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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 constitutes a significant 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

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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

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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 of particle-bound organic compounds (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). Most of these source apportionment studies, however, were focused on characterization of fresh emissions and emissions of either particle-phase or gas-phase compounds.

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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. 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). 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). There is still a lack of understanding, however, regarding (1) major organic compounds emitted from BB, (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., 2018b), 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,

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104 monocarboxylic acids, aromatic acids, resin acids, and anhydrosugars). In the analyzed
105 anhydrosugars, we paid special attention to levoglucosan, a derivative from cellulose (Simoneit et
106 al., 1999), since levoglucosan has been widely used as a molecular tracer of BB emissions
107 (Bonvalot et al., 2016; Maenhaut et al., 2016). Methoxyphenols also have been used in source
108 apportionment studies (Schauer et al., 2001a; Schmidl et al., 2008b, 2008a). These source
109 apportionment studies, however, haven't combined such a wide range of different groups in a
110 single investigation. Here we provide a detailed targeted chemical analysis of both gas- and
111 particle-phase BB emissions from the combustion of individual biomass fuels from diverse
112 geographical locations for both fresh and aged emissions. EFs of gas- and particulate-phase
113 individual polar organic species are presented for six groups of compounds (methoxyphenols,
114 dicarboxylic acids, monocarboxylic acids, aromatic acids, anhydrosugars, and resin acids) and are
115 discussed in separate sections for fresh and OFR-aged BB samples. The fresh-to-aged ratio and
116 top contributing organic species also are discussed. The comparison between fresh and OFR-aged
117 BB emissions helps to understand the chemical evolution of BB plumes in the atmosphere and the
118 obtained data can be used in future source apportionment and atmospheric modeling studies.
119

120 ## 2. Experiments

121 ### 2.1 Fuel Description

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

126 Peatland ecosystems, generally wetland or mesic ecosystems underlain by soils composed
127 primarily of partially-decomposed biomass, contain mostly organic carbon and more than 20%
128 mineral content, represent a vast terrestrial carbon pool, and are potentially vast sources of carbon
129 flux to the atmosphere during wildfires that consume peat (Harden et al., 2000). Peatlands in high-
130 latitude temperate and boreal regions are particularly vulnerable to increased fire-related carbon
131 emissions resulting from climatic warming and increases in fire season length, while peatlands in
132 low-latitude and tropical regions are threatened by factors such as deforestation for agriculture,

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133 urbanization, and drainage (Turetsky et al., 2015). We collected Alaskan peat samples from the
134 upper 10 cm of soils within black spruce (*Picea mariana*) near crown forest (Chakrabarty et al.,
135 2016). High-latitude and Eurasia samples here are from *Sphagnum*- and cotton grass- (*Eriphorum*
136 spp.) dominated communities, collected from the Moscow (Odintsovo and Shatura districts) and
137 Pskov regions of Russia. These regions are representative of oligotrophic peat bogs found widely
138 across Siberia as well. Tropical peat in this study includes samples from two areas in Malaysian
139 Borneo. One set of samples is from a *Dipterocarp*-dominated lowland forest with largely intact
140 native land cover, while the second set is from a cleared agricultural area in the Kota Snamarahan
141 region.

142

143 We selected Eucalyptus because of its prevalence across Australia and its important contribution
144 to Australian wildland fires. In addition, economic losses and risk to life and property from fires
145 in eucalypt forests are magnified by their proximity to both fire-prone ecosystems and large urban
146 areas; often eucalypt-dominated stands form boundaries between these two land-use types. There
147 are nearly 900 species of the genera *Eucalyptus*, *Corymba*, and *Angophora*, which collectively
148 comprise woody plants known as eucalypts. Native to Australia, eucalypt-dominated forests cover
149 nearly 92 million ha (Hills, W.E.; Brown, 1978). In addition, the fast and hardy growth
150 characteristics of eucalypts have made them popular in warm ecoregions of Europe as well as
151 North and South America, where they readily escape cultivation and become established, dominant
152 community types near urban areas where they were originally introduced. Because of their high
153 oil content, rapid and dense growth, and vegetative structure, eucalypts are highly flammable and
154 contribute to high fire risk in areas where they occur (Goodrick and Stanturf, 2012).

155

156 **2.2 Reagents and Materials**

157 We obtained high-performance liquid chromatography (HPLC) grade methanol and hexane from
158 Fisher Scientific (Fair Lawn, NJ, USA) and used the following filters for sampling and further
159 chemical analyzes: pre-fired (900 °C for 4 h) 47 mm diameter quartz-fiber filter (2500 Pallflex
160 QAT-UP, Pall Life Sciences, Ann Arbor, MI, USA) for thermo-optical Elemental Carbon/Organic
161 carbon (EC/OC) analysis, Teflon® filters (2500 Pallflex QAT-UP, Pall Life Science, Ann Arbor,
162 MI, USA) for gravimetric particulate matter (PM) mass analysis, and Teflon-impregnated glass

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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, benzoic-d5 acid, succinic-d4 acid, decanoic-d19 acid, adipic-d10 acid, suberic-d12 acid, levoglucosan-13C6, homovanillic-2,2-d2 acid, myristic-d27 acid, heptadecanoicd33 acid, oleic-9,10-d2 acid, tetradecanedioic-d24 acid, and cholesterol-2,2,3,4,4,6-d6.

2.3 Biomass Burning (BB) Experiments

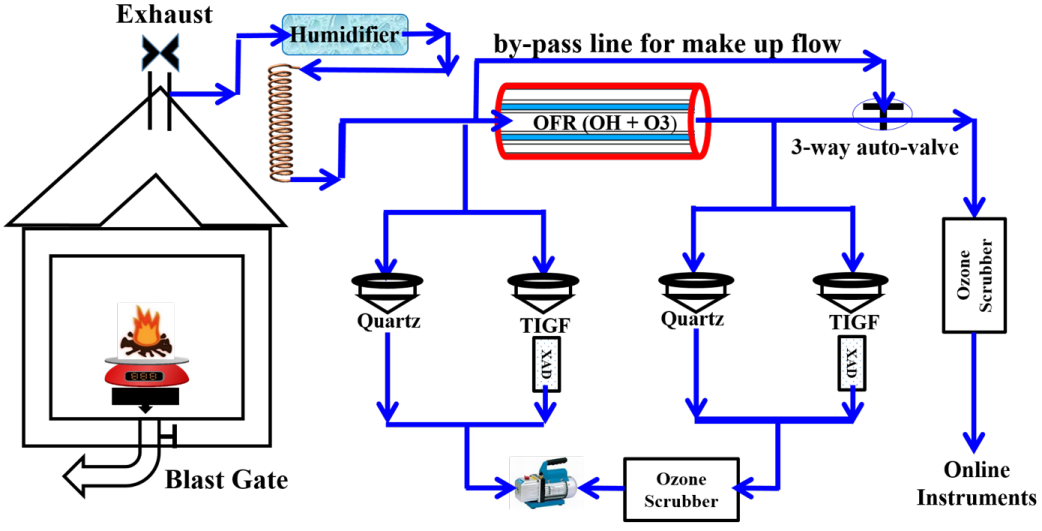

Figure 1. Desert Research Institute (DRI) biomass burning (BB) facility with oxidative flow reactor (OFR) and flow setup.

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

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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., 2018a). 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.

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

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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.

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

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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.

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**.**

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 are 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

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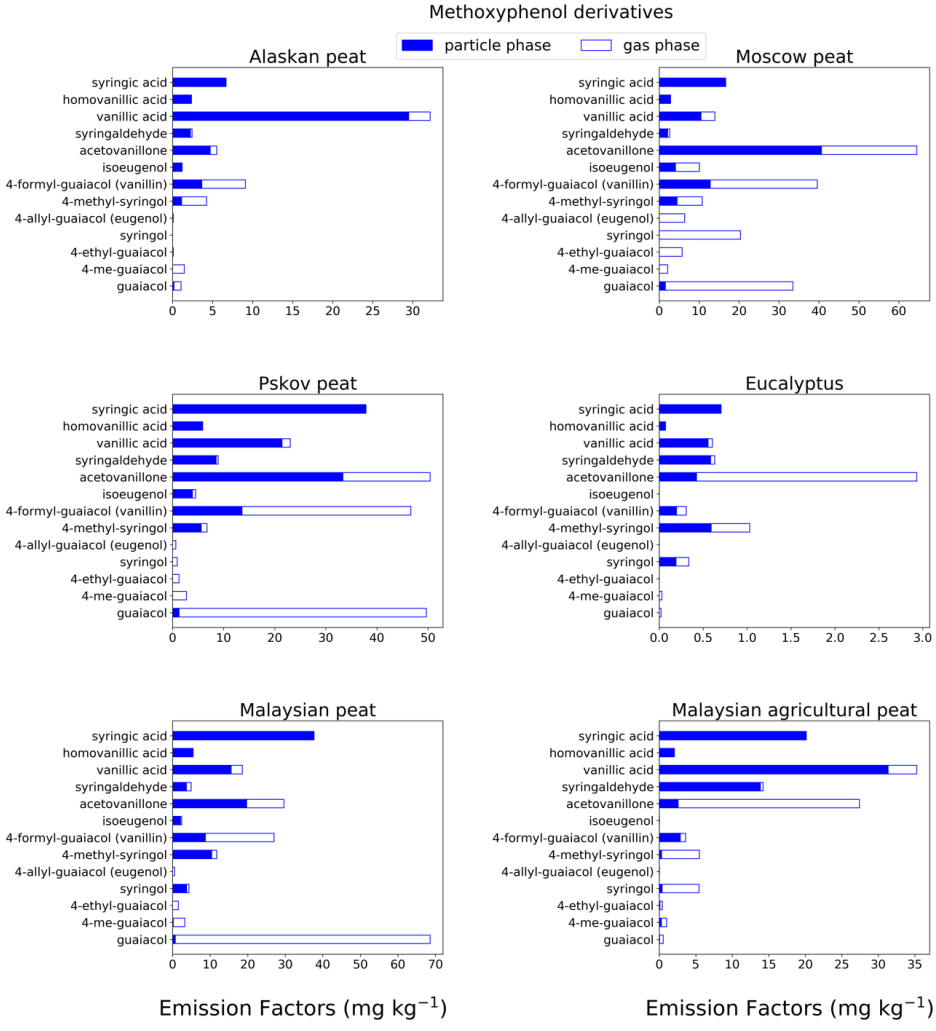

Figure 2a. EFs for methoxyphenols in both particulate phase (solid bars, filter samples) and gas-phase (open bars, XAD samples) from fresh biomass burning emissions for six different fuel types. We did not burn fuels in replicates, and standard deviations (SD) were calculated based on replicate analysis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

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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., 2001b) 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., 2001a), 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., 2001a). 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 molecular weight methoxyphenols (e.g., guaiacol) are expected to be found in the gas phase (Yatavelli et al., 2017b), 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 molecular weight 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).

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

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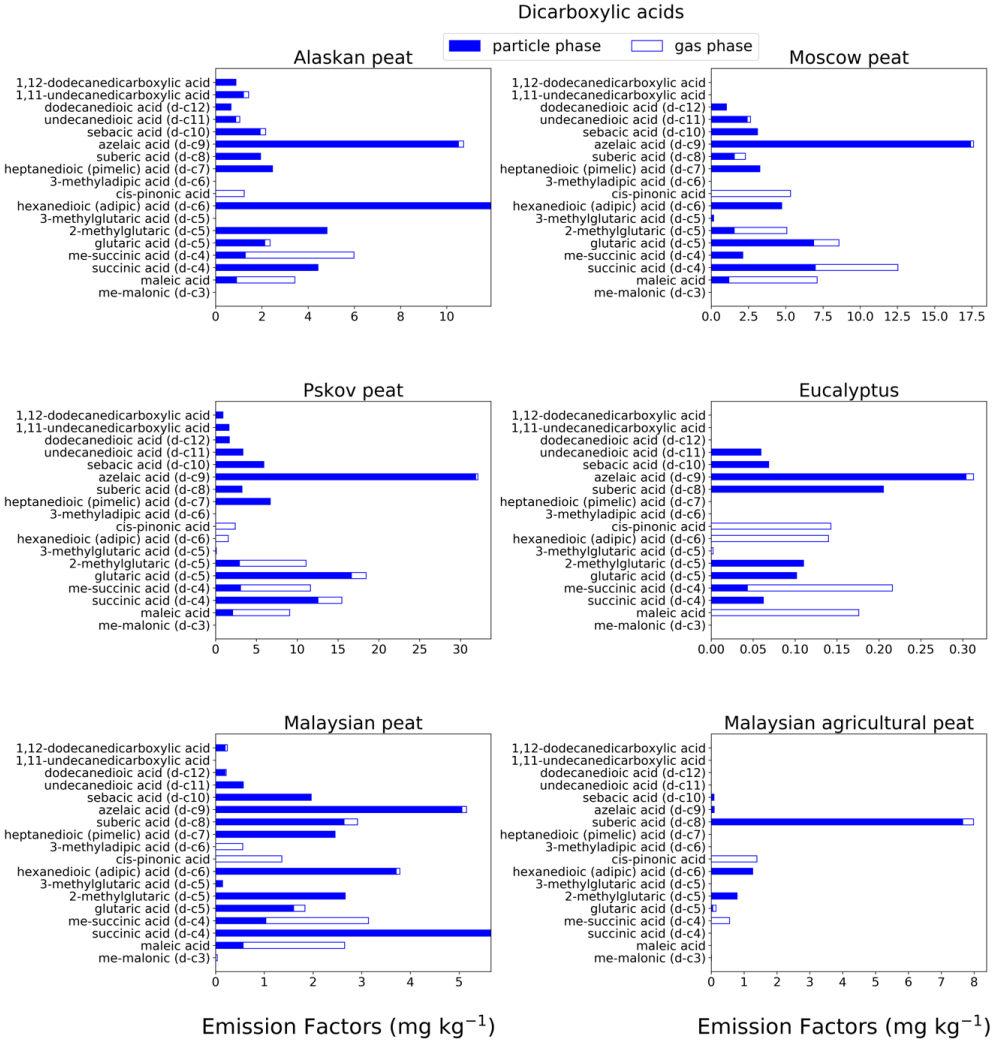
339 ***3.1.2 Dicarboxylic Acids***



340

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

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348 Dicarboxylic acids play a significant role in the atmospheric organic aerosols budget (Samburova
349 et al., 2013; Yatavelli et al., 2017b) via secondary organic aerosol formation that either changes
350 radiative forcing directly, or indirectly by acting as cloud condensation nuclei (Kawamura and
351 Bikkina, 2016). The EF_{group} for dicarboxylic acids (Fig. 3b) varied among the fuels with the highest
352 EF for fresh Pskov peat samples (123±10 mg kg^{-1}) and with the lowest for Eucalyptus (1.5±0.1
353 mg kg^{-1}). This range in EFs can be attributed to difference in fuel type and burning conditions
354 (smoldering vs. flaming). We also observed, however, a difference in the EF_{group} of dicarboxylic
355 acid between two tropical peats from the same geographical area (Malaysian peat: EF=35.33±2.9
356 mg kg^{-1} and Malaysian agricultural peat: 12.29 ±1.02 mg kg^{-1}). The highest EF for individual
357 dicarboxylic acids was observed for azelaic acid. For example, for Pskov peat the EF was 32.1±4.1
358 mg kg^{-1}; and for Moscow peat it, was 17.6±2.6 mg kg^{-1}. Azelaic acids were mostly found in the
359 particulate phase (Fig. 2b, Table S1) and their relative abundances in the gas phase varied between
360 0.77% (for Pskov peat) and 2.85% (for Eucalyptus. Maleic acid was mostly found in the gas phase
361 (73%–83%), since it is a lower MW compound (MW=116.0 g mol^{-1}) compared to azelaic
362 (MW=188.22 g mol^{-1}) and adipic (146.14 g mol^{-1}) acids. Succinic and methyl-succinic acids are
363 found in both gas and particulate phases (Table S1), and their abundance in the particulate phase
364 was 19–59% and 53–100%, respectively. For Malaysian peat BB emissions, succinic acid was
365 present only in the particulate phase. A distinguishable increase in dicarboxylic acid mass
366 concentrations was observed for ambient aerosols followed by a biomass burning event (Cao et
367 al., 2017) compared to normal ambient concentrations. The formation of saturated dicarboxylic
368 acids (e.g., succinic acid) and unsaturated dicarboxylic acids (e.g., maleic acid) also was reported
369 for ambient aerosols collected near a biomass-burning event (Graham et al., 2002; Kundu et al.,
370 2010; Zhu et al., 2018) and in ice core records historically affected by biomass burning (Müller-
371 Tautges et al., 2016).

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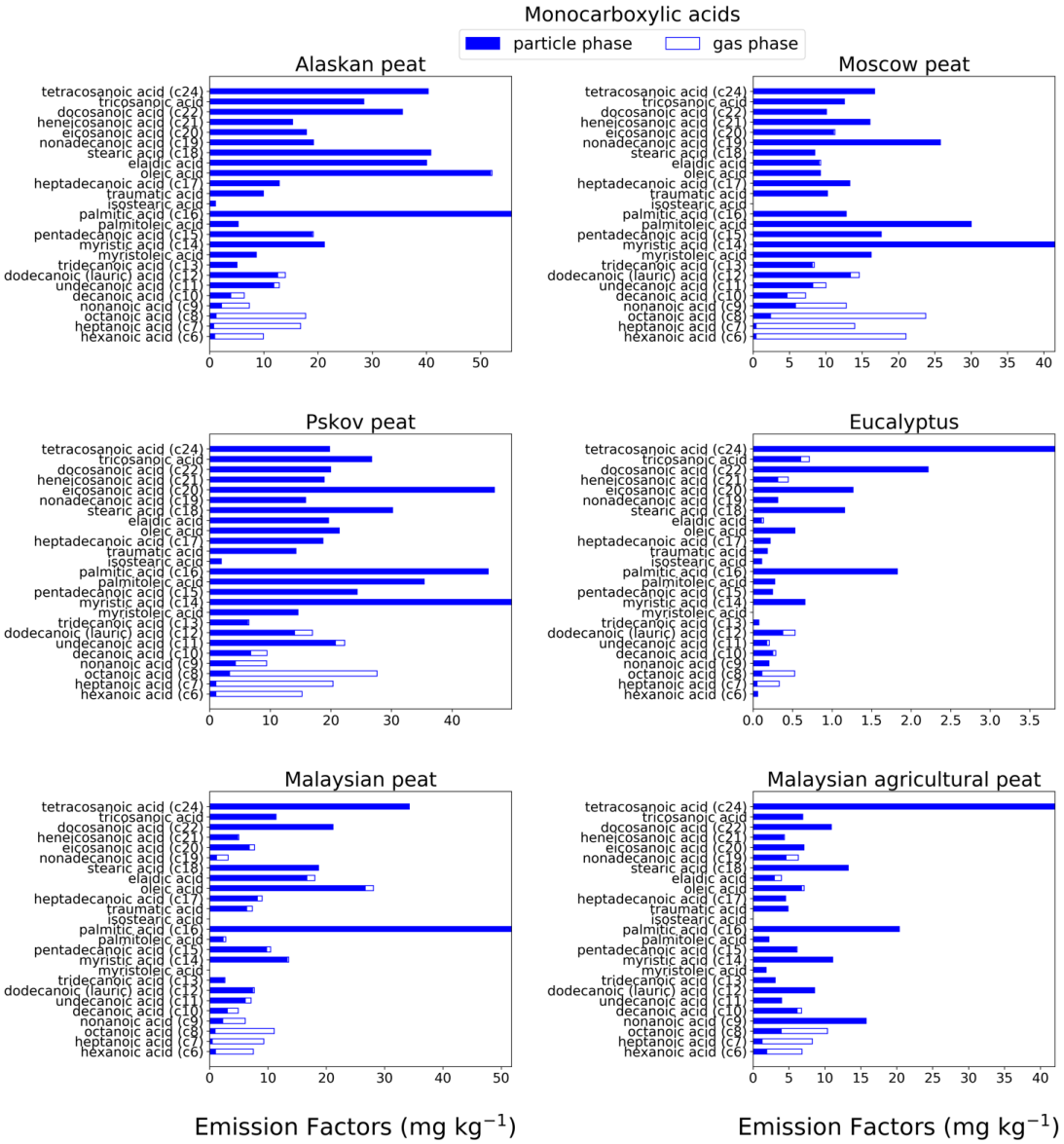
372 ***3.1.3 Monocarboxylic Acids***



373

374 Figure 2c. EFs for monocarboxylic acids in both particulate phase (solid bars, filter samples) and
375 gas-phase (open bars, XAD samples) from fresh biomass burning emissions for six different fuel
376 types. We did not burn fuels in replicates and standard deviations (SD) were calculated based on

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377 replicate analysis of emissions from similar fuels (with identical experimental conditions) during
378 our previous combustion campaigns (Yatavelli et al., 2017a) where SD ranged between 9.4 and
379 12% for monocarboxylic acids.

380

381 Monocarboxylic acids can constitute up to 30–40% of total identified organic aerosol mass from
382 BB emissions (Oros et al., 2006). In our study, we characterized the range from C_6 –C_{24}, where
383 some unsaturated monocarboxylic acids (e.g., oleic acid) also are included. For Alaskan and
384 Malaysian peat fresh emissions (Fig. 2c), the highest EF (gas + particle) among all analysed
385 monocarboxylic acids was for hexadecanoic acid (C_{16}) with EFs of 55.7±6.6 mg kg^{-1} and 51.8±6.2
386 mg kg^{-1}, respectively. The dominance of hexadecanoic acid among other monocarboxylic acids in
387 combustion emissions also was observed in ambient measurements during biomass-burning events
388 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
390 and Malaysian agricultural peat fresh samples, the largest contributor to monocarboxylic acids was
391 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.
392 As we expected, low molecular weight 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
394 Malaysian agricultural peat) and 98% (for Moscow peat). Similar trends were observed for other
395 low molecular weight monocarboxylic acids. For example, the relative abundance of octanoic acid
396 (C_8) in the gas phase was 93.4% for Alaskan peat. High molecular weight monocarboxylic acids
397 (C_{16}>) abundance in the gas phase was < 2% for all analyzed fuels.

398

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

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(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.

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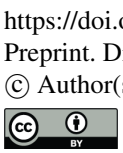

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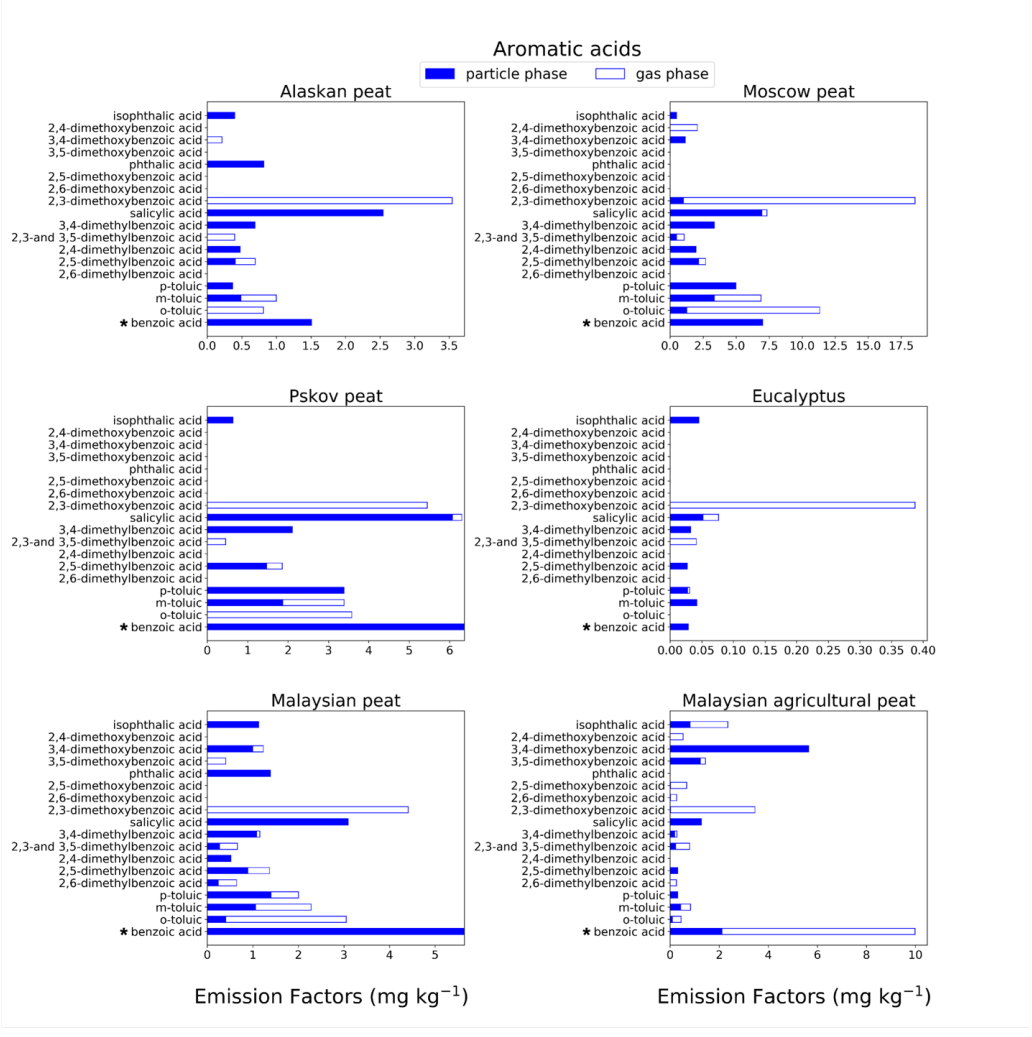
436 ***3.1.4 Aromatic Acids***



437

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

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445

446 Aromatic acids from BB emissions can contribute up to 20–35 % of total identified organic mass
447 (Wan et al., 2019). In our study, the aromatic acids (e.g., p-hydroxy benzoic acid), excluded
448 methoxyphenol derivatives and resin acids. For most of the fuels, LMW aromatic acids (MW <150
449 g mol^{-1}) (e.g., benzoic acid, o-/m-/p-toluic acids) contributed more (almost 40% of total aromatic
450 acid emissions) toward total fresh emissions, compared to HMW aromatic acids (MW >150 g mol^{-1}).
451 For example, the benzoic acid EF for Malaysian agricultural peat fresh emission (Fig. 2d) is
452 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).
453 Although, o-toluic and p-toluic acids are found in gas phase with 50%–100% abundance in
454 Alaskan and Moscow peat, benzoic acid is found only in particulate phase. Benzoic acid was found
455 in high concentrations in the XAD blanks that introduced a substantial uncertainty to quantification
456 of this compound . One of the most abundant aromatic acids in fresh peat emissions was 2,3-
457 dimethoxy benzoic acid. For example in Moscow peat, the EF was 18.6±4.7 mg kg^{-1}. The acid was
458 mostly found in gas phase (91%–100%) for all fuels (Fig. 2d, Table S1). 2,3-dimethoxy benzoic
459 acid is potentially derived from combustion of lignin moieties of biomass, and the emission of this
460 compound is more than an order of magnitude lower in emissions from flaming combustion
461 samples (EF=0.38 ±0.09 mg kg^{-1}) than in emissions from smoldering combustion emissions
462 (EF=5.44±1.36 mg kg^{-1}). Emissions of 3,4 dimethoxy benzoic acid were only observed for peats
463 from tropical regions (EF=5.64±0.8 mg kg^{-1}) with 80–100% abundance in particulate phase. This
464 compound can be used for source apportionment of aerosols emitted from burning of tropical peat
465 and also can potentially help to distinguish between emissions from tropical and high latitude
466 peatland fires.

467

468 The EF_{group} for aromatic acids in fresh combustion emissions from eucalyptus fuel is extremely
469 low (0.71±0.05 mg kg^{-1}) compared to that for peat fuels (13–69 mg kg^{-1}). Among all peat samples,
470 the Alaskan peat fresh EF was the lowest EF (13.5±0.9 mg kg^{-1}), whereas Moscow peat fresh
471 emissions yielded the highest EF (69±4.4 mg kg^{-1}). The difference in total aromatic acid emissions
472 can be attributed to the variation in the lignin content of the fuels and burning conditions (Simoneit,
473 2002).

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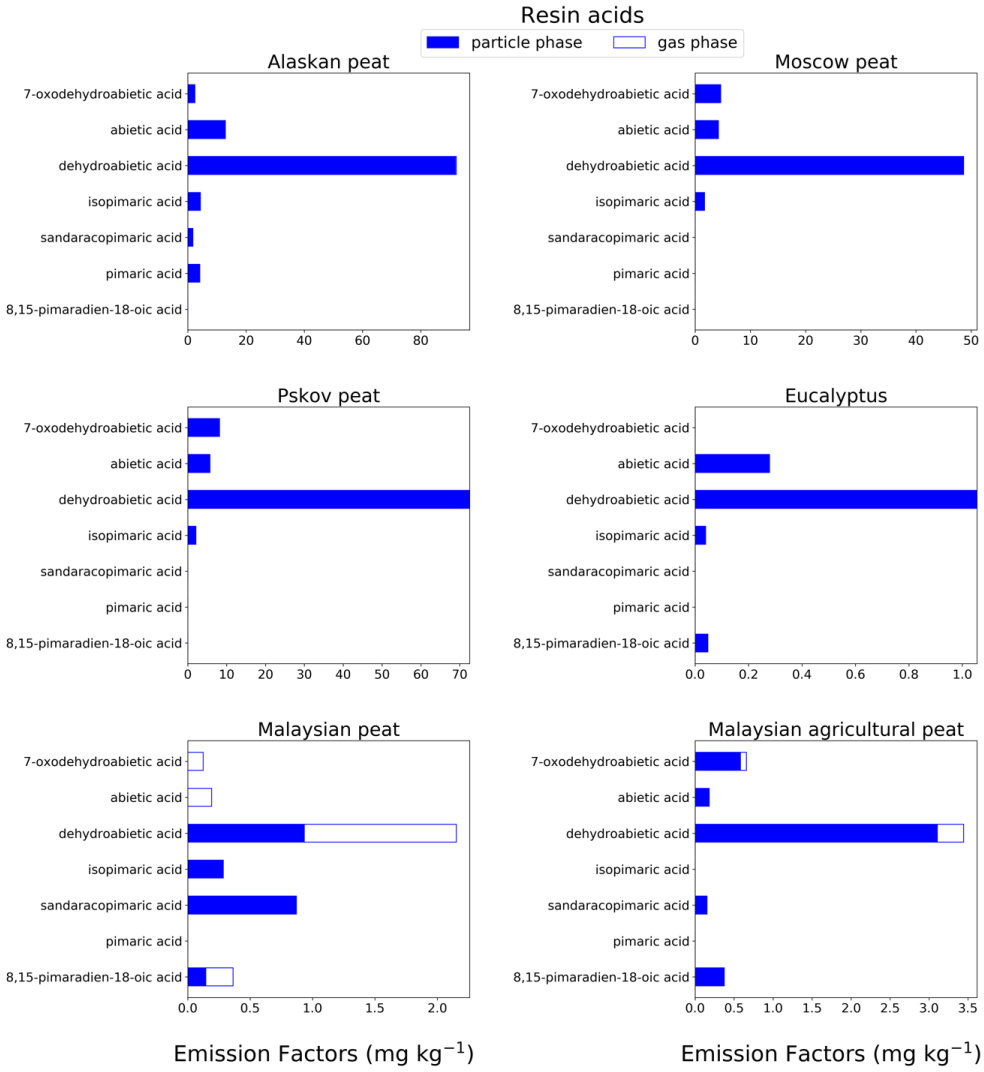
475

476 ***3.1.5 Resin Acids***



477

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

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(Yatavelli et al., 2017a) 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 molecular weight and functional groups (Asher et al., 2002; Pankow and Asher, 2008)(Karlberg et al., 1988), 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.

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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).

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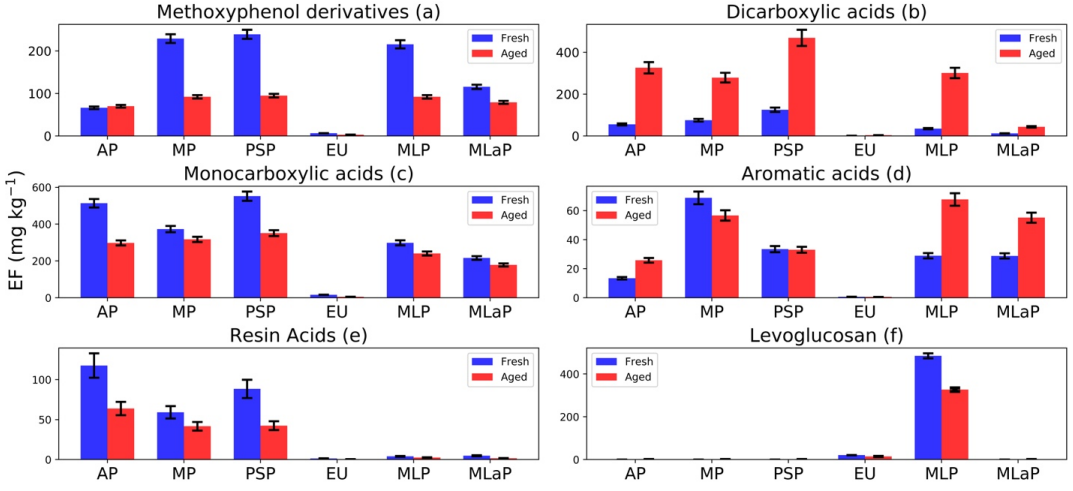
524 **3.2. Emission factors of total (gas + particle) organic compounds of six chemical groups and**
525 **their changes upon OFR oxidations**
526
527 Here we describe changes in the EF_{group} followed by OFR oxidation for all six chemical groups.
528 Levoglucosan and the most abundant resin acid, dehydroabietic acid also are reported in this
529 section.



530

531 Figure 3. Fuel-based emission factors (EFs) of organic compounds assigned to six chemical groups
532 for six different fuels: Alaskan peat (AP), Moscow peat (MP), Pskov peat (PSP), Eucalyptus (EU),
533 Malaysian peat (MLP), Malaysian agricultural peat (MLaP). EFs are presented as a sum of gas-
534 and particle-phase species mass measured in fresh and OFR-aged BB emissions in units of mg kg^{-}
535 ^{1} (mass of emissions per fuel mass combusted). We did not burn fuels in replicates, and standard
536 deviations (SD) of all chemical groups were calculated based on replicate analysis of similar fuels
537 (with same experimental conditions) from our previous campaign based on the data reported by
538 Yatavelli et al. (2017).

539

540 *3.2.1. Methoxyphenol derivatives after OFR oxidation (Fig. 3a)*

541 Methoxyphenols can undergo gas-phase oxidation reactions via either aromatic ring
542 fragmentation/opening to form short-chain ketones, acids, esters, and double bonds in conjugations

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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 molecular weight (LMW) 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

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572 al., 2004). This is consistent with our results (Figs. 3b, 3c, Table S2b) Moreover, monocarboxylic
573 acids, during their atmospheric transformations, can produce a potential precursor for formation
574 of high molecular weight compounds, such as HUmic Like Substance (HULIS) (Carlton et al.,
575 2007; Tan et al., 2012).

576

577 *3.2.4. Aromatic acid group after OFR oxidation (Fig. 3d)*

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

589

590

591 *3.2.5. Resin acids after OFR oxidation (Figs. 3d and 4e)*

592 Resin acids can be oxidized to corresponding oxo-acids (e.g., 7-oxodehydroabietic acid (Karlberg
593 et al., 1988)), and they are considered to be stronger contact allergens than the resin acids
594 themselves (Sadhra et al., 1998). Our data showed a small decrease in 7-oxodehydroabietic acid
595 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
596 decrease in the EF_{group} of resin acids from 117±15 mg kg^{-1} (fresh) and 63±8 mg kg^{-1} (aged) for
597 Alaskan peat after OFR oxidation, mostly because of some individual compounds like
598 dehydroabietic acid. Although resin acids are considered to be stable atmospheric tracers for
599 biomass burning (Simoneit et al., 1993a), we observed a decrease in dehydroabietic acid (most
600 abundant) EF after the OFR-oxidation of emissions from all fuels (Fig. S2b). For example, for

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601 Alaskan peat (Fig. S2b), the decrease was from 92±14 mg kg^{-1} to 57±8 mg kg^{-1} after OFR-
602 oxidation. The fate of resin acids during OFR aging, however, was beyond the scope of this work
603 and may be the subject of future investigations.

604

605 *3.2.6. Levoglucosan after OFR oxidation (Fig. 3f)*

606 Levoglucosan is one of the most popular tracers of BB emissions, since it has been considered a
607 stable compound in the atmosphere (Oros et al., 2006; Simoneit, 2002; Simoneit et al., 1999).
608 Several laboratory studies, however, have demonstrated degradation of levoglucosan in the
609 presence of OH radicals (Hennigan et al., 2010). Here we observed a decrease of 30% in
610 levoglucosan levels following OFR oxidation. For example, Malaysian peat decreased from
611 485±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
612 mg kg^{-1}. This decrease also can be attributed to the degradation process during OH oxidation
613 (Hoffmann et al., 2010). Levoglucosan oxidation should be studied more, so it can be adequately
614 used as a tracer of BB emissions.

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616 **3.3. Aged-to-fresh ratios of total (gas + particle) emission factors of individual organic**
617 **compounds assigned to six chemical groups and their changes upon OFR oxidation**

618 We computed aged-to-fresh ratios of individual compounds for all fuels. If the aged-to-fresh ratio
619 of one compound is greater than one, this implies that the compound is formed during OFR
620 oxidations; if the ratio is less than one, then the compound must have decomposed inside the OFR.
621

622 ***3.3.1 Methoxyphenol Derivatives***

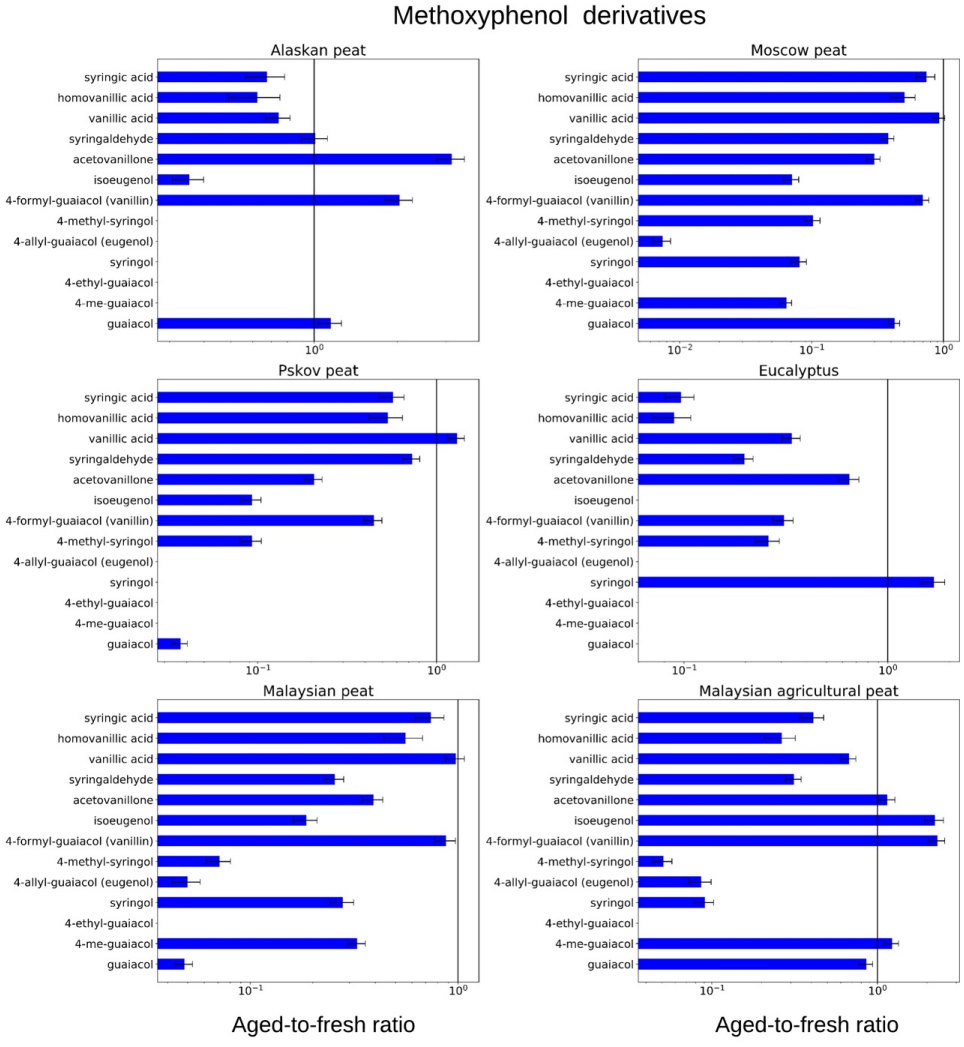

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Figure 4a. Aged-to-fresh ratios of total (gas + particle) EFs for methoxyphenols from biomass burning emissions for six different biomass types presented in log scale. We did not burn fuels in replicates, and standard deviations (SD) were calculated 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±0.01 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 molecular weight products, such as succinic acid and maleic acid (Schnitzler and Abbatt, 2018).

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3.3.2 Dicarboxylic Acids

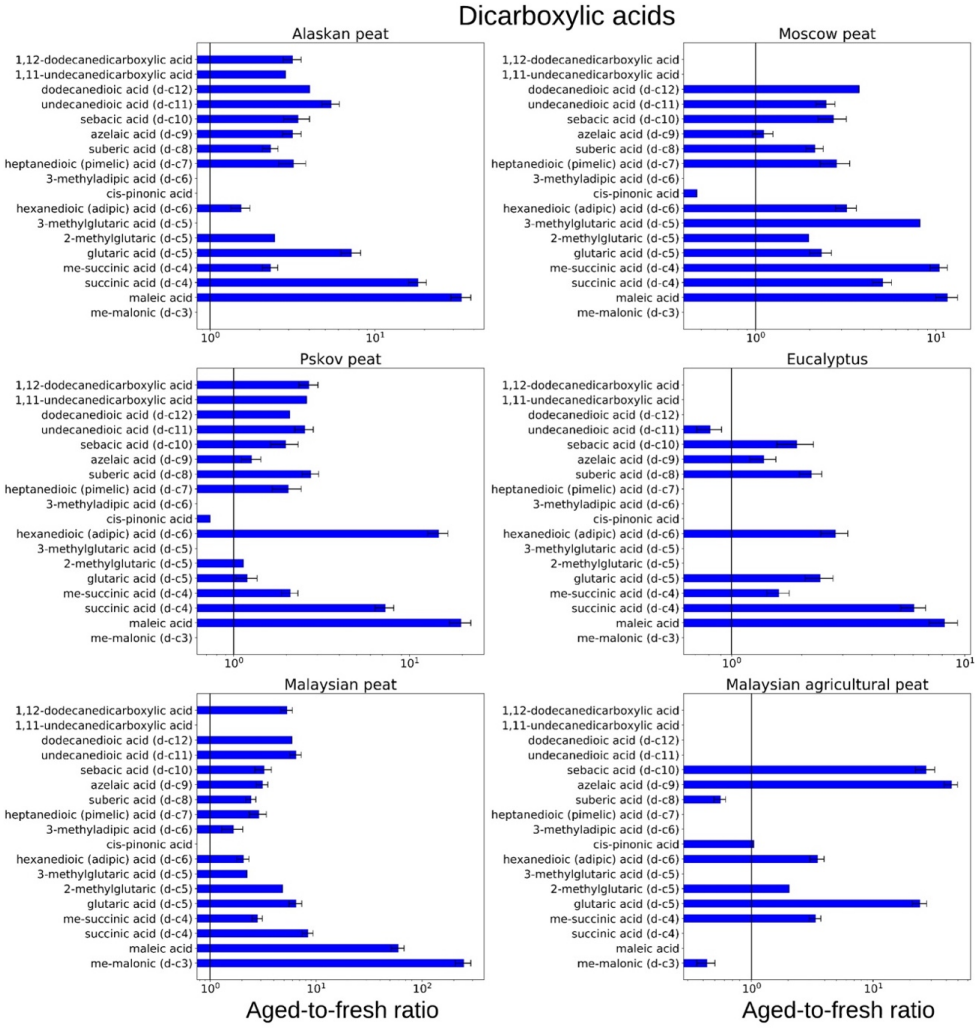

Figure 4b. Aged-to-fresh ratios of total (gas + particle) EFs for dicarboxylic acids from biomass burning emissions for six different biomass types presented in log scale. We did not burn fuels in replicates, and SD were calculated based on replicate analysis of similar fuels (with same experimental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

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659 In the case of dicarboxylic acids, we observed 2–20 times increase in EFs, but the degree of
660 enhancement of low-MW (LMW) dicarboxylic acids EFs was higher than for high-MW (HMW)
661 dicarboxylic acids EFs. For example, a 20-fold increase in maleic acid, a LMW dicarboxylic acid
662 (MW= 116.07 g mol^{-1}), was observed during OFR oxidation of Pskov peat emissions (aged-to-
663 fresh ratio = 19.6±2.8), whereas 1,11-undecanedicarboxylic acid, an HMW dicarboxylic acid
664 (MW = 244.33 g mol^{-1}), EF increased 2.6 times (aged-to-fresh ratio = 2.6±0.001) for the same fuel.
665 Similarly, the concentration of succinic acid, an LMW dicarboxylic acid (MW= 118.09 g mol^{-1}),
666 increased almost by five times after OFR oxidation (aged-to-fresh ratio = 5.07±0.62), whereas that
667 of undecanedioic acid, an HMW dicarboxylic acid (MW = 230.30 g mol^{-1}), increased 2.5 times
668 (aged-to-fresh ratio = 2.46±0.30) for Moscow peat. This trend was in accord with results from
669 ambient observations after BB events (Cao et al., 2017; Kawamura and Bikkina, 2016).
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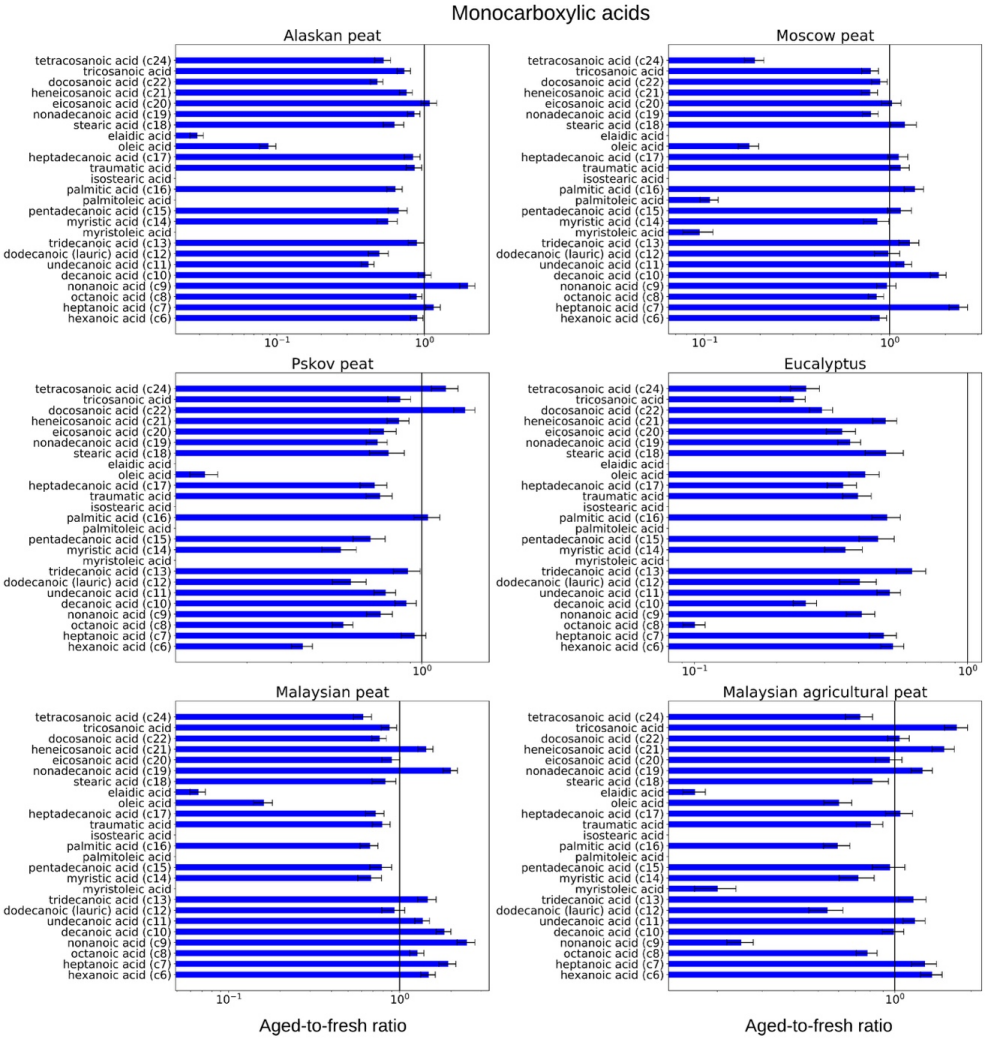
683 ### *3.3.3 Monocarboxylic Acids*



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

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Our analysis of OFR-aged samples showed that concentrations of monocarboxylic acids with different molecular weights 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 HMW monocarboxylic acids and formation of LMW 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.

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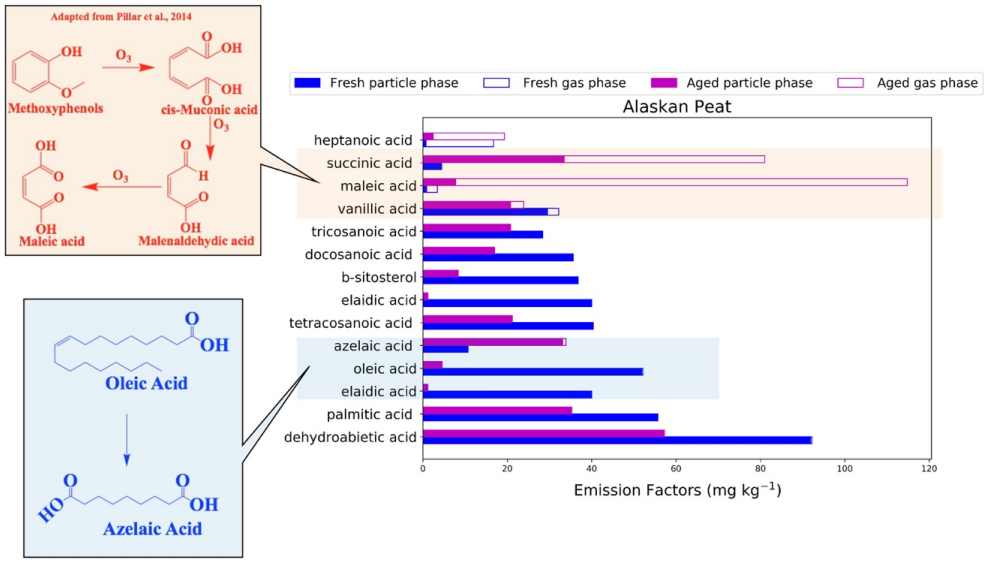
721 **3.4. Most Contributing Compounds**



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

730

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

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739 Dehydroabietic acid, a resin acid, is the compound with the highest EF (92.2 mg kg^{-1}) for fresh
740 combustion emissions from Alaskan peat. Moncarboxylic acids including palmitic acid (EF = 55.7
741 mg kg^{-1}), tetracosanoic acid (EF = 40.35 mg kg^{-1}), and docosanoic acid (EF = 35.38 mg kg^{-1}) were
742 also found in high abundance in fresh emissions from the combustion of this fuel. The high
743 contributions of β-sitosterol (EF = 36.84 mg kg^{-1}) and alkenoic acids (e.g., oleic acid EF = 52.1
744 mg kg^{-1}) to emissions are unique to Alaskan peat. All the compounds described above are found
745 in particulate phase. After the OFR-oxidation, both dehydroabetic acid and β-sitosterol, considered
746 to be potential markers for biomass burning emissions (Simoneit et al., 1993b), decreased from
747 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.
748 This reduction in EF because of OFR oxidation for both dehydroabetic acid and β-sitosterol must
749 be considered when using these compounds as biomass-burning markers. We observed the
750 formation of low molecular weight organic compounds, particularly in gas phase, from OFR
751 oxidation. For example, the EF of heptanoic acid increased from 2.42 mg kg^{-1} to 16.9 mg kg^{-1} and
752 that of maleic acid increased from 7.8 mg kg^{-1} to 107 mg kg^{-1} in the gas phase because of OFR
753 oxidation. Such a significant increase in the EF of maleic acid can be explained by the aqueous
754 phase oxidation of methoxyphenols (El Zein et al., 2015) in the presence of ozone. We found that
755 the oxidation inside the chamber was happening under dry conditions and understand that the
756 reactions of organic compounds with OH radicals inside the OFR chamber will prevail over
757 reactions with ozone. As we had our ozone scrubbers placed after sampling media (Fig. 1) to
758 prevent the pumps and online instruments from ozone-induced damage, we suspect that the maleic
759 acid was not formed inside the OFR chamber but rather by potential oxidation of organic
760 compounds on filters with relatively longer exposure of ozone (40–60 min for smoldering
761 combustion). Succinic acid EFs increased in both the gas phase (from 0.0 mg kg^{-1} to 47.5 mg kg^{-1})
762 and the particulate phase (from 4.43 mg kg^{-1} to 33.5 mg kg^{-1}). Azelaic acid EFs showed mainly
763 an increase in the particulate phase (from 10.5 mg kg^{-1} to 33.1 mg kg^{-1}), and we think that this was
764 because of the oxidation of oleic and eladic acid during OFR oxidation.

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772 **3.5 Contribution of polar fraction to total organic carbon**
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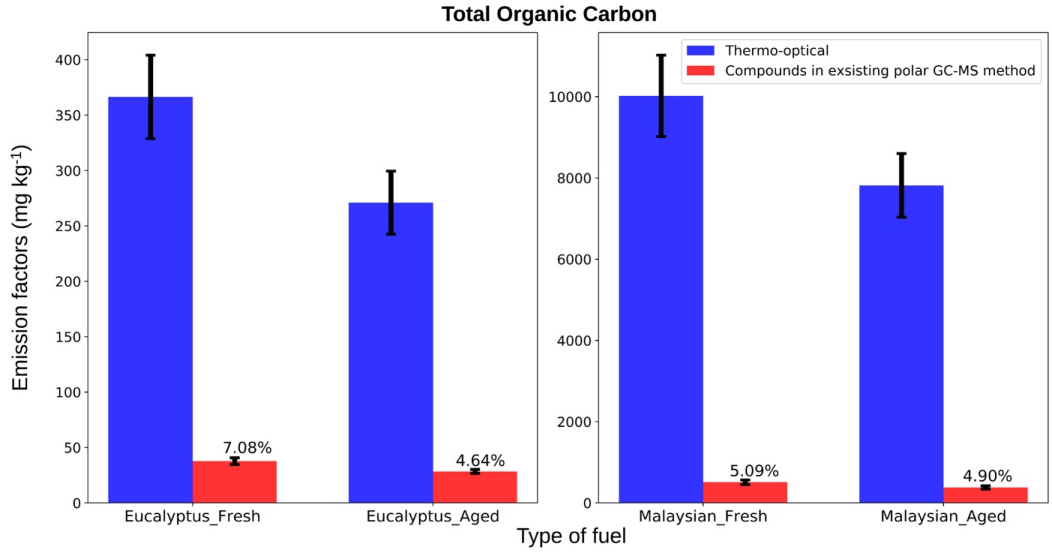

774

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

781

782 For Figure 6, we calculated the carbon content of total GC-MS characterized mass of identified
783 polar organic compounds and compared results with the total OC mass characterized by the
784 thermo-optical technique to estimate the contribution of polar compounds. The OC emissions were
785 higher for smoldering combustion (10,209 ± 5 mg kg^{-1} for Malaysian peat fresh emissions) than
786 for flaming combustion (366.5 ± 7 mg kg^{-1} for eucalyptus fresh emissions) samples, similar to the
787 observation of flaming and smoldering combustion by Akagi et al. (2011). Total OC emissions
788 are highly dependent on the type of fuel. For example, the fuel-based OC emission factor for rice
789 crop residue burning is 1960 mg kg^{-1} (Cao et al., 2008), whereas burning of corn and conifer forest

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yields emission factors of ~1457 mg kg $^{-1}$ (Andreae and Rosenfeld, 2008) and ~7800 mg kg^{-1} (Akagi et al., 2011a), 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.

3. 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 molecular weight compounds are mostly found in gas phase (e.g., guaiacol found in gas phase 82–100%), whereas high molecular weight (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

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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 molecular weight 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 molecular weight 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 and data collection. 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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