in the manuscript, however, as we mentioned in our previous comment, because of the inherent complexity of the data we are inclined to keep the current structure of our manuscript.

The lack of replicate tests is another serious study limitation. It appears that standard deviations were taken from another set of tests and applied. This makes it difficult to judge the quality of the concentration data given here and calls into question how exactly the statistics were performed. It also complicates the interpretation of evidence showing what reacted or formed. This is a major limitation that needs to be addressed by providing the readers with sample population (N) and a detailed description of how the standard deviation was calculated and used to determine statistical significance and so on.

AC: We recognize the lack of replicate analysis is a limitation of the current study. Unfortunately, due to resource (limited quantity of fuels available) and budget limitations of the project, we were able to perform only single-burning experiments with each fuel. However, in our previous BB experiments which were run with comparable conditions (Samburova et al., 2016; Yatavelli et al., 2017), we were able to perform triplicate burns for each fuel (including peats) and we argue that the uncertainties from our previous campaigns can be used for the current burning experiments. A detailed description was added to the section 2.5 The uncertainty of the emission factor values reported in the current manuscript includes: 1) burn to burn variability, 2) wall losses in the OFR, and 3) analytical uncertainty of the GC-MS method. In our previous campaigns, we clearly observed that the burn-to-burn variability is much higher than the wall losses and the analytical uncertainty of our method. There is no reason to beleave that burn-to-burn variability, as well as other uncertainties in the current study are different from those observed in our previous studies. Therefore, we think that the best approach is to use the levels of uncertainty that we calculated for our previous combustion campaigns (calculated based on three replicate burns where a comparable experimental set up was used) and use these values for the present data set. For levoglucosan analysis with IC-PAD technique, we were able to calculate only analytical uncertainty.

Finally, no new emissions compounds or SOA markers were measured that weren't part of the original compound suite. At the very least a set of chromatograms should be provided showing the raw emissions and the OFR effluent. That way we can see the major changes in these emissions.

AC: We thank the reviewer for this proposition. We could not agree more that finding new SOA markers is really important in this area of atmospheric research. As mentioned in the current manuscript, we actually performed GC-MS full scan runs on our samples and we are currently working on the data for a future publication discussing compounds that fall outside of the current method.

Specific comments:

1. *line 13: conserve use of the term 'significant' for describing statistics results.*

   AC: We changed "significant" on " prominent" (**Page 1, Line 12**). The word "significant" related to statistical results was also reviewed and changed through the text

2. *line 48: Biomass burning particles exhibit a variety of toxicological properties other than mutagencity. It is worth being clear about that.*

   AC: We agree, BB particle and gas exhibits wide toxicological properteies and mutagenicity is one of them. Hence, we have rephrased the sentence and added a few more refences on the toxicity of BB aerosols (**Page 3, lines 47 – 49**)

3. *lines 54-59: **[MAJOR]** Resolving the organic chemical composition of biomass burning particles is indeed challenging and improvements in speciation are needed. However, this particular study doesn't improve speciation technology in any way. It examines a common set of polar organic compounds and simulates their potential to photooxidize in the atmosphere. The suggestion is to focus on the reactivity of these molecules not on the improved speciation seeing that there are no methodological improvements in molecular level speciation being presented per se. After this study, we are still near 80% w/w for the unknown chemical fraction.*

   AC: We appreciate reviewer's point and agree that this study is not novel in identification of new BB species. The goal of this research was to compare fresh and OFR aged BB emissions of known compounds, which have been already identified in previous studies. We deleted this part of the text from the main manuscript to avoid a wrong impression that we also characterized unknown BB compounds (**Page 3, lines 55-60**). Also, we added a sentence (**Pages 5-6, lines 132-135** of the marked manuscript) that clarifies the goal of this study.

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: This is a good recommendation. Analysis of both fresh and aged peat burning emissions is indeed one of the strengths of this work. We added a paragraph that explains the importance of the peat emissions (**Pages 3-4, lines 71-79**).

5. *lines 80:81: I think the paper needs to be written around this sentence. This is what will make this study novel, important, and worth reading to many. Try and get to this point sooner. It would be better to couch this paper as one that attempts to examine the stability of commonly used polar atmospheric organic markers in an oxidizing environment.*

   AC: We do agree that in our paper we attempted to investigate the stability of commonly identified polar organic compounds in laboratory oxidizing environment. However, we also wanted to analyze and discuss the difference in EFs of these compounds between different fuels as total (gas + particulate phases) and as well as individual gas and particulate phases.

6. *lines 81-93: Describe the advantages and disadvantages of each of these studies, how these pertain and give rise to the current study. Describe more than what these studies did, i.e, mention why these studies are important and are worthy of further discussion. Otherwise, there is not much value here.*

   AC: This is a great suggestion. We added both advantages and disadvantages of the studies to the manuscript (**Pages 4-5, lines 101-113**).

7. *lines 95-96: All peats except Eucalyptus? Why not just focus on peats?*

   AC: We understand the reviewer's recommendation to focus on peat fuels only. However, Eucalyptus fuel is ubiquitous and has a large contribution to recent Australian wildfire emissions. Therefore, presenting our results for eucalyptus emissions is timely and we prefer to keep them in our manuscript with respect to global emission perspectives. The importance of eucalyptus is now highlighted in section 2.1 (**Page 7, lines 167 -171**)

8. *lines 97-98: Describe why the focus here was isolated to polar compounds. It may have been more interesting to focus on the most reactive compounds in the aerosol mixture instead of presenting the study as an exercise in chemical accounting.*

   AC: We understand the reviewer point. 84 polar compounds were selected and analyzed based on our established "polar compound" method, since there are no data how these compounds behave during OFR-aging in the complex mixture of real BB emissions.

9. *lines 135-140: At what depth were the tropical and Russian peats extracted?*

   AC: The peat soils were extracted from the top 15cm of the soil profile, in accordance with convention and also to represent the depths at which soil combustion is most likely to occur. More detailes were added to the Experimental section (**Page 7, lines 163-165**)

10. *lines 176-179: Briefly mention the mass of fuel used per test and how the fuels were configured for burning.*

    AC: Masses of all fuels were added to the Experimental section and the description of fuels' configuration during burning experiments was also added (**Page 7, lines 179-180**)

11. *lines 203-207: Figure 1 does not indicate which on-line instruments were used. These instruments should be described. Please explain how they were used. If they aren't being*

used as part of this study please explain why. There is no modified combustion efficiency evidence showing the levels of smoldering or flaming combustion for each fuel type. Perhaps that can be included here.

AC: The following on-line instruments were used during our combustion experiments: Scanning Mobility Particle Sizer (SMPS), Photo Acoustic Soot Spectrometer (PASS-3), CO and CO_2 analyzer. More detailed description of the instrumental set-up can be found in our previous publication (Bhattarai et al., 2018). PASS and SMPS results will be used in our following manuscript, which will focus on optical properties of BB emissions. During this campaign, the CO_2 analyzer malfunctioned and thus we were unable to use/present the continuous CO_2 data and hence the modified combustion efficiency.

12. *lines 229-231 and lines 251-258: It is mentioned that a 13C radio-labeled levoglucosan samplewas added as internal standard. Wouldn't the 13C isotope elute at the same time as the unlabeled compound? How was that accounted for in this study. The radio isotopes are typically applied for GC-MS. How did things work with the IC-PAD method knowing that the PAD is a non-specific detector and that the radio isotope may interfere?*

    AC: Thank you for catching this error. Levoglucosan-d7 was used as an internal standard for the quantitative analysis of levoglucosan with GC/MS. For the IC-PAD analysis of levoglucosan (see comment #17) the filters were not spiked with any internal standards. This error was corrected (**Page 8, lines 194-195**).

13. *lines 236-237: What is the value of reporting these separately considering that the equilibrium partitioning changes and was specific to the sampling conditions used for this particular study? Please discuss briefly. Also, was any thermodynamics-based check performed on how well the equilibrium partitioning was measured here? Such a relatively straightforward check on select compounds can verify that the sampling worked as planned.*

    AC: This is definitely an interesting scientific question. We agree that the equilibrium partitioning can change under different sampling conditions. However, a compound's phase also affects its reaction rates. Thus, we beleave it is important to report gas and particle concentrations as they were observed during the experiments. We did check whether the observed partitioning is thermodynamically reasonable – it is for most compounds, at least qualitatively. A quantitative assment, however, is complicated for the heavy and light compounds due to the very low concentrations in one of the phases.

We are working on resolving these issues, but the complexity of this process is well beyond the scope of this manuscript .

14. *lines 275-280: [MAJOR] Please clarify how the SDs were calculated. It's unclear where the standard deviations (SDs) came from and the reader should know exactly what and how many experiments were used to report SD values. The suggestion that the SDs came from another study and therefore can be applied here is questionable analytical-chemical practice. SDs should be experiment-specific, not just assumed and carried-over from study to study. At the very least, multiple injections of the same extract should be performed. What is meant by 'similar' fuels? This comment applies to all of the experimental data being reported.*

    AC: In the section 2.5 we added a description how the SDs were calculated for the present data set (**Page 11, lines 280 – 293**). In our analytical method we have replicates for few samples with multiple injections that we have used for calculating analytical uncertainties. However, burn-to-burn variability during the combustion experiments governs the overall uncertainties and hence we have included that variability calculated from the data collected in our previous combustion campaigns. It is worth mentioning that analytical uncertainties are also discussed along with burn-to-burn variability.
    The uncertainties for the peat combustion experiments were computed based on the results for Alaskan peat emissions (triplicate burns), while the uncertainties for eucalyptus were calculated using our previous Cheatgrass results (triplicate burns). The expression "Similar fuels" refers to similar combustion conditions (smoldering type peat combustion vs. flaming type eucalyptus combustion) **(Page 13, line 320)**

15. *lines 282-328: This information about methoxy-phenol emissions from biomass burning is already available 'ad naseum' in the literature and can be further consolidated. Instead of focusing on whatwe already know, examine how the peat emissions are different (if they indeed are) and how these differences may be important to the atmospheric processing and oxidation. Knowing more about the extent of smoldering and flaming combustion can help properly develop this discussion.*

    AC: We have this discussion (differences in EFs between fuels) in our manuscript and we also compared our EFs with EFs from other studies. (**Section 3.1.1**).

16. *lines 381-508: [MAJOR] Again, virtually all of this chemical information is already available. Much of this can be condensed into a brief paragraph or two unless there is something salient and different for the fuels being examined here that merits further attention. Suggestions: Develop one section that discusses 'Polar organic chemistry' of these emissions. Move the figures of individual compound emissions into supporting information. Develop a new emission figure that combines everything by compound class and shows the reader some sort of chemical mass balance so they can understand the aerosol fraction of interest (more like Figure 3, but include a mass balance). Only if needed, focus on some of the unique chemical or physical state attributes of individual compounds emitted during burning of these particular fuels. In other words, if the chemical structure or physical state of a compound is important to understanding its oxidation then discuss these attributes and the results. This requires a reorganization of the paper as some of these results are presented elsewhere.*

    AC: We really appreciate reviewer's recommendation of creating a new section and figures that exhibit a mass balance. We have addressed that issue in the general comment section too. Here, we give an example that explains why attaining closure in mass balance with the our results is a difficult task and beyond the scope of this manuscript.
    For example, aromatic acids can be produced during oxidation of methoxyphenols (reported in this study) and also from oxidation of PAHs and substituted PAHs (Wang et al., 2007) (not reported). Similarly, monocarboxylic acids can form by fragmentation (during oxidation) of compounds, form the same homologous series, and at the same time they also can be derived from oxidations of alkanes and alkenes. Because of the chemical complexity, it is very challenging to derive adequate mass balance results based only on analyzed polar compounds without considering other species.

17. *line 509: It would be interesting to learn if any of the levoglucosan was found in the gas phase. Levoglucosan elutes from a GC column with and without derivatization. Was there any indication of levoglucosanin the gas-phase?*

    AC: For the quantitative analysis of levoglucosan we selected IC-PAD analysis over the GC-MS technique that includes BSTFA-derivatisation of this polar compound. Due to the high levels of levoglucosan in the extracts, the MS detector was oversaturated; that made it impossible to perfom adequate quantitative analysis of this compound. Therefore, further investigation of levoglucosan in the gas phase emissions was not feasible.

18. *lines 524-530: The important part of the study begins here. Figure 3 is a good figure that captures the essence of what was tested, measured, and and accomplished.*

    AC: We thank the reviewer for this recognition

19. *Figure 3: Again, are these error bars taken from other studies? If so, please remove them from the figure. One idea is to combine all of the peat samples measured here and calculate a standard deviation and use that to report global error for experimental peat burning. That can be added as a panel to one of the figures or presented separately.*
    AC: The uncertainties calculations are added to the text (**Page 11, lines 280-293**)

20. *lines 605-614: The importance of associating meaningful error with concentration data cannot be understated. For example, the error associated with levoglucosan measurement using GC-MS is approximately20%. Although, the combustion test error can bring this value closer to 30%-50%. If we knew the exact error associated with repeating these peat experiments, we'd have a better understanding of this decrease being real or not. This may also explain why the same compound appears to be eitherformed or degraded for some fuels (see lines 631-632 and lines 691-699 (e.g., hexanoic acid).*

    AC: This is an interesting point. However, we believe that this is not only due to the error assignment. Hexanoic acid can be formed by oxidation of alkanes and decomposition of high molecular weight mono carboxylic acids (McNeill et al., 2008) This is why it is difficult to predict the fate of this compound by just looking at a matrix of polar compounds. Moreover, the occurance of multiple generation of oxidations inside OFR (Li et al., 2015) leads to further complexity and as a result the same compounds can be either formed or degraded during oxidations of emissions from different fuels.

21. *line 696: Please describe the type of statistical tests being applied here and how they are being applied. Please report the sample population (N). Additionally, provide more information about how the error was calculated and applied to conduct the statistics tests.*

    AC: We have described earlier how we calculated SD at the end of section 2.5 (**Page 11, lines 280-293**). In order to evaluate changes associated with oxidation experiments, we need to perform "Pairwise-T-test" with fresh and aged samples. However, in our case we have computed the uncertainties from our previous campaign with only fresh samples, propagated that to both fresh and aged samples, and we refrained from performing pairwise T-test for this analysis. We agree with the reviewer's perspective that without replicate burns, we need to be conservative while describing some change as "statistically significant/insignificant". We have deleted such strong words to make the message less categorical. Changes in the main manuscript related to this comment are highlighted (**Lines 621, 681, 733, 747, 750**).

22. *lines 724-733: Please describe the criteria for a "top" contributing compound. Was it concentration?*

    AC: The reviewer is correct, the "top" contribution compounds refer to compounds with highest levels of concentration (EFs.). We rephrased the figure caption (**Page 35, lines 762-763**)

23. *lines 736-737: Isn't it also possible that the combustion was different?*

    AC: We agree with the reviewer and added the "nature of combustion" to the text (**Page 36, line 776**).

References:

Bhattarai, C., Samburova, V., Sengupta, D., Iaukea-Lum, M., Watts, A.C., Moosmüller, H. and Khlystov, A.Y., 2018. Physical and chemical characterization of aerosol in fresh and aged emissions from open combustion of biomass fuels. Aerosol Science and Technology, 52(11), pp.1266-1282.

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RESPONSES TO REVIEWER #2 (ACP-2019-1179)
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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 responded 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 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 online (Fortenberry et al., 2018) and offline (Jen et al., 2019) sample collection techniques. Those studies also tried to extablish mass balance closure of different compound classes but only with identified fraction of organic aerosol mass. However, no attempt was made to compare the indentified 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.*

   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**.

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

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Polar semi-volatile organic compounds in biomass burning emissions and their chemical transformations during aging in an oxidation flow reactor

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Abstract

Semi-volatile organic compounds (SVOCs) emitted from open biomass-burning (BB) can contribute to chemical and physical properties of atmospheric aerosols and also may cause adverse health effects. The polar fraction of SVOCs is a prominent part of BB organic aerosols, and thus it is important to characterize the chemical composition and reactivity of this fraction. In this study, globally and regionally important representative fuels (Alaskan peat, Moscow peat, Pskov peat, Eucalyptus, Malaysian peat, and Malaysian agricultural peat) were burned under controlled conditions using the combustion chamber facility at the Desert Research Institute (DRI). Gas- and particulate-phase biomass-burning emissions were aged in an oxidation flow reactor (OFR) to mimic 5–7 days of atmospheric aging. Fresh and OFR-aged biomass-burning aerosols were collected on Teflon impregnated glass fiber filters (TIGF) in tandem with XAD resin media for organic compound (OC) speciation. The polar fraction extracted with dichloromethane and acetone was analyzed with gas chromatography mass spectrometry (GC-MS) for 84 polar organic compounds—including mono and dicarboxylic acids, methoxylated phenols, aromatic acids, anhydrosugars, resin acids, and sterols. For all these compounds, fuel-based emission factors (EFs) were calculated for fresh and OFR-aged samples. The carbon mass of the quantified polar compounds was found to constitute 5% to 7% of the total OC mass. High abundance of methoxyphenols (239 mg kg^{-1} for Pskov peat; 22.6% of total GC-MS characterized mass) and resin acids (118 mg kg^{-1} for Pskov peat; 14.5 % of total GC-MS characterized mass) was found in peat burning emissions (smoldering combustion). Concentration of some organic compounds (e.g., tetracosanoic acid) with molecular weight (MW) above 350 g mol^{-1} decreased after the OFR aging, while abundances of low MW compounds (e.g., hexanoic acid) increased. This indicated a significant extent of fragmentation reactions in the OFR. Methoxyphenols decreased after OFR aging, while a significant increase (3.7 to 8.6 times) in abundance of dicarboxylic acids emission factors (EFs), especially maleic acid (10 to 60 times), was observed. EFs for fresh and ratios from fresh-to-aged BB samples reported in this study can be used to perform source apportionment and predict processes occurring during atmospheric transport.

Keywords. Biomass burning, organic aerosols, semi-volatile organic compounds (SVOCs), gas chromatography, mass spectrometry, polar organic compounds, oxidation flow reactor

1 Introduction

Biomass burning (BB), including both wildfires and prescribed burns, is a major source of carbonaceous aerosols in the atmosphere (Penner et al., 1991) and can contribute up to 75% of total atmospheric aerosol mass loading (Andreae et al., 2001; Park et al., 2007). These carbonaceous aerosols have significant impact on both regional and global radiative forcing (Ramanathan and Carmichael, 2008). BB emissions also can cause adverse health effects (Arbex et al., 2007; Regalado et al., 2006) because of the ~~mutagenic property~~ toxicological properties of particle-bound organic compounds (Chen et al., 2017; Pardo et al., 2020; Pavagadhi et al., 2013; Sigsgaard et al., 2015; Yang et al., 2010) ~~(for example, mutagenicity (Yang et al., 2010)).~~ Therefore, comprehensive, molecular-level characterization of BB emissions is essential for understanding health effects. Such molecular characterization of BB carbonaceous aerosols in the atmosphere, however, is challenging as these aerosols are composed of tens of thousands of compounds (Goldstein and Galbally, 2007).

~~Current atmospheric chemistry models use a limited number of organic species because of the complexity of atmospheric aerosol chemical composition and the lack of aerosol chemical speciation data. Approximately 80% of BB organic mass emissions, especially aged emissions, are not identified in such models (Bertrand et al., 2018; Jen et al., 2019), limiting the capabilities of atmospheric organic aerosol modeling. Thus, improvement is needed in molecular-level speciation of both fresh and aged BB emissions for more accurate model estimations.~~

Simulation of natural fires in a laboratory environment using a BB chamber is one way to characterize the chemical composition of BB emissions (Yokelson et al., 2003). A number of studies characterizing the molecular composition of combustion emissions from fuels that represent different geographical regions have been completed: temperate conifers (Oros and Simoneit, 2001a), deciduous trees (Oros and Simoneit, 2001b), grasses (Oros et al., 2006), and peats (Samburova et al., 2016; Iinuma et al., 2007). Akagi et al. (2011) compiled fuel-based emission factors (EFs) from different fuels from throughout the world, including the peatlands of south Asia, and found that burning condition (flaming/smoldering) can influence the EFs of individual compounds~~.~~ These data have been used for modeling work in predicting ozone-forming potential and other air quality impacts (Alvarado et al., 2015). Very few studies (e.g. (Samburova et al., 2016) have focused on peat emissions. However, the importance of investigating the combustion products from burning peat soils is multifaceted. Peat soils, comprised predominantly of partially decomposed organic material, represent one-fourth to one-third of global terrestrial carbon and are under threat of increased fire activity in both boreal and tropical latitudes, areas of widespread peatland occurrence (Turetsky et al., 2015). In addition to the implications of peat fires for the global C cycle, local impacts from burning of peatlands include public health and safety problems from degraded to air quality, as well as ecological changes due to altered surface hydrology in low-relief areas (Watts et al., 2015). Most source apportionment studies, however, focused on characterization of fresh emissions and emissions of either particle-phase or gas-phase compounds.

Significant changes in organic aerosol composition during atmospheric transport have been reported (Liu et al., 2017; Decker et al., 2019). These changes can impact local and regional air quality. Also, the role of Siberian peat burning in haze formation in the Korean peninsula (Jung et al., 2016) demonstrates the global impact of BB emissions and their atmospheric transport on regional air quality. Some laboratory studies found an increase in organic aerosol (OA) mass after photochemical aging (Ortega et al., 2013; Grieshop et al., 2009) while others observed a modest decrease (Bhattarai et al., 2018). There is still limited data on evolution of chemical composition of primary organic aerosols (POAs) during atmospheric aging. Some laboratory experiments demonstrated degradation of levoglucosan (Hennigan et al., 2010; Kessler et al., 2010) and oxidation of methoxyphenols in the gas phase (Yee et al., 2013) and aqueous phase (Net et al., 2011). These studies have more mechanistic implications than quantifying gross change after atmospheric oxidation. The reactivity of a pool of organic compounds in a complex mixture such as BB emissions is expected to be different mechanistically from individual compounds. This necessitates the need for studies of the evolution of organic compounds through bulk molecular level characterization of BB emissions. Recently, Fortenberry et al. (2018) characterized the chemical fingerprints of aged biomass-burning aerosols (leaf and hardwood of white oak) by performing oxidation in a potential aerosol mass oxidation flow reactor (PAM-OFR) and chemical analysis with a thermal desorption aerosol gas chromatograph aerosol mass spectrometer (TAG-AMS). In this study, denuders were used to remove gases and particles were introduced to OFR to evaluate only the changes in particulate BB emissions during OFR oxidation. However, the presence of both gas and particulate phase emissions in real BB emission and the partitioning of organic compounds in such a complex mixture can affect the reactivity inside the OFR and hence the fate of organic compounds during OFR aging. Bertrand et al. (2018) analyzed 71 organic compounds in BB emissions, sampled from a smog chamber, with high resolution time of flight mass spectrometry (HR-ToF-AMS). This study confirms that nitro-aromatic compounds are formed after OFR oxidation and that they can be used as SOA tracer. However, this study was focused on controlled wood (pellet) burning that is substantially different from wildland BB emissions. There is still a lack of understanding, however, regarding (1) major organic compounds emitted from BB (especially from peat fuels), (2) their roles in atmospheric photochemical reactions, and (3) what compounds are responsible for light absorption of fresh and aged BB emissions.

In this study, emissions from laboratory combustion of six globally important fuels (Alaskan peat, Moscow peat, Pskov peat, Eucalyptus, Malaysian peat, and Malaysian agricultural peat) were quantitatively analyzed for more than 250 individual organic species, and analyses of 84 polar organic species is presented in this paper. BB emissions generated in a combustion chamber were run though the OFR, mimicking approximately 5 to 7 days of atmospheric oxidation (Bhattarai et al., 2018), and the OFR output was analyzed to characterize aged BB emissions. BB emissions were collected on filter and XAD media to identify distribution of organic species between the gas and particle phases. For the polar fraction of collected organic compounds, we quantitatively analyzed a total of 84 compounds (methoxyphenol derivatives, dicarboxylic acids, monocarboxylic acids, aromatic acids, resin acids, and anhydrosugars). In the analyzed anhydrosugars, we paid special attention to levoglucosan, a derivative from cellulose (Simoneit et al., 1999), since levoglucosan has been widely used as a molecular tracer of BB emissions (Bonvalot et al., 2016; Maenhaut et al., 2016). Methoxyphenols also have been used in source apportionment studies (Schauer et al., 2001; Schmidl et al., 2008b, 2008a). These source apportionment studies, however, haven't combined such a wide range of different groups in a single investigation. Here we provide a detailed targeted chemical analysis of both gas- and particle-phase BB emissions from the combustion of individual biomass fuels from diverse geographical locations for both fresh and aged emissions. The goal of this research was to characterize EFs of gas- and particulate-phase individual polar organic species ~~are presented~~ for six compound groups ~~of compounds~~ (methoxyphenols, dicarboxylic acids, monocarboxylic acids, aromatic acids, anhydrosugars, and resin acids) and to analyze their fate after the-OFR oxidation. In separate sections we discussed EFs obtained for fresh and OFR-aged BB samples. The fresh-to-aged ratio and top contributing organic species also are discussed. The comparison between fresh and OFR-aged BB emissions helps to understand the chemical evolution of BB plumes in the atmosphere and the obtained data can be used in future source apportionment and atmospheric modeling studies.

2. Experiments

2.1 Fuel Description

We selected six globally and regionally important BB fuels: Alaskan peat, Moscow peat, Pskov peat, Eucalyptus, Malaysian peat, and Malaysian agricultural peat. Five of these were peat fuels selected from different geographical locations, representing smoldering combustion and one (Eucalyptus) representing flaming combustion.

Peatland ecosystems, generally wetland or mesic ecosystems underlain by soils composed primarily of partially-decomposed biomass, contain mostly organic carbon and more than 20% mineral content, represent a vast terrestrial carbon pool, and are potentially vast sources of carbon flux to the atmosphere during wildfires that consume peat (Harden et al., 2000). Peatlands in high-latitude temperate and boreal regions are particularly vulnerable to increased fire-related carbon emissions resulting from climatic warming and increases in fire season length, while peatlands in low-latitude and tropical regions are threatened by factors such as deforestation for agriculture, urbanization, and drainage (Turetsky et al., 2015). We collected Alaskan peat samples from the upper 10 cm of soils within black spruce (*Picea mariana*) near crown forest (Chakrabarty et al., 2016). High-latitude and Eurasia samples here are from *Sphagnum*- and cotton grass- (*Eriphorum* spp.) dominated communities, collected from the Moscow (Odintsovo and Shatura districts) and Pskov regions of Russia. These regions are representative of oligotrophic peat bogs found widely across Siberia as well. Tropical peat in this study includes samples from two areas in Malaysian Borneo. One set of samples is from a *Dipterocarp*-dominated lowland forest with largely intact native land cover, while the second set is from a cleared agricultural area in the Kota Snamarahan region. All peat soils were extracted from the top 15 cm of the soil profile. The mass of the dry peat fuels varied from 70-100 g. The peat fuels were burned inside a metal pot which contains thermally insulating materials at its bottom and sides.

We selected Eucalyptus as a test fuel because of its prevalence across Australia and its important contribution to Australian wildland fires. In addition, economic losses and risk to life and property from fires in eucalypt forests are magnified by their proximity to both fire-prone ecosystems and large urban areas; often eucalypt-dominated stands form boundaries between these two land-use types. There are nearly 900 species of the genera *Eucalyptus*, *Corymba*, and *Angophora*, which collectively comprise woody plants known as eucalypts. Native to Australia, eucalypt-dominated forests cover nearly 92 million ha (Hills, W.E.; Brown, 1978). In addition, the fast and hardy growth characteristics of eucalypts have made them popular in warm ecoregions of Europe as well as North and South America, where they readily escape cultivation and become established, dominant community types near urban areas where they were originally introduced. Because of their high oil content, rapid and dense growth, and vegetative structure, eucalypts are highly flammable and contribute to high fire risk in areas where they occur (Goodrick and Stanturf, 2012). The mass of the Eucalyptus fuel burned (i.e., ~650 g) was higher than that of peat fuels and this fuel was arranged similar to a common arrangement for campfires.

2.2 Reagents and Materials

We obtained high-performance liquid chromatography (HPLC) grade methanol and hexane from Fisher Scientific (Fair Lawn, NJ, USA) and used the following filters for sampling and further chemical analyzes: pre-fired (900 °C for 4 h) 47 mm diameter quartz-fiber filter (2500 Pallflex QAT-UP, Pall Life Sciences, Ann Arbor, MI, USA) for thermo-optical Elemental Carbon/Organic carbon (EC/OC) analysis, Teflon® filters (2500 Pallflex QAT-UP, Pall Life Science, Ann Arbor, MI, USA) for gravimetric particulate matter (PM) mass analysis, and Teflon-impregnated glass fiber (TIGF) 47 mm diameter filters (Fiber FilmT60A20, Pall Life Sciences, Ann Abor, MI, USA) for organic analysis. We purchased the following deuterated internal standards from Cambridge isotope laboratories (Tewksbury, MA, USA) and CDN isotopes (Pointe-Claire, Quebec, Canada): hexanoic-d11 acid, , succinic-d4 acid, decanoic-d19 acid, adipic-d10 acid, suberic-d12 acid, homovanillic-2,2-d2 acid, myristic-d27 acid, heptadecanoicd33 acid, oleic-9,10-d2 acid tetradecanedioic-d24 acid (CDN Isotopes, Quebec, Canada) and benzoic-d5 acid, levoglucosan-d7 and cholesterol-2,2,3,4,4,6-d6 (Cambridge Isotope Laboratories, Inc., MA, USA)

2.3 Biomass Burning (BB) Experiments

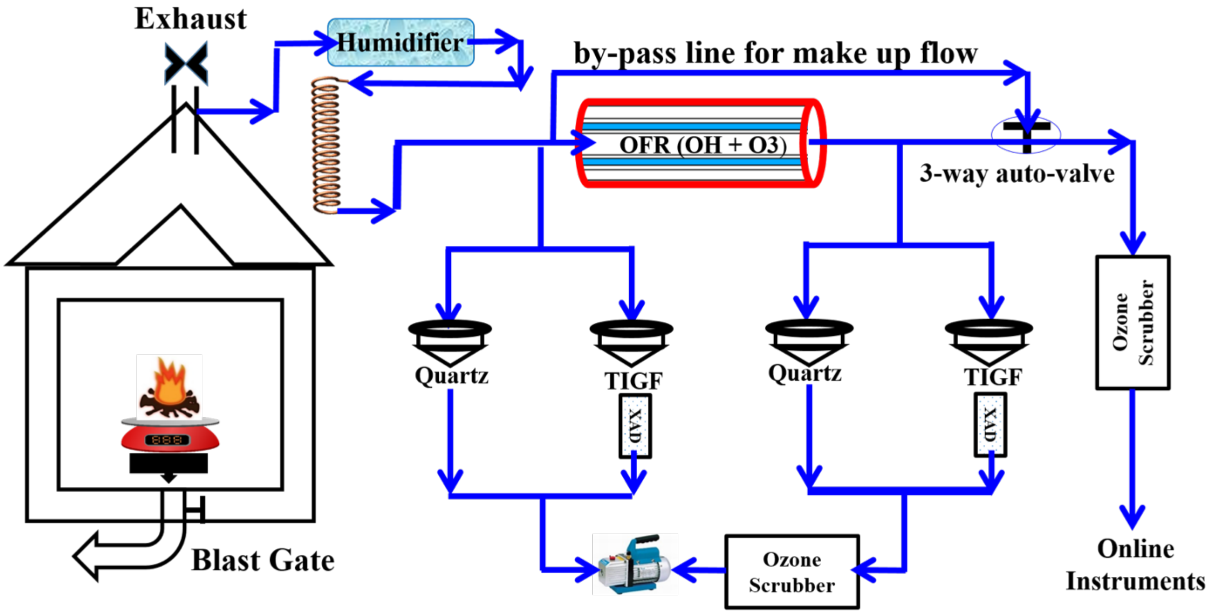

Figure 1. Desert Research Institute (DRI) biomass burning (BB) facility with oxidative flow reactor (OFR) and flow setup.

BB experiments were conducted using DRI's BB facility for combustion of the selected fuels under controlled conditions. A close replicate of this facility was described previously (Tian et al., 2015), and a detailed description of the experimental setup was presented elsewhere (Bhattarai et al., 2018; Sengupta et al., 2018).

We mixed laboratory-generated BB emissions with humidified zero air (Airgas Inc., Sparks, NV, USA) using 4 m long spiral copper tubing (12.7 mm OD). Before it was mixed with the BB emissions, the zero air was humidified by bubbling through Nano-pure water in a glass 500 mL volume impinger. The flow rate was controlled with a mass flow controller (810C-CE-RFQ-1821, Sierra Instruments, Monterey, CA, USA). An oxidation flow reactor (OFR) (Aerodyne Research

Inc., Billerica, MA, USA) was used to mimic approximately seven days of equivalent atmospheric aging (Bhattarai et al., 2018). The OFR consisted of an alodine-coated aluminum cylinder (46 cm length and 22 cm diameter) with an internal volume of 13.3 L. Two sets of lamps emitted UV radiation at wavelengths of 185 and 254 nm (Atlantic Ultraviolet Corporation, Hauppauge, NY, USA) in the OFR to produce ozone and OH radicals (Li et al., 2015). UV irradiance in the OFR was quantified using a photodiode detector with a wavelength range of 225 to 287 nm (TOCON_C6; Sglux GmbH, Berlin, Germany). Ultra-high-purity nitrogen (Airgas Inc., Reno, NV, USA) was used to purge the UV lamp compartments to prevent the lamps from overheating. A probe that monitored relative humidity and temperature inside the OFR (from Aerodyne Inc., MA, USA) was mounted toward the outlet side of the OFR. A detailed characterization of the OFR—such as particle loss, OH production rate, and time scales of various processes—can be found in Bhattarai et al. (2018).

The duration of smoldering combustion experiments ranged from 69 to 255 min, whereas the average duration of flaming combustion experiments was 50 min. During all experiments, both fresh (directly from the chamber) and aged (oxidized in the OFR) emissions were continuously collected on a TIGF filter (for particle phase) followed by an XAD cartridge (for gas phase) for detailed chemical speciation. We used several online instruments to characterize gas- and particle-phase pollutants (see Fig. 1). Simultaneous collection of samples for thermal optical carbon analysis on quartz fiber filters (Pall-Gelman, 47 mm diameter, pre-heated) was conducted, but only for Eucalyptus and Malaysian peat. The online instruments alternated every 10 min between sampling fresh and aged emissions using a computer-controlled valve system. A description of all instruments and the detailed experimental set up can be found elsewhere (Bhattarai et al., 2018).

We employed a bypass flow to keep the flow from the BB chamber and through the OFR constant when online instruments switched between sampling fresh and aged emissions. To protect online instruments from high ozone concentrations produced in the OFR, ozone scrubbers were installed in front of the instruments' inlets. The ozone scrubbers were loaded with charcoal followed by Carulite 200 catalyst (Carus Corp., Peru, IL, USA). There were no ozone scrubbers before the filter-XAD set up, which could cause further oxidation of organic compounds on filter surfaces during sampling. The reaction rates between organics and ozone, however, are orders of magnitude lower than OH oxidation reactions (Finlayson-Pitts and Pitts Jr, 1999). Therefore, we assumed that reactions with OH radicals were primarily responsible for changes in organic compounds associated with fresh gas and particulate emissions. We also acknowledge that the ozone-oxidation on the filters during the sampling can affect chemistry of the collected BB aerosols (section 3.4).

2.4. Organic and Elemental Carbon (OC/EC) Analysis

Emissions from the combustion of two fuels (Eucalyptus and Malaysian peat) were sampled with quartz-fiber filters, collected simultaneously with TIGF filters, for both fresh and aged BB aerosols (Supplementary Material, Fig. S1). Punches (area = 1.5 cm^2) from these quartz filters were analyzed with a thermal-optical carbon analyzer (Atmoslytic Inc., Calabasas, CA, USA) following the IMPROVE protocol (Chow et al., 1993, 2004) for total organic carbon (OC_{Total}) and elemental carbon (EC) mass.

2.5 Analytical Methodology for GC-MS

We extracted filter and XAD samples for GC/MS analysis (SI Table S1) yielding concentrations of 84 polar organic compounds. In addition, levoglucosan concentrations were determined using ion chromatography coupled with a pulsed amperometric detector (IC-PAD). Prior to the extraction, sampled TIGF filters and XAD-resin cartridges were spiked with deuterated internal standards (see “Reagents and Materials” section). The TIGF filters and XAD cartridges were extracted separately with an accelerated solvent extractor (Dionex ASE-300, Sunnyvale, CA, USA) at the following conditions: 80° C temperature, 250 mL extraction volume, and subsequent extraction with dichloromethane and acetone. The XAD and filters were treated separately to evaluate the speciation of gas- and particle-phase semi-volatile polar compounds. The extracts were concentrated with a rotary evaporator (Buchi-R124, Switzerland), filtered using 0.2 µm pore size syringe filters (Thermo Scientific, Redwood, TN, USA), and pre-concentrated with nitrogen to a volume of 4 mL. Then we split the extracts into two fractions. One fraction was transferred to 2.0 mL volume deactivated glass maximum recovery vials (Waters Corporation, Milford, MA, USA), pre-concentrated to 50 µL volume under ultra-high-purity nitrogen (Airgas, Reno, NV, USA), and derivatized with N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA with 1% of trimethylchlorosilane; Thermo-Scientific, Bellefonte, PA, USA) and pyridine as described elsewhere (Rinehart et al., 2006). Derivatized samples were analyzed by electron impact ionization using a Varian CP-3400 gas chromatograph with a CP-8400 auto-sampler and interfaced to a Varian 4000 ion trap mass spectrometer (Varian Inc. Palo Alto, CA, USA). The second fraction of non-derivatized extracts was kept for further analysis of non-polar organic species (e.g., alkanes and PAHs), and those results will be presented in future publications.

Since, we have not performed any replicate burning experiments in this study, we used uncertainty values from our previous work (Yatavelli et al., 2017) as follows. We took mean (μ_c) and standard deviation (σ_c) values for all 84 compounds from Alaskan peat (3 replicates) and Cheatgrass (3 replicates) combustion and calculated fractional uncertainties (f_c) using equation 1.

$$f_c = \frac{\mu_c}{\sigma_c} \qquad \text{Eq. 1}$$

These fractional uncertainty values are multiplied by the emission factors for each compound (both fresh and aged) from the current study to obtain individual uncertainties or standard deviation (SD) values as demonstrated in equation 2.

$$SD_c = f_c \times EF_c \qquad \text{Eq. 2}$$

The group uncertainties for each different subclass were computed from individual uncertainties by applying standard propagation of error method (root sum of squares).

Considering the different nature of combustion, the fractional uncertainties derived from Alaskan peat combustion were applied to emissions from all peat fuels and the uncertainties obtained from cheatgrass combustion were applied to emissions from Eucalyptus combustion.

2.6. Levoglucosan Analysis

Portions of quartz filters collected for OC/EC analysis also were used for quantitative analysis of levoglucosan concentration with IC-PAD. Prior to the analysis, quartz filters were extracted with 15 ml of deionized water (18.2 MΩ), sonicated for one hour, and refrigerated overnight. The column temperature for IC was 25° C. Analytes along with a mixture of two eluents (48% hydroxide solution and 52% deionized water) were passed through the IC column with a 0.4 ml min^{-1} eluent flow rate and detected using an electrochemical detector. See Chow and Watson (2017) for details. Uncertainties or standard deviations associated with levoglucosan results indicate only analytical uncertainties of the IC-PAD method.

3. Results and Discussion

3.1. Gas- and Particulate-Phase Emission Factors

Organic compounds (84 in total) in fresh emissions identified and quantified in this study were assigned to six major groups (Table S1): methoxyphenol derivatives, dicarboxylic acids, mono-carboxylic acids, aromatic acids, resin acids, and levoglucosan. First, we report individual emission factors (EF) belonging to a particular group calculated by summation of gas- and particle-phase EFs of individual compounds. Relative abundance of these compounds is reported next followed by a comparison of the contributions of each group (EF_{group}) among fuels and a comparison with previously reported results.

3.1.1 Methoxyphenol Derivatives

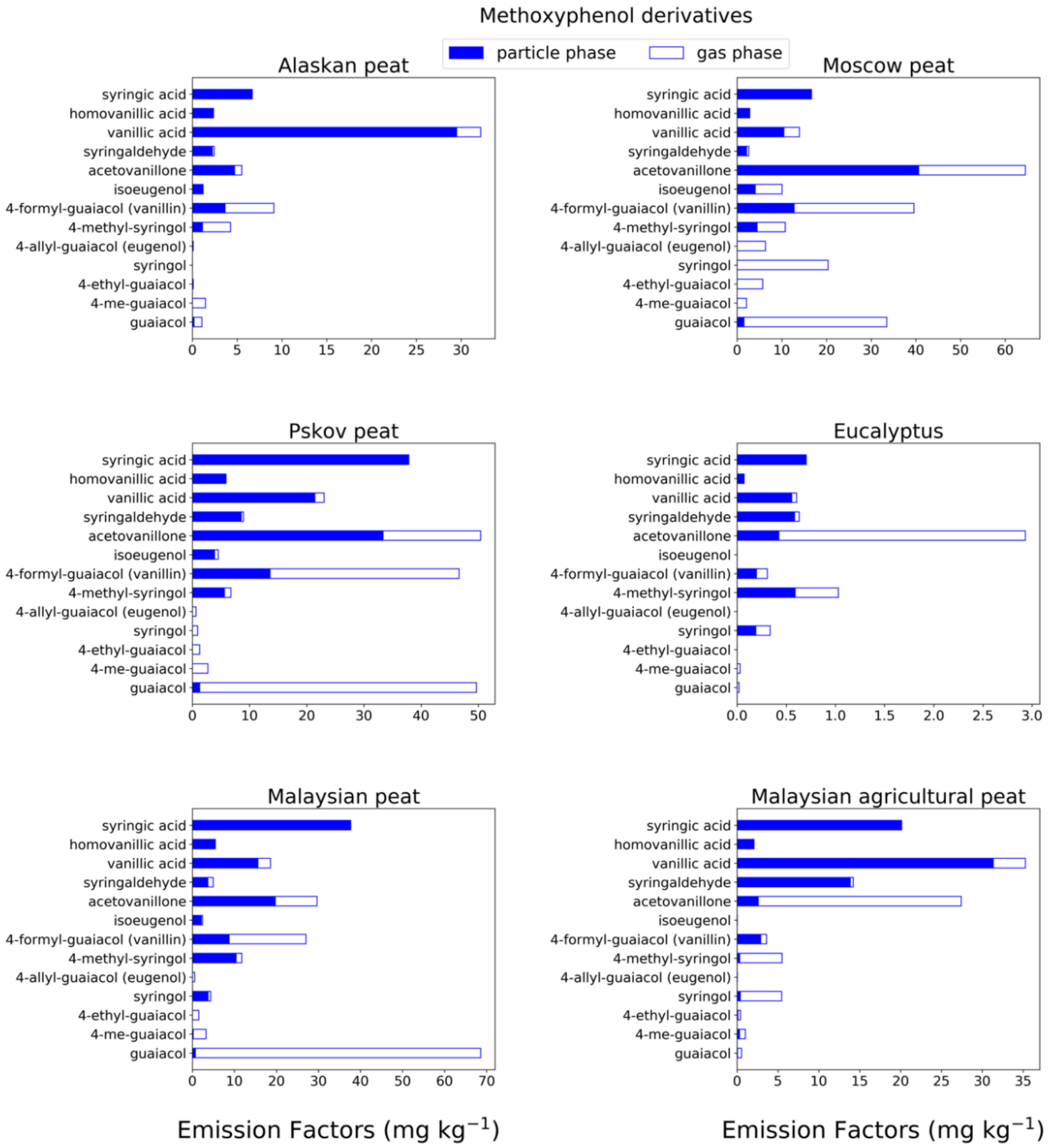

Figure 2a. EFs for methoxyphenols in both particulate phase (solid bars, filter samples) and gas-phase (open bars, XAD samples) from fresh biomass burning emissions for six different fuel types. We did not burn fuels in replicates, and standard deviations (SD) were calculated based on replicate analysis of emissions from similar fuels (with identical experimental conditions) during our previous combustion campaigns (Yatavelli et al., 2017) where SD ranged between 9.7 and 22% for methoxyphenol derivatives.

Methoxyphenols are key compounds in BB smoke since they constitute from 20 to 40% of total identified organic aerosol mass (Hawthorne et al., 1989; Yee et al., 2013). For this reason, these compounds are considered potential markers for wood combustion (Schauer et al., 2001) and have been used as probable biomarkers to determine human exposure to BB emissions (Simpson and Naeher, 2010; Dills et al., 2006). Our analysis of 13 methoxyphenols (Fig. 2a, Table S1) showed that guaiacol (MW = 124~~±12~~ g mol^{-1}) was the major contributor to EFs of the measured methoxyphenols in Moscow peat (33.5±3.3 mg kg^{-1}), Pskov peat (49.7±4.8 mg kg^{-1}), and Malaysian peat (68.6±6.7 mg kg^{-1}). Syringol, another methoxyphenol commonly found in BB emissions (Schauer et al., 2001), had the highest EF for Moscow Peat fresh emissions (20.4±2.7 mg kg^{-1}), while for the other fuels, the EF was much lower (0–5.5 mg kg^{-1}). EFs for syringic acids (MW = 198 g mol^{-1}) were in the range of 0.06–37.9 mg kg^{-1} for all fresh emissions. Syringols are generally not formed during pyrolysis of coniferous lignin, but during pyrolysis of deciduous lignin, where both guaiacols and syringols are formed (Mazzoleni et al., 2007). Presence of both guaiacol and syringol moieties in fresh emissions indicates that the part of the plant material that was responsible for peat formation was probably from deciduous trees, and this signature of deciduous trees from peat burning emission is irrespective of geographical origin of those peats (also shown by Schauer et al., 2001). Acetovanillone, vanillin, and vanillic acid also were observed in fresh emissions with high abundance (5–50 mg kg^{-1}). For example, vanillin is an abundant methoxyphenol in the fresh emissions from Pskov peat (46.7±5.4 mg kg^{-1}) which contributed 4.4% of the total mass of the 84 analyzed compounds.

Low MW methoxyphenols (e.g., guaiacol) are expected to be found in the gas phase (Yatavelli et al., 2017), in close agreement with our results. For example, guaiacol and substituted guaiacols were mostly present in gas phase (82–100%) for emissions from the combustion of different fuels (Fig. 2a, Table S1). With the addition of more oxygenated functional groups to a molecule, and thus with MW increase, the equilibrium gas-particle partitioning of the compound tends to shift toward the particulate phase, which also was confirmed by our results (e.g., for acetovanillone, a keto form of lignin derivative, from Malaysian peat combustion, 33.5% of its mass was found in gas phase; for more oxygenated syringic acid, 99% of its mass was found in particulate phase emissions from the same fuel).

The highest methoxyphenol EF_{group} from combustion of all fuels was observed in the fresh Pskov peat (Fig. 3a) emissions (239±11 mg kg^{-1}). For Moscow peat, which was sampled close to the geographical region of Pskov peat, the EF_{group} of methoxyphenols was 229±10 mg kg^{-1} (Fig. 3a), very similar to that for Pskov peat. The methoxyphenol EF_{group} for peat samples were in the range of 66 to 239 mg kg^{-1} (Fig. 3a) for our 13 analyzed compounds. A previous study analyzed for 30 different compounds (Schauer et al., 2001) and consequently found a larger value EF_{group} of up to 1330 mg kg^{-1}, at least partially a result of the larger number of compounds analyzed. Formation of methoxyphenols during biomass combustion is mainly because of pyrolysis of lignin (e.g., Simonelt et al., 1993). Lignin, an essential biopolymer of wood tissue, is primarily derived from three aromatic alcohols: p-coumaryl, coniferyl, and sinapyl alcohols (Hedges and Ertel, 1982). Lignins of hardwoods (angiosperms) are enriched with products from sinapyl alcohol; softwoods (gymnosperms) instead have a high proportion of products from coniferyl alcohol with a minor contribution from sinapyl alcohol; grasses have mainly products from p-coumaryl alcohol. The relative proportions of these bio-monomers vary considerably among the major plant classes (Sarkanen and Ludwig, 1971), reflected in our total emission factors estimate for 13 methoxyphenols.

3.1.2 Dicarboxylic Acids

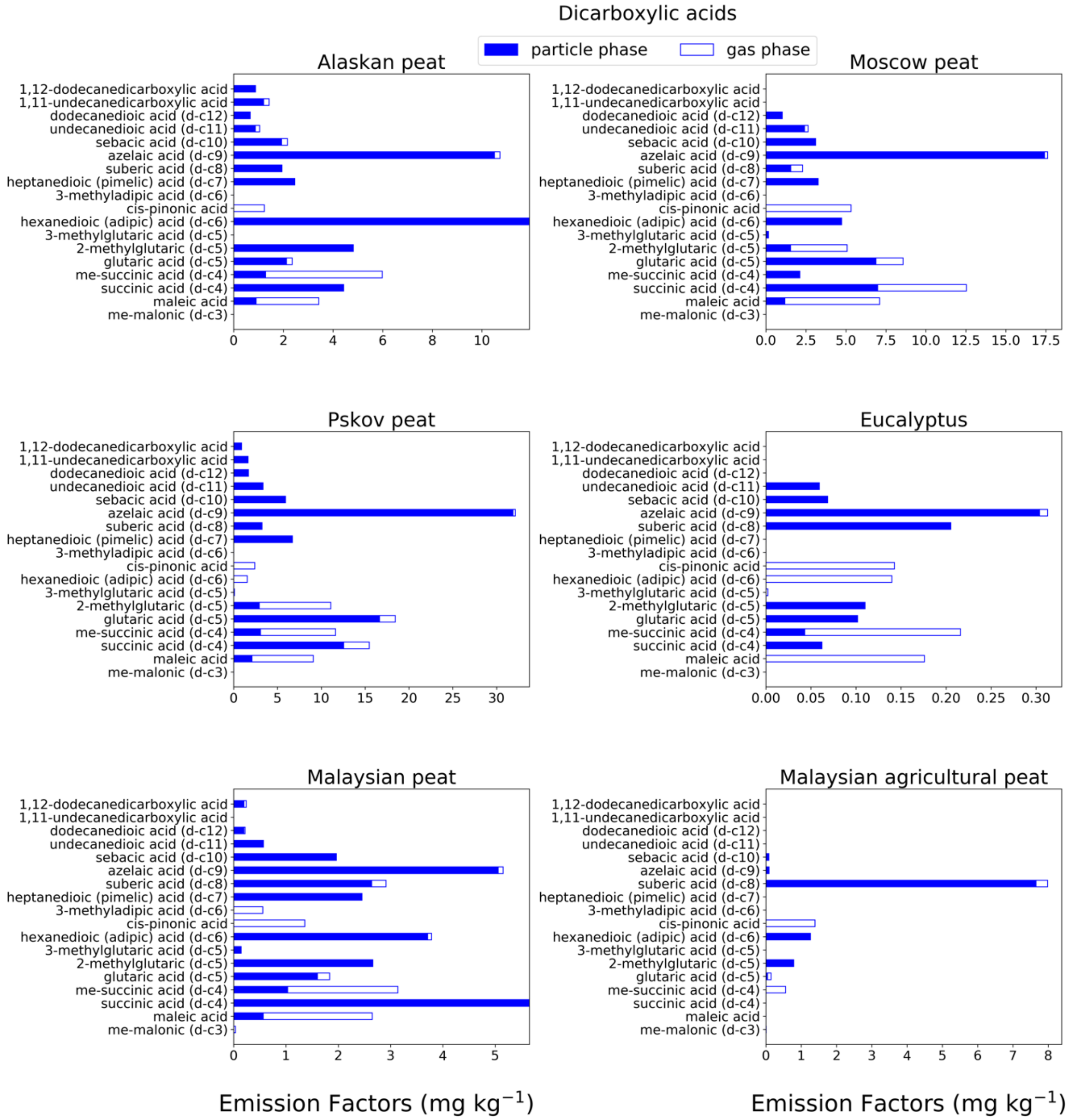

Figure 2b. EFs for dicarboxylic acids in both particulate phase (solid bars, filter samples) and gas-phase (open bars, XAD samples) from fresh biomass-burning emissions for six different fuel types. We did not burn fuels in replicates, and standard deviations (SD) were calculated based on replicate analysis of emissions from similar fuels (with identical experimental conditions) during our previous combustion campaigns (Yatavelli et al., 2017) where SD ranged between 10 and 17% for dicarboxylic acids.

Dicarboxylic acids play a significant role in the atmospheric organic aerosols budget (Samburova et al., 2013; Yatavelli et al., 2017) via secondary organic aerosol formation that either changes radiative forcing directly, or indirectly by acting as cloud condensation nuclei (Kawamura and Bikkina, 2016). The EF_{group} for dicarboxylic acids (Fig. 3b) varied among the fuels with the highest EF for fresh Pskov peat samples (123±10 mg kg $^{-1}$) and with the lowest for Eucalyptus (1.5±0.1 mg kg^{-1}). This range in EFs can be attributed to difference in fuel type and burning conditions (smoldering vs. flaming). We also observed, however, a difference in the EF_{group} of dicarboxylic acid between two tropical peats from the same geographical area (Malaysian peat: EF=35.33±2.9 mg kg^{-1} and Malaysian agricultural peat: 12.29 ±1.02 mg kg^{-1}). The highest EF for individual dicarboxylic acids was observed for azelaic acid. For example, for Pskov peat the EF was 32.1±4.1 mg kg^{-1}; and for Moscow peat it, was 17.6±2.6 mg kg^{-1}. Azelaic acids were mostly found in the particulate phase (Fig. 2b, Table S1) and their relative abundances in the gas phase varied between 0.77% (for Pskov peat) and 2.85% (for Eucalyptus). Maleic acid was mostly found in the gas phase (73%–83%), since it is a lower MW compound (MW=116.0 g mol^{-1}) compared to azelaic (MW=188.22 g mol^{-1}) and adipic (146.14 g mol^{-1}) acids. Succinic and methyl-succinic acids are found in both gas and particulate phases (Table S1), and their abundance in the particulate phase was 19–59% and 53–100%, respectively. For Malaysian peat BB emissions, succinic acid was present only in the particulate phase. A distinguishable increase in dicarboxylic acid mass concentrations was observed for ambient aerosols followed by a biomass burning event (Cao et al., 2017) compared to normal ambient concentrations. The formation of saturated dicarboxylic acids (e.g., succinic acid) and unsaturated dicarboxylic acids (e.g., maleic acid) also was reported for ambient aerosols collected near a biomass-burning event (Graham et al., 2002; Kundu et al., 2010; Zhu et al., 2018) and in ice core records historically affected by biomass burning (Müller-Tautges et al., 2016).

3.1.3 Monocarboxylic Acids

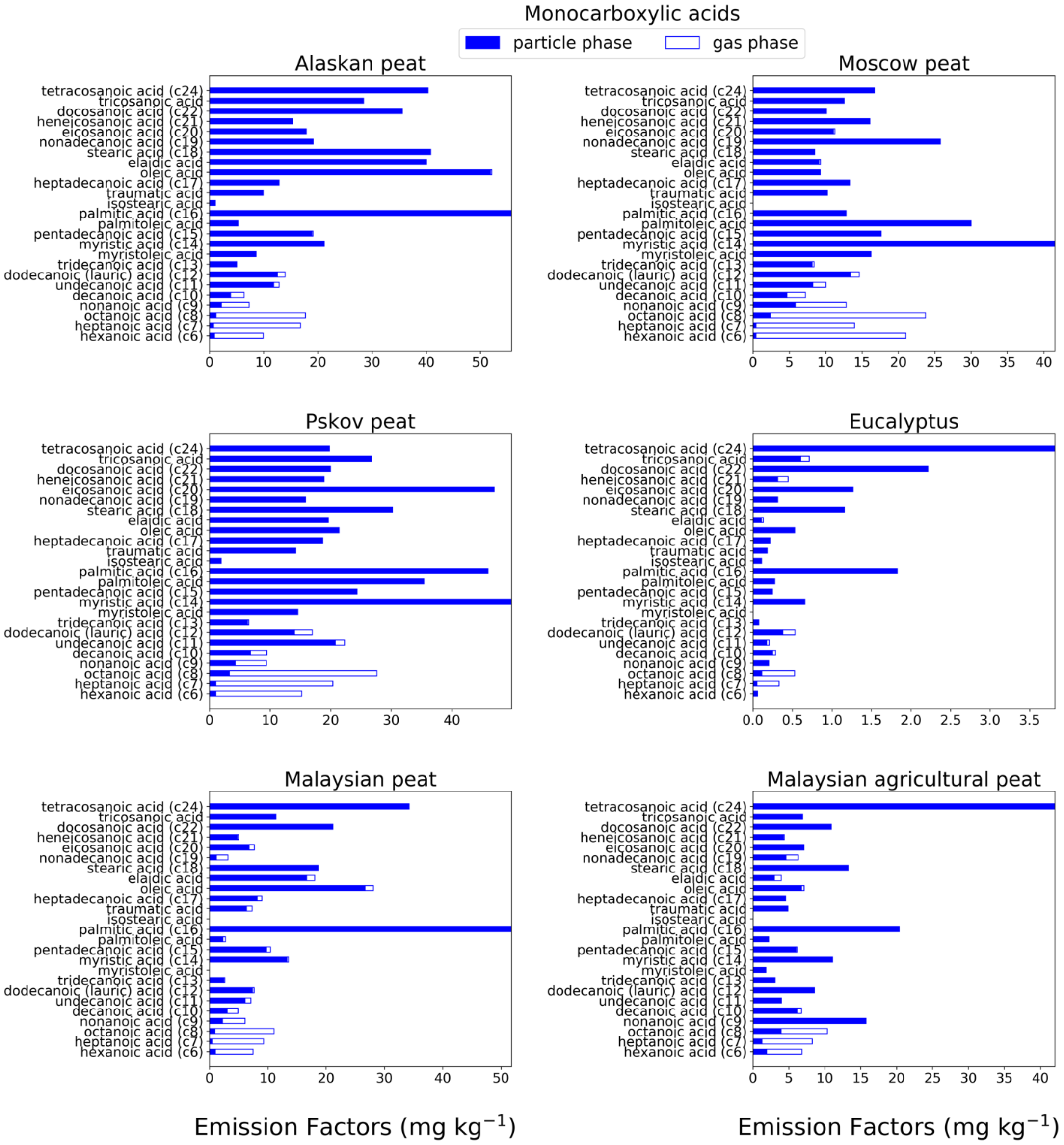

Figure 2c. EFs for monocarboxylic acids in both particulate phase (solid bars, filter samples) and gas-phase (open bars, XAD samples) from fresh biomass burning emissions for six different fuel types. We did not burn fuels in replicates and standard deviations (SD) were calculated based on replicate analysis of emissions from similar fuels (with identical experimental conditions) during our previous combustion campaigns (Yatavelli et al., 2017) where SD ranged between 9.4 and 12% for monocarboxylic acids.

Monocarboxylic acids can constitute up to 30–40% of total identified organic aerosol mass from BB emissions (Oros et al., 2006). In our study, we characterized the range from C_6 –C_{24}, where some unsaturated monocarboxylic acids (e.g., oleic acid) also are included. For Alaskan and Malaysian peat fresh emissions (Fig. 2c), the highest EF (gas + particle) among all analysed monocarboxylic acids was for hexadecanoic acid (C_{16}) with EFs of 55.7±6.6 mg kg^{-1} and 51.8±6.2 mg kg^{-1}, respectively. The dominance of hexadecanoic acid among other monocarboxylic acids in combustion emissions also was observed in ambient measurements during biomass-burning events in southeast Asia (Fang et al., 1999). For Moscow (41.5±6.5 mg kg^{-1}) and Pskov (49.8±7.8 mg kg^{-1}) peats, tetradecanoic acid (C_{14}) had the highest EFs in fresh samples (Fig. 2c). For Eucalyptus and Malaysian agricultural peat fresh samples, the largest contributor to monocarboxylic acids was tetracosanoic acid (C_{24}) (Fig. 2c) with EFs of 3.81±0.5 mg kg^{-1} and 42.0±5.1 mg kg^{-1}, respectively. As we expected, low MW monocarboxylic acids like hexanoic acid (MW=116 g mol^{-1}) was mostly present in the gas phase, and the gas phase mass fraction varied between 72% (for Malaysian agricultural peat) and 98% (for Moscow peat). Similar trends were observed for other low MW monocarboxylic acids. For example, the relative abundance of octanoic acid (C_8) in the gas phase was 93.4% for Alaskan peat. High MW monocarboxylic acids (C_{16}>) abundance in the gas phase was < 2% for all analyzed fuels.

Carbon preference index (CPI) is generally used for source apportionment of organic aerosols (Fang et al., 1999). We also computed the carbon preference index for monocarboxylic acids from all analyzed fuel combustion emissions by taking even carbon number over odd carbon number ratio on EFs of monocarboxylic acids ranges from C_6 to C_{24} (Fig. S1). For fresh emission samples, the CPI values ranged from 1.28 (for Moscow peat) to 4.53 (for Eucalyptus). The CPI values are higher for fresh emissions of tropical peats (for example, 2.78 for Malaysian peat) than for emissions from peats from high latitudes (for example, 1.74 for Pskov peat). An average CPI index of 3.7 for monocarboxylic acids was reported for combustion emissions from sedimentary bogs (Freimuth et al., 2019), in the range of our reported values (CPI: 1.3–4.5).

The sums of the EFs for 25 monocarboxylic acids are shown in Fig. 3c. The EF_{group} was in the range of 5 and 515 mg kg^{-1} for all fuels. This range is comparable to the EF_{group} reported previously for grass (tundra, cotton, Pampas and ryegrass) combustion (32–250 mg kg^{-1}) (Oros et al., 2006). Overall, the trend of low EFs associated with flaming combustion of Eucalyptus (16±0.7 mg kg^{-1}) compared to smoldering peat combustion is also evident for this compound category. Combustion of peat fuels from tropical regions (e.g., Malaysian agricultural peat) resulted in monocarboxylic acids EFs of 212±9.6 mg kg^{-1} compared to higher EFs from Alaskan peat combustion (505±23 mg kg^{-1}). The origin of monocarboxylic acid is mostly plant wax and oils (Simoneit, 2002). The relative proportion of plant wax and oils can vary widely among vegetation taxa and also their concentrations in peat depend on biogeochemical processes involved in peat formation. The differences in relative abundance of waxes and plant oils in living vegetation and the differences between biogeochemical processes involved in peat formation for arctic and tropical regions may be responsible for diverse EFs for monocarboxylic acids.

3.1.4 Aromatic Acids

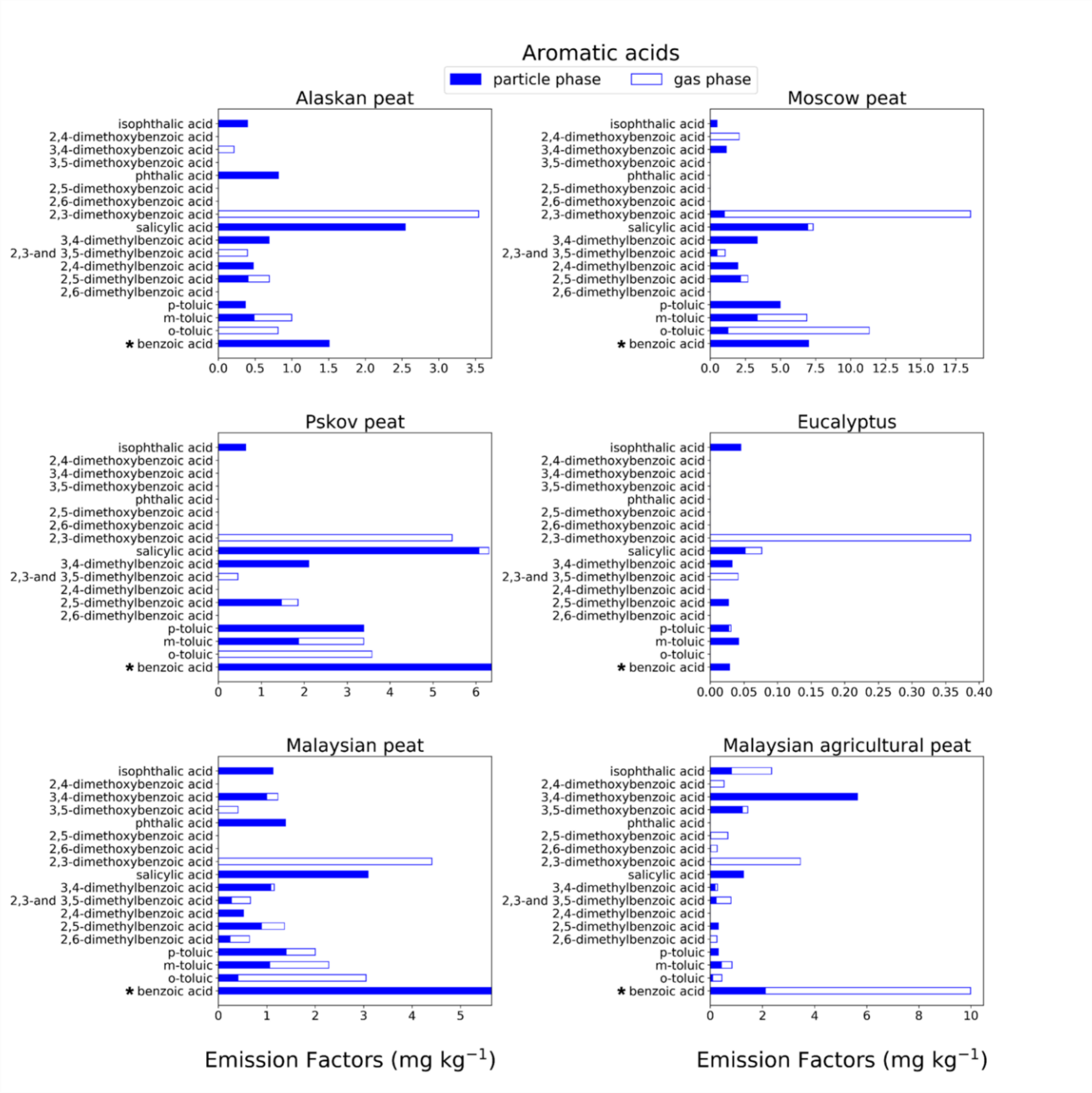

Figure 2d. EFs for aromatic acids in both particulate phase (solid bars, filter samples) and gas-phase (open bars, XAD samples) from fresh biomass burning emissions for six different fuel types. We did not burn fuels in replicates, and SD were calculated based on replicate analysis of emissions from similar fuels (with identical experimental conditions) during our previous combustion campaigns (Yatavelli et al., 2017) where SD ranged between 9.5 and 15% for aromatic acids; *Benzoic acid was found in high concentrations in the XAD blanks that introduced a substantial uncertainty to quantification of this compound.

Aromatic acids from BB emissions can contribute up to 20–35 % of total identified organic mass (Wan et al., 2019). In our study, the aromatic acids (e.g., p-hydroxy benzoic acid), excluded methoxyphenol derivatives and resin acids. For most of the fuels, ~~LMW~~ low MW aromatic acids (MW <150 g mol^{-1}) (e.g., benzoic acid, o-/m-/p-toluic acids) contributed more (almost 40% of total aromatic acid emissions) toward total fresh emissions, compared to high MW aromatic acids (MW >150 g mol^{-1}). For example, the benzoic acid EF for Malaysian agricultural peat fresh emission (Fig. 2d) is 9.98±1 mg kg^{-1}, and the EF for the same benzoic acid is 6.36±0.6 mg kg^{-1} for Pskov peat (Fig. 2d). Although, o-toluic and p-toluic acids are found in gas phase with 50%–100% abundance in Alaskan and Moscow peat, benzoic acid is found only in particulate phase. Benzoic acid was found in high concentrations in the XAD blanks that introduced a substantial uncertainty to quantification of this compound. One of the most abundant aromatic acids in fresh peat emissions was 2,3-dimethoxy benzoic acid. For example, for Moscow peat the EF was 18.6±4.7 mg kg^{-1}. The acid was mostly found in gas phase (91%–100%) for all fuels (Fig. 2d, Table S1). 2,3-dimethoxy benzoic acid is potentially derived from combustion of lignin moieties of biomass, and the emission of this compound is more than an order of magnitude lower in emissions from flaming combustion samples (EF=0.38 ±0.09 mg kg^{-1}) than in emissions from smoldering combustion emissions (EF=5.44±1.36 mg kg^{-1}). Emissions of 3,4 dimethoxy benzoic acid were only observed for peats from tropical regions (EF=5.64±0.8 mg kg^{-1}) with 80–100% abundance in particulate phase. This compound can be used for source apportionment of aerosols emitted from burning of tropical peat and also can potentially help to distinguish between emissions from tropical and high latitude peatland fires.

The EF$_{group}$ for aromatic acids in fresh combustion emissions from eucalyptus fuel is extremely low (0.71±0.05 mg kg^{-1}) compared to that for peat fuels (13–69 mg kg^{-1}). Among all peat samples, the Alaskan peat fresh EF was the lowest EF (13.5±0.9 mg kg^{-1}), whereas Moscow peat fresh emissions yielded the highest EF (69±4.4 mg kg^{-1}). The difference in total aromatic acid emissions can be attributed to the variation in the lignin content of the fuels and burning conditions (Simoneit, 2002).

3.1.5 Resin Acids

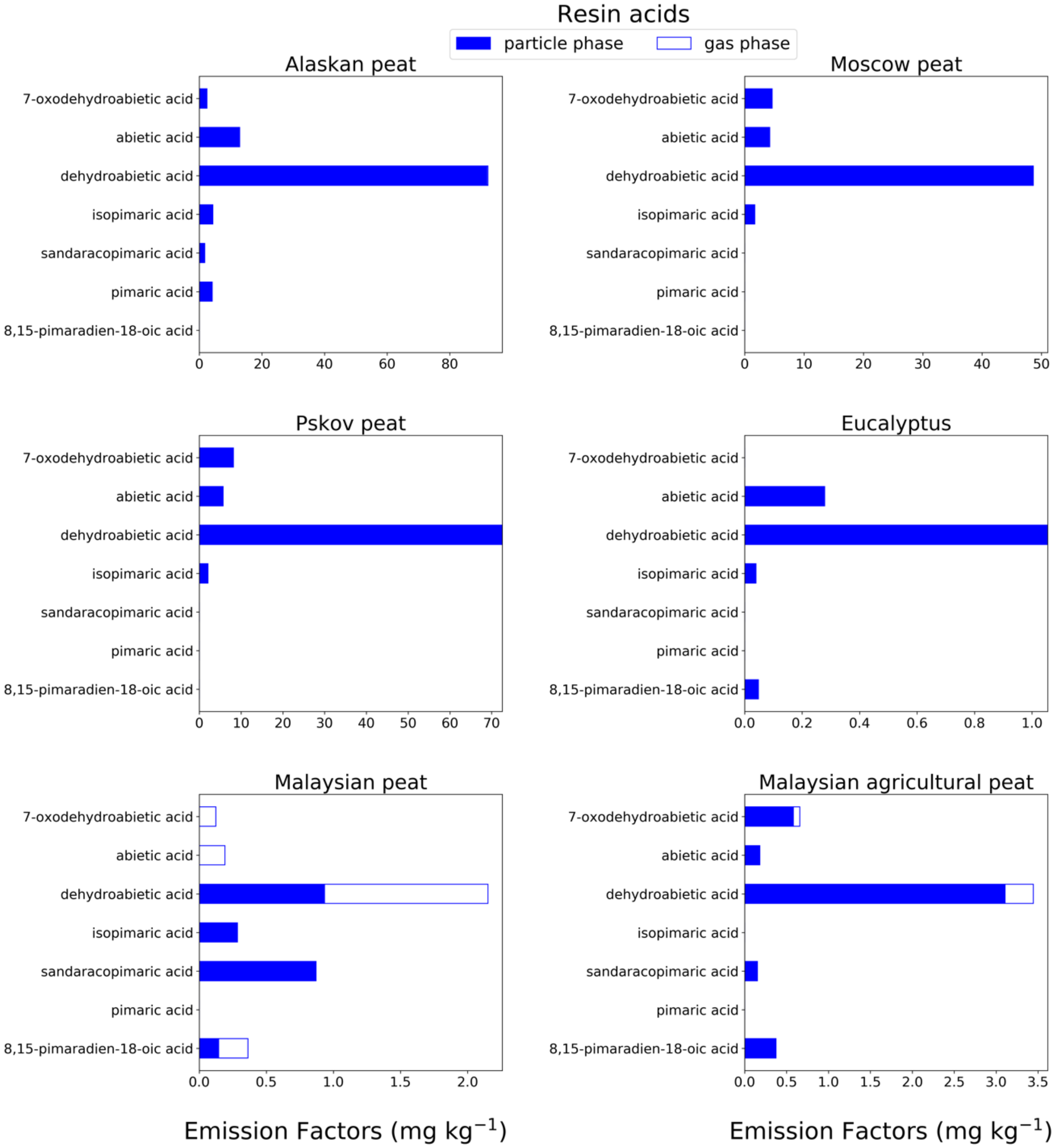

Figure 2e. EFs of resin acids in both particulate phase (solid bars, filter samples) and gas-phase (open bars, XAD samples) from fresh biomass-burning emissions for six different biomass types. As in prior cases, we did not burn fuels in replicates, and SD were calculated based on replicate analysis of similar fuels (with same experimental conditions) from our previous campaigns (Yatavelli et al., 2017) and SD varies from 9.7–15% for resin acids

We quantitatively analyzed combustion emissions for isomers in six resin acids (Table S1). The most abundant resin acid (78% of total resin acid emission) is dehydroabietic acid (C_{20}) that does not have isomers. The preponderance of this acid over other resin acids in emissions from oak and pine biomass burning was reported by Simoneit et al. (1993). We found that dehydroabietic acid (C_{20}) content in fresh emissions is 15–30 times higher in fuels from high-latitude peatlands than in those of tropical origin. For example, the EF for dehydroabietic acid in fresh Alaskan peat emissions is 92.2±14 mg kg^{-1} (Fig. 2e), whereas the same in fresh Malaysian peat emissions is 3.44±0.5 mg kg^{-1} (Fig. 2e). Resin acids are supposed to be found mostly in particulate phase based on their MW and functional groups (Asher et al., 2002; Karlberg et al., 1988; Pankow and Asher, 2008), confirmed by our results (80–100% in particulate phase) with the exception of Malaysian peat emissions where 56.6% abundance of dehydroabietic acid was found in gas phase. Although a distinct peak of dehydroabietic acid was observed at the desired retention time for this sample during GC-MS analysis, we believe this result can be attributed to some unknown interreference from our analysis procedure.

The EF_{group} for seven resin acids are presented in Fig. 3e. High EF_{group} was observed for Alaskan (117±15 mg kg^{-1}), Pskov (89±12 mg kg^{-1}), and Moscow (59±7.7 mg kg^{-1}) peats representing mid latitude and arctic peats. Resin acids (e.g., pimaric acid) are biosynthesized mainly by conifers (gymnosperms) in temperate regions. In previous work, Iinuma et al. (2007) gave a range of resin acids EFs from 0 to 110 mg kg^{-1}, in agreement with our results. Very low resin acids EFs were found for peat from tropical regions (e.g., 4 mg kg $^{-1}$ for Malaysian peat fresh samples). As deciduous trees in tropical zones are not prolific resin and mucilage (gum) producers, compositional data on smoke from such sources should not be expected to show moderate concentrations of resin acids. This is supported by earlier work by Iinuma et al. (2007), where resin acids were not even detectable for emissions from Indonesian peat combustion.

3.1.5 Levoglucosan

Levoglucosan can be found mostly in particulate phase (Simoneit, 2002). We report levoglucosan EFs from our analysis of the quartz filter using the IC-PAD technique (no gas phase EFs reported).

The EFs of levoglucosan (Fig. 3f) were found to be 20.9±0.68 mg kg^{-1} and 485±11.8 mg kg^{-1} for Eucalyptus and Malaysian peat, respectively, and their carbon content is approximately 1.8% and 2.5 % of the total organic carbon mass characterized by the thermo-optical technique. Fine et al. (2002) reported 9% to 16% contribution of levoglucosan to total OC from residential wood combustion, a relatively higher percentage than values obtained in our study. Anhydrosugars (e.g., levoglucosan and its isomers) are found in great abundance and have been widely used as a BB tracer because of their atmospheric stability, as summarized by Bhattarai et al. (2019). We found that levoglucosan constituted 36% and 51% of GC-MS characterized polar (listed in our method) organic aerosol mass for eucalyptus and Malaysian peat, respectively, which also is consistent with the previous BB literature assembled in the recent review article by Bhattarai et al. (2019).

3.2. Emission factors of total (gas + particle) organic compounds of six chemical groups and their changes upon OFR oxidations

Here we describe changes in the EF$_{group}$ followed by OFR oxidation for all six chemical groups. Levoglucosan and the most abundant resin acid, dehydroabietic acid also are reported in this section.

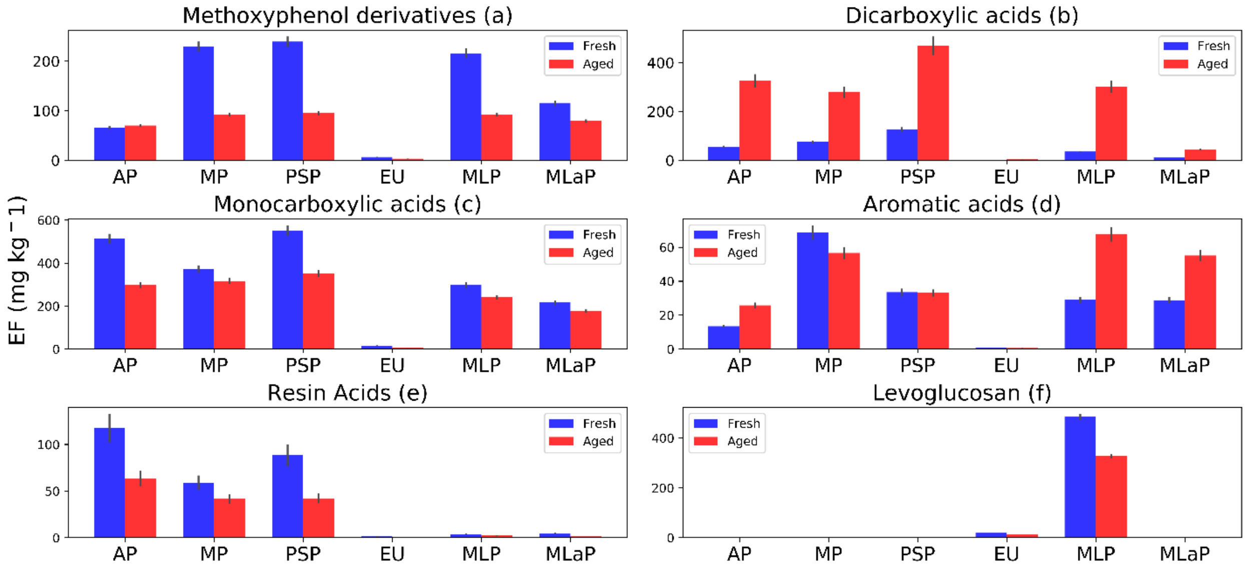

Figure 3. Fuel-based emission factors (EFs) of organic compounds assigned to six chemical groups for six different fuels: Alaskan peat (AP), Moscow peat (MP), Pskov peat (PSP),

Eucalyptus (EU), Malaysian peat (MLP), Malaysian agricultural peat (MLaP). EFs are presented as a sum of gas- and particle-phase species mass measured in fresh and OFR-aged BB emissions in units of mg kg^{-1} (mass of emissions per fuel mass combusted). We did not burn fuels in replicates, and standard deviations (SD) of all chemical groups were calculated based on replicate analysis of similar fuels (with same experimental conditions) from our previous campaign based on the data reported by Yatavelli et al. (2017).

3.2.1. Methoxyphenol derivatives after OFR oxidation (Fig. 3a)

Methoxyphenols can undergo gas-phase oxidation reactions via either aromatic ring fragmentation/opening to form short-chain ketones, acids, esters, and double bonds in conjugations with all functional groups or further hydroxylation of aromatic rings to form multiple substituted aromatic compounds (Yee et al., 2013). In either case, a decrease in methoxyphenols after oxidation was expected. In our study, a decrease in methoxyphenol's EF_{group} with OFR oxidations were observed for all fuels (e.g., for Pskov peat from 239±11 mg kg^{-1} to 95±4 mg kg^{-1}) except for Alaskan peat, where an insignificant increase from 66±3 mg kg^{-1} to 70±3 mg kg^{-1} after the OFR oxidation was observed.

3.2.2. Dicarboxylic acid group after OFR oxidation (Fig. 3b)

A significant increase (2.5–8.5 times) in the EF_{group} of dicarboxylic acids was observed for OFR-aged samples. For example, the EF_{group} of dicarboxylic acids increased from 35±3 mg kg^{-1} to 301±25 mg kg^{-1} for Malaysian peat and from 56±5 mg kg^{-1} to 326±27 mg kg^{-1} for Alaskan peat. Oxidation of aerosols potentially produces more oxygenated functional groups (Jimenez et al., 2009), demonstrated by an increase in O:C ratios (from 0.45 to 0.65) in recent laboratory oxidation of BB emissions by Bertrand et al. (2018), where TAG-AMS was used to identify the fate of organic compounds. In this work, however, the number of identifiable compounds with highly functional groups is constrained by the elution technique used in the TAG method. Our results on the fate of BB organic aerosols with 18 dicarboxylic acids can provide better mechanistic understanding about the processes inside OFR.

3.2.3. Monocarboxylic acid group after OFR oxidation (Fig. 3c)

We observed a decrease in monocarboxylic acids EF_{group} from OFR aging for all fuels. For example, the EF_{group} for monocarboxylic acids from Alaskan peat combustion decreased from 514±23 mg kg^{-1} (fresh) to 298±14 mg kg^{-1} (aged). A relatively small decrease compared to Alaskan peat was observed for Malaysian agricultural peat (from 216±10 mg kg^{-1} [fresh] to 179±8 mg kg^{-1} [aged]) and Malaysian peat (from 298±14 mg kg^{-1} [fresh] to 240±11 mg kg^{-1} [aged]) too. This is probably because of the formation of low MW monocarboxylic acids (e.g., hexanoic acids; MW=116 g mol^{-1}) after OFR oxidation demonstrated in Fig. 4c and Table S2c and will be discussed further in section 3.3. Monocarboxylic acids can be oxidized in the atmosphere (Charbouillot et al., 2012), leading to the formation of dicarboxylic acids from C_2 to C_6 (Ervens et al., 2004). This is consistent with our results (Figs. 3b, 3c, Table S2b) Moreover, monocarboxylic acids, during their atmospheric transformations, can produce a potential precursor for formation of high MW compounds, such as HUmic Like Substance (HULIS) (Carlton et al., 2007; Tan et al., 2012).

3.2.4. Aromatic acid group after OFR oxidation (Fig. 3d)

Levels of aromatic acids from peat burning increased for Alaskan peat, Malaysian peat, and Malaysian agricultural peat (e.g., from 29±2 mg kg^{-1} to 68±4 mg kg^{-1} for Malaysian peat) by OFR aging (Fig. 3e, Table S2e). This increase could be from oxidation of phenols and methoxyphenols in the OFR chamber (Akagi et al., 2011; Legrand et al., 2016). For eucalyptus, Moscow and Pskov peats it was an insignificantly small decrease (e.g., from 69±4 mg kg^{-1} to 57±3 mg kg^{-1} for Moscow peat and from 34±2 mg kg^{-1} to 33±2 mg kg^{-1} for Pskov peat). This small decrease in the EF_{group} of monocarboxylic acids is ~~statistically~~ insignificant. The oxidation processes occurring in the OFR are complex, especially in the case of multi-component BB emissions. The decrease observed for aromatic acids after the OFR may be attributed, however, to multiple generations of oxidation leading to the breaking of aromatic rings and formation of low MW organic compounds via fragmentation (Jimenez et al., 2009).

3.2.5. Resin acids after OFR oxidation (Figs. 3d and 4e)

Resin acids can be oxidized to corresponding oxo-acids (e.g., 7-oxodehydroabietic acid (Karlberg et al., 1988)), and they are considered to be stronger contact allergens than the resin acids themselves (Sadhra et al., 1998). Our data showed a small decrease in 7-oxodehydroabietic acid levels after the OFR (e.g., from 8.2±0.8 to 4.8±0.5 mg kg^{-1} for Pskov peat). We noted a significant decrease in the EF_{group} of resin acids from 117±15 mg kg^{-1} (fresh) and 63±8 mg kg^{-1} (aged) for Alaskan peat after OFR oxidation, mostly because of some individual compounds like dehydroabietic acid. Although resin acids are considered to be stable atmospheric tracers for biomass burning (Simoneit et al., 1993a), we observed a decrease in dehydroabietic acid (most abundant) EF after the OFR-oxidation of emissions from all fuels (Fig. S2b). For example, for Alaskan peat (Fig. S2b), the decrease was from 92±14 mg kg^{-1} to 57±8 mg kg^{-1} after OFR-oxidation. The fate of resin acids during OFR aging, however, was beyond the scope of this work and may be the subject of future investigations.

3.2.6. Levoglucosan after OFR oxidation (Fig. 3f)

Levoglucosan is one of the most popular tracers of BB emissions, since it has been considered a stable compound in the atmosphere (Oros et al., 2006; Simoneit, 2002; Simoneit et al., 1999). Several laboratory studies, however, have demonstrated degradation of levoglucosan in the presence of OH radicals (Hennigan et al., 2010). Here we observed a decrease of 30% in levoglucosan levels following OFR oxidation. For example, Malaysian peat decreased from 485±12 mg kg^{-1} to 327±8 mg kg^{-1}. For eucalyptus, the decrease was from 20±0.7 mg kg^{-1} to 14±0.6 mg kg^{-1}. This decrease also can be attributed to the degradation process during OH oxidation (Hoffmann et al., 2010). Levoglucosan oxidation should be studied more, so it can be adequately used as a tracer of BB emissions.

3.3. Aged-to-fresh ratios of total (gas + particle) emission factors of individual organic compounds assigned to six chemical groups and their changes upon OFR oxidation

We computed aged-to-fresh ratios of individual compounds for all fuels. If the aged-to-fresh ratio of one compound is greater than one, this implies that the compound is formed during OFR oxidations; if the ratio is less than one, then the compound must have decomposed inside the OFR.

3.3.1 Methoxyphenol Derivatives

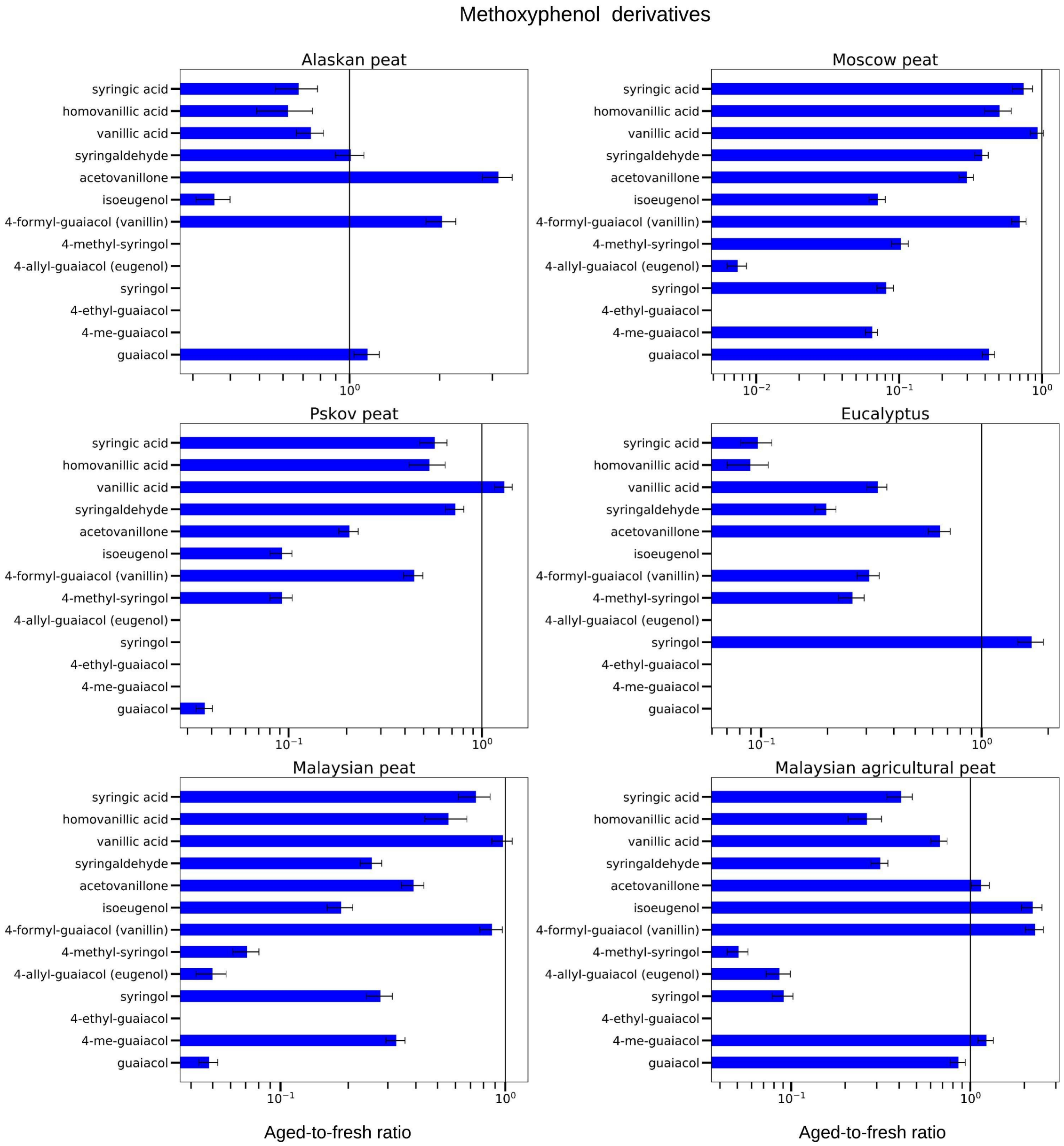

Figure 4a. Aged-to-fresh ratios of total (gas + particle) EFs for methoxyphenols from biomass burning emissions for six different biomass types presented in log scale. We did not burn fuels in replicates, and standard deviations (SD) were calculated based on replicate analysis of similar fuels (with same experimental conditions) from our previous campaigns. SD values derived from EFs were scaled to ratio.

Overall, we found that abundances for methoxyphenol derivatives rapidly decreased upon OFR-oxidation (Fig. 4a, Table S2a). Some compounds—vanillic acid, acetovanillone, and syringic acids— demonstrated both increasing and decreasing trends. For example, for Pskov peat, the aged-to-fresh ratio of guaiacol was 0.04±0.0,1 reflecting a significant decrease during OFR oxidation. For Pskov peat, we also observed a ratio less than one for vanillin (0.44 ± 0.05), indicating vanillin also decreased during OFR oxidation for the same fuel but not to the extent of guaiacol. At the same time and for the same fuel, a slight increase (aged-to-fresh ratio >1) in vanillic acid was observed (1.30±0.13) in the OFR-oxidized sample. This increase in vanillic acid concentration can be attributed to the oxidation of vanillin, one of the abundant methoxyphenol in the fresh emissions from Pskov peat (Fig. 4a, Table S2a). For combustion of other peats, vanillic acid concentrations also decreased (e.g., aged-to-fresh ratios were 0.74±0.08 and 0.67±0.07 for Alaskan peat and Malaysian agricultural peat, respectively). Acetovanillone increased by a factor of three during OFR oxidation for Alaskan peat and around 15 % for Malaysian agricultural peat (aged-to-fresh ratio 1.15±0.13), but the increase for Malaysian agricultural peat was not ~~statistically~~ significant. For other fuels, acetovanillone decreased during the OFR oxidation. For example, for Moscow Peat, the aged-to-fresh ratio for acetovanillone was 0.30±0.03. We still need to investigate the reason why both acetovanillone and vanillic acid increased for some fuels and decreased for others. The reduction of acetovanillone and vanillic acid was because of a photo-chemical decomposition process in the OFR with formation of lower MW products, such as succinic acid and maleic acid (Schnitzler and Abbatt, 2018).

3.3.2 Dicarboxylic Acids

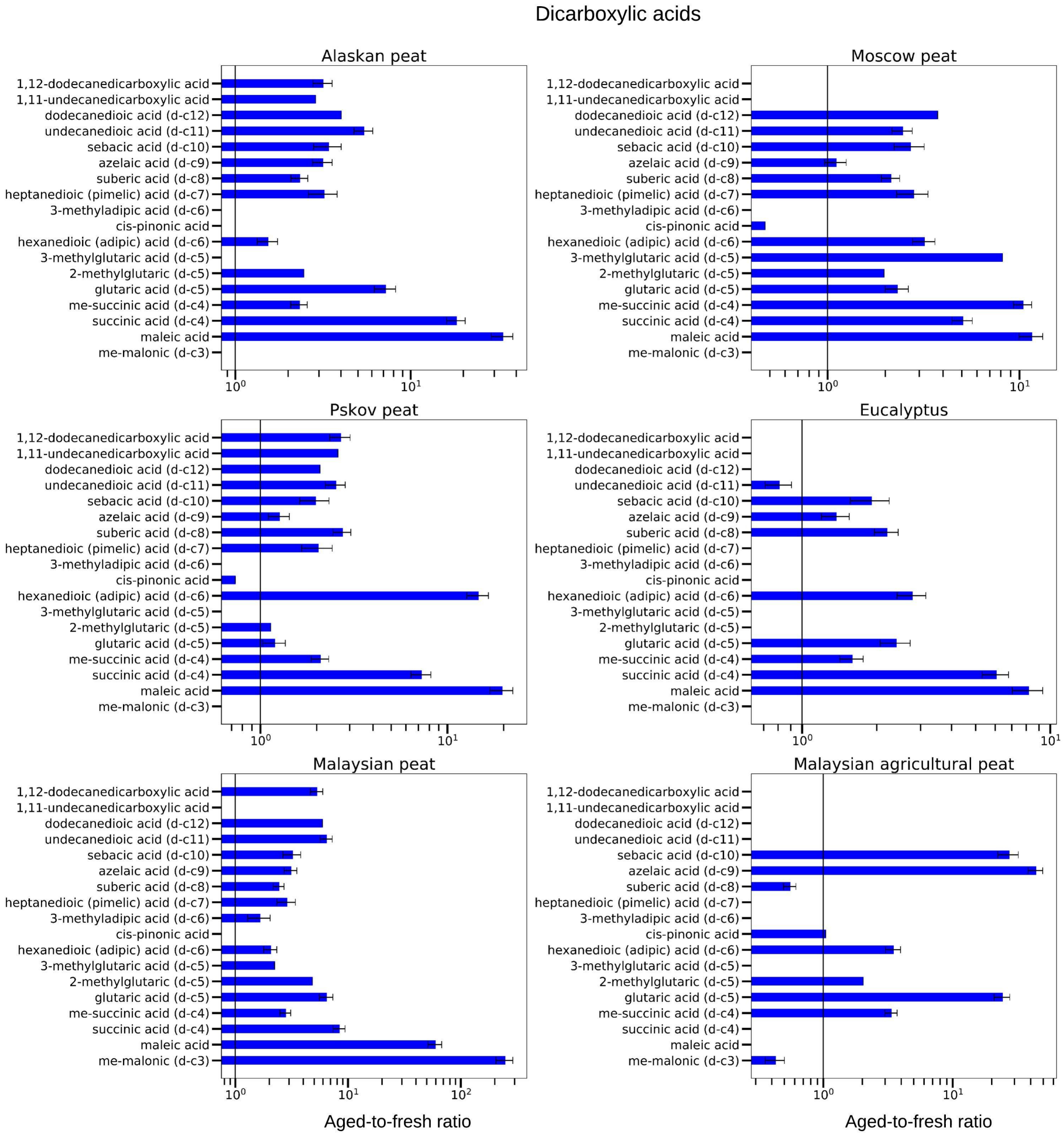

Figure 4b. Aged-to-fresh ratios of total (gas + particle) EFs for dicarboxylic acids from biomass burning emissions for six different biomass types presented in log scale. We did not burn fuels in replicates, and SD were calculated based on replicate analysis of similar fuels (with same experimental conditions) from our previous campaigns. SD values derived from EFs were scaled to ratio.

In the case of dicarboxylic acids, we observed 2–20 times increase in EFs, but the degree of enhancement of low MW dicarboxylic acids EFs was higher than for high MW dicarboxylic acids EFs. For example, a 20-fold increase in maleic acid, a low MW dicarboxylic acid (MW= 116.07 g mol^{-1}), was observed during OFR oxidation of Pskov peat emissions (aged-to-fresh ratio = 19.6±2.8), whereas 1,11-undecanedicarboxylic acid, a high MW dicarboxylic acid (MW = 244.33 g mol^{-1}), EF increased 2.6 times (aged-to-fresh ratio = 2.60±0.01) for the same fuel. Similarly, the concentration of succinic acid, a low MW dicarboxylic acid (MW= 118.09 g mol^{-1}), increased almost by five times after OFR oxidation (aged-to-fresh ratio = 5.07±0.62), whereas that of undecanedioic acid, a high MW dicarboxylic acid (MW = 230.30 g mol^{-1}), increased 2.5 times (aged-to-fresh ratio = 2.46±0.30) for Moscow peat. This trend was in accord with results from ambient observations after BB events (Cao et al., 2017; Kawamura and Bikkina, 2016).

3.3.3 Monocarboxylic Acids

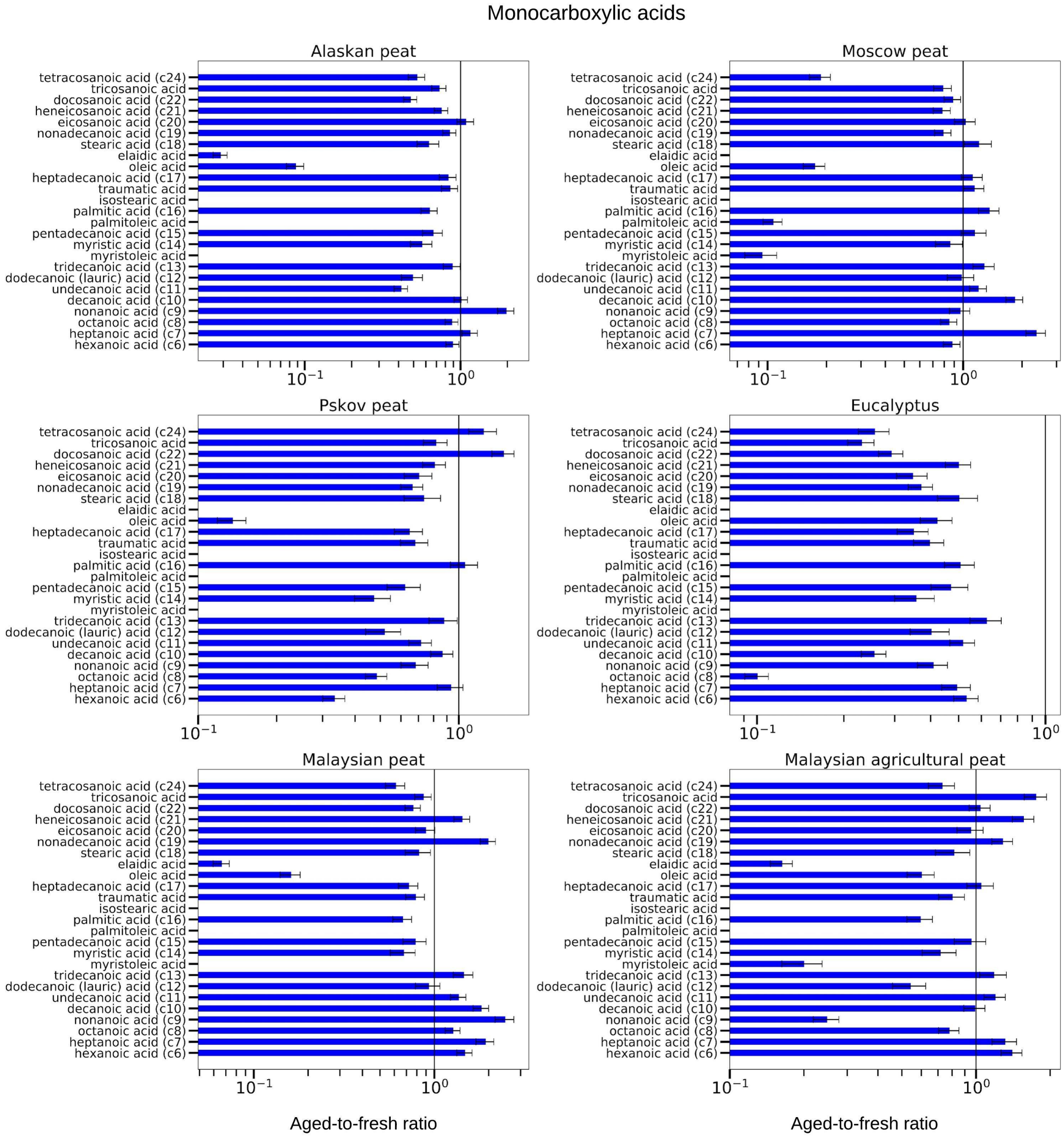

Figure 4c. Aged-to-fresh ratios of total (gas + particle) EFs for monocarboxylic acids from biomass burning emissions for six different biomass types presented in log scale. We did not burn fuels in replicates, and SD were calculated based on replicate analysis of similar fuels (with same experimental conditions) from our previous campaigns. SD values derived from EFs were scaled to ratio.

Our analysis of OFR-aged samples showed that concentrations of monocarboxylic acids with different MWs changed during OFR oxidation, but the changes varied from one fuel to another. For example, the EF of hexanoic acid (C_6) was reduced for Eucalyptus (aged-to-fresh ratio = 0.5±0.05) and fuels from other high-latitude peatlands like Alaskan (aged-to-fresh ratio = 0.89±0.09), Moscow (aged-to-fresh ratio = 0.88±0.09) and Pskov peat (aged-to-fresh ratio = 0.33±0.03). The reduction of hexadecenoic acid was ~~statistically~~ insignificant for Alaskan and Moscow peat. The peats from tropical regions showed exactly the opposite change. Hexanoic acid increased for both Malaysian (aged-to-fresh ratio = 1.47±0.14) and Malaysian agricultural peat (aged- to-fresh ratio = 1.40±0.14). We observed a similar trend for heptanoic acid (C_7) during OFR oxidation. The tropical peats clearly demonstrated increases (for example, aged-to-fresh ratio = 1.92±0.22 for Malaysian peat) in heptanoic acid concentration. For Moscow peat, even though hexanoic acid concentrations were insignificantly decreased, heptanoic acid concentrations increased significantly (aged-to-fresh ratio = 2.37±0.27). This contrast between changes in hexanoic and heptanoic acid can be explained by a decrease in CPI indices during OFR oxidations (for example, from 2.78 to 1.7 for Malaysian peat). The reduction of CPI indices indicated that during oxidation more monocarboxylic acids with odd carbon numbers were formed than monocarboxylic acids with even carbon numbers. The abundance of hexadecenoic acid (C_{16}) was reduced during OFR oxidation for all fuels (for example, aged-to-fresh ratio = 0.63±0.08 for Alaskan peat) except for Moscow and Pskov peat aged-to-fresh ratio = 1.05±0.13 for peat), and we believe this small increase is ~~statistically~~ insignificant. Similarly, tetracosanoic acid (C_{20}) was reduced for all fuels (for example, aged-to-fresh ratio = 0.61±0.07 for Malaysian peat) except for Pskov peat (aged-to-fresh ratio = 1.24±0.15). The small increase in tetracosanoic acid (C_{20}) concentration was again ~~statistically~~ insignificant. Even though our results indicated the possibility of fragmentation of high MW monocarboxylic acids and formation of low MW monocarboxylic acids, this was because of the complexity of the OFR oxidation environment. We are not able to hypothesize what is the main reactive mechanism.

3.4. Most Contributing Compounds

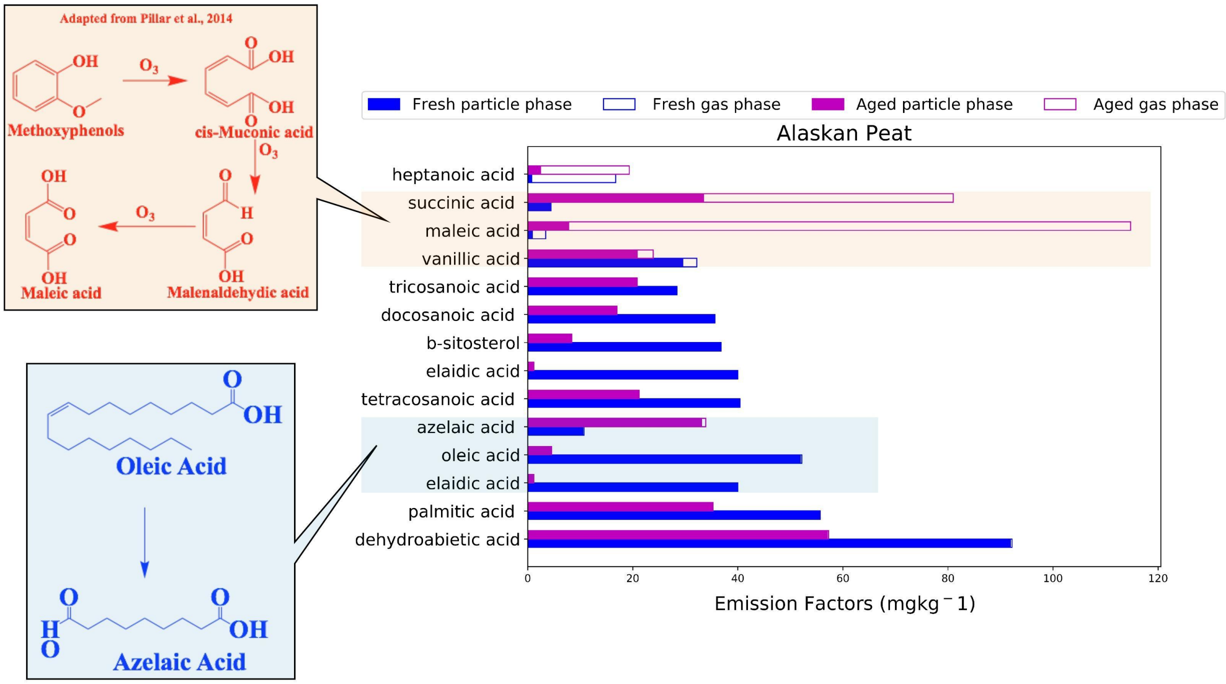

Figure 5. Emission factors (EF) of top contributing organic compounds assigned to Alaskan peat. Top 10 contributing ~~EFs~~ compounds were selected from both fresh and aged emissions based on EF values. Since fresh and aged samples do not have the same set of compounds after the selection, we included the top 10 compounds for both fresh and aged emissions. Hence, the number of top contributing compounds varies from one fuel to another. Solid bars of each type represent a chemical group from particulate emission of BB fuels and open bars of the same color represent gas phase BB emissions.

We have identified top contributing compounds for both fresh and aged BB emissions of each fuel to understand how emissions vary from one fuel to another. The top 10 compounds for fresh and aged emission were different, and we merged the top 10 compounds from fresh and aged emissions resulting in different numbers of total top compounds for different fuels. Here we discuss Alaskan peat emissions in their particulate phase (with solid bars) and gas phase (with open bars) as an example, while the remaining results are given in the SM (Fig. S3 and Fig. S4). It is clear that the top compounds vary between fuels, likely because of both different chemical nature of these fuels and nature of combustion.

Dehydroabietic acid, a resin acid, is the compound with the highest EF (92.2 mg kg^{-1}) for fresh combustion emissions from Alaskan peat. Moncarboxylic acids including palmitic acid (EF = 55.7 mg kg^{-1}), tetracosanoic acid (EF = 40.35 mg kg^{-1}), and docosanoic acid (EF = 35.38 mg kg^{-1}) were also found in high abundance in fresh emissions from the combustion of this fuel. The high contributions of β-sitosterol (EF = 36.84 mg kg^{-1}) and alkenoic acids (e.g., oleic acid EF = 52.1 mg kg^{-1}) to emissions are unique to Alaskan peat. All the compounds described above are found in particulate phase. After the OFR-oxidation, both dehydroabetic acid and β-sitosterol, considered to be potential markers for biomass burning emissions (Simoneit et al., 1993b), decreased from 91.9 mg kg^{-1} to 57.2 mg kg^{-1} and 36.8 mg kg^{-1} to 8.38 mg kg^{-1} in particulate phase, respectively. This reduction in EF because of OFR oxidation for both dehydroabetic acid and β-sitosterol must be considered when using these compounds as biomass-burning markers. We observed the formation of low MW organic compounds, particularly in gas phase, from OFR oxidation. For example, the EF of heptanoic acid increased from 2.42 mg kg^{-1} to 16.9 mg kg^{-1} and that of maleic acid increased from 7.8 mg kg^{-1} to 107 mg kg^{-1} in the gas phase because of OFR oxidation. Such a significant increase in the EF of maleic acid can be explained by the aqueous phase oxidation of methoxyphenols (El Zein et al., 2015) in the presence of ozone. We found that the oxidation inside the chamber was happening under dry conditions and understand that the reactions of organic compounds with OH radicals inside the OFR chamber will prevail over reactions with ozone. As we had our ozone scrubbers placed after sampling media (Fig. 1) to prevent the pumps and online instruments from ozone-induced damage, we suspect that the maleic acid was not formed inside the OFR chamber but rather by potential oxidation of organic compounds on filters with relatively longer exposure of ozone (40–60 min for smoldering combustion). Succinic acid EFs increased in both the gas phase (from 0.0 mg kg^{-1} to 47.5 mg kg^{-1}) and the particulate phase (from 4.43 mg kg^{-1} to 33.5 mg kg^{-1}). Azelaic acid EFs showed mainly an increase in the particulate phase (from 10.5 mg kg^{-1} to 33.1 mg kg^{-1}), and we think that this was because of the oxidation of oleic and eladic acid during OFR oxidation.

3.5 Contribution of polar fraction to total organic carbon

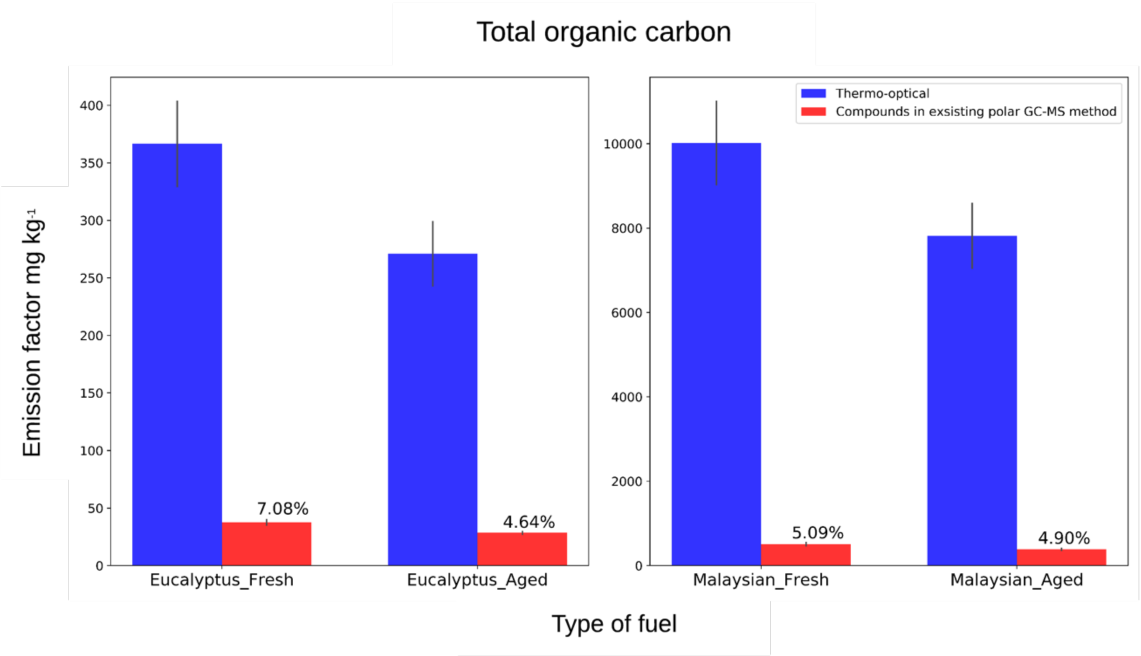

Figure 6. Contribution of GC-MS characterized polar compound carbon mass to total thermo-optical organic carbon mass. The y-axis shows the total carbon mass with dimensions of mass per mass. The error bars represent analytical uncertainties of the methods. For the thermo-optical method, uncertainties are the standard deviation of results from multiple punches on the same filter and for the GC-MS method, uncertainties were computed by taking the square root of sum of the squares of individual analytical uncertainties of all compounds included.

For Figure 6, we calculated the carbon content of total GC-MS characterized mass of identified polar organic compounds and compared results with the total OC mass characterized by the thermo-optical technique to estimate the contribution of polar compounds. The OC emissions were higher for smoldering combustion (10,209 ± 5 mg kg^{-1} for Malaysian peat fresh emissions) than for flaming combustion (366.5 ± 7 mg kg^{-1} for eucalyptus fresh emissions) samples, similar to the observation of flaming and smoldering combustion by Akagi et al. (2011). Total OC emissions are highly dependent on the type of fuel. For example, the fuel-based OC emission factor for rice crop residue burning is 1960 mg kg^{-1} (Cao et al., 2008), whereas burning of corn and conifer forest yields emission factors of ~1457 mg kg $^{-1}$ (Andreae and Rosenfeld, 2008) and ~7800 mg kg^{-1} (Akagi et al., 2011), respectively. Figure 6 shows that the 84 identified polar compounds in our study constituted 4.5% to 7% of total OC mass for both fresh and aged emissions. From Indonesian peat combustion emissions, Jayarathne et al. (2018) were able to identify polar compounds that constituted 5.446% of total organic carbon mass. In recent work, based on both a field campaign with prescribed burning and laboratory investigations, Jen et al. (2019) quantified a fraction (10–65%) of only identified compounds (not a fraction of total mass) by the use of the 2D-GC-MS technique. In our work, we identified only up to 7% (Fig. 6) of the total particle phase OC, and further analysis of unidentified compounds is needed to improve understanding of atmospheric chemistry of BB emissions.

4. Summary and conclusions

In this study, we chemically characterized the polar fraction of biomass-burning aerosols from laboratory combustion of six different globally and regionally important fuels—five of them representing smoldering and one of them representing flaming combustion. Our objective was to understand how emissions of the polar compounds (e.g., methoxyphenols) varied from one fuel to another during these combustion experiments and what are the relative distribution of these polar compounds in gas and particulate phase. We also identified the fates of these polar compounds following laboratory oxidation/aging (OFR aging). Resin acids were found mostly in emissions from combustion of peats from high latitude regions but not in emissions of tropical peatlands (e.g., EF_{group} = 117±15 mg kg^{-1} for Alaskan peat and EF_{group} = 4.0±0.5 mg kg^{-1} for Malaysian peat). Similarly, monocarboxylic acids were found in higher abundance in emissions from high latitude peatlands compared to tropical peatland emissions (e.g., EF_{group} = 505±36 mg kg^{-1} for Alaskan peat and EF_{group} = 212±15 mg kg^{-1} for Malaysian agricultural peat). The presence of both guaiacol and syringol moieties in all fuels indicated a part of the biomass, considered as representative of a particular geographical region, is deciduous for all fuels. Low MW compounds are mostly found in gas phase (e.g., guaiacol found in gas phase 82–100%), whereas high MW (e.g., ~~high molecular weight~~ monocarboxylic acids [>C_{16}] more than 98% for all fuels) and highly oxygenated compounds (e.g., syringic acid and acetovanillone 65–100% in particulate phase) are found in particulate phase with high abundance. Monocarboxylic acids (1.2–3 times) and methoxyphenols (1.5–2.5 times) decreased after OFR oxidation, whereas dicarboxylic acids increased by 3–9 times followed by OFR oxidation. Relatively low MW hexanoic acid increased for both Malaysian (aged-to-fresh ratio = 1.47±0.14) and Malaysian agricultural peat (aged- to-fresh ratio = 1.40±0.14), whereas high MW tetracosanoic acid (C_{20}) was reduced for all fuel increases (e.g., aged-to-fresh ratio = 0.61±0.07 for Malaysian peat). This indicated fragmentation occurring inside the OFR chamber. With relative distribution of the top 10–15 compounds from Alaskan peat, we were able to identify transformation of unsaturated fatty acids (e.g., oleic acid) to dicarboxylic acids (e.g., azelaic acid). We identified only up to 7% of the total particle phase OC and further analysis of unidentified compounds with GC-MS full scan is needed for better understanding of atmospheric chemistry of BB emissions.

Data availability. Data can be provided upon request: <andrey.khlystov@dri.edu>.

Author contributions. DS, VS, and AK designed experiments. DS and CB performed sample, data collection, and extraction. DS performed ~~extractions,~~ derivatizations, GC-MS analysis, summarized data, and wrote the paper. AW provided biomass fuels. VS, AK, and HM provided input on interpretation of results. VS, HM, and AK revised the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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