Polycyclic Aromatic Hydrocarbons in Biomass-Burning Emissions and Their Contribution to Light Absorption and Aerosol Toxicity

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Abstract

In recent years, brown carbon (BrC) has been shown to be an important contributor to light absorption by biomass-burning atmospheric aerosols in the blue and near-ultraviolet (UV) part of the solar spectrum. Emission factors and optical properties of 113 polycyclic aromatic hydrocarbons (PAHs) were determined for combustion of five globally important fuels: Alaskan, Siberian, and Florida swamp peat, cheatgrass (*Bromus tectorum*), and ponderosa pine (*Pinus ponderosa*) needles. The emission factors of total analyzed PAHs were between $1.9 \pm 0.4 - 3.0 \pm 0.6$ and $9.6 \pm 1.2 - 42.2 \pm 5.4$ $\text{mg}_{\text{PAH}} \text{kg}^{-1}_{\text{fuel}}$ for particle- and gas phase, respectively. Spectrophotometric analysis of the identified PAHs showed that perinaphthenone, methylpyrenes, and pyrene contributed the most to BrC light absorption with 17.2%, 3.3 - 10.5%, and 7.6% of the total particle-phase PAH absorptivity averaged over analyzed emissions from the fuels. In the gas phase, the top three PAH contributors to BrC were acenaphthylene (32.6%), anthracene (8.2%), and 2,4,5-trimethylnaphthalene (8.0%). Overall, the identified PAHs were responsible for 0.087-0.16% (0.13% on average) and 0.033-0.15% (0.11% on average) of the total light absorption by dichloromethane-acetone extracts of particle and gas emissions, respectively. Toxic Equivalency Factor (TEF) analysis of 16 PAHs prioritized by the United States Environmental Protection Agency (EPA) showed that benzo(a)pyrene contributed the most to the PAH carcinogenic potency of particle phase

emissions (61.8 – 67.4 % to the total carcinogenic potency of $\Sigma 16_{\text{EPA}}$ PAHs), while naphthalene played the major role in carcinogenicity of the gas phase PAHs in the biomass-burning emission analyzed here (35.4 – 46.0 % to the total carcinogenic potency of $\Sigma 16_{\text{EPA}}$ PAHs). The 16 EPA-prioritized PAHs contributed only $22.1 \pm 6.2\%$ to total particle and $23.4 \pm 11\%$ to total gas phase PAH mass, thus toxic properties of biomass-burning PAH emissions are most likely underestimated.

Additional keywords: biomass-burning, polycyclic aromatic hydrocarbons, potential carcinogen, brown carbon, UV-Vis spectra, peat smoldering

1. Introduction

Emissions from wildland fires and biomass fuel use contribute to regional air pollution events (Aiken et al., 2009; Duan et al., 2004; Hays et al., 2005; Koren et al., 2004), global scale radiative forcing and climate change (Finlayson-Pitts and Pitts, 1999; Stocker et al., 2013), and cause severe health effects (Kim et al., 2011; Naeher et al., 2007). Global inventories of black carbon (BC) and organic carbon (OC) particulate mass emitted from combustion show that approximately 88% of total carbonaceous aerosol mass is emitted from biomass combustion (Bond et al., 2004). Approximately 80% of this (or 70% of the total) is emitted from the smoldering combustion phase (Einfeld et al., 1991) – a low-temperature, flameless surface oxidation of solid fuel (Reid et al., 2005). As reported by the World Health Organization (WHO), around 3 billion people use open fires and simple stoves for cooking and for heating their homes with over 4 million premature deaths per year attributed to illnesses from smoke exposure (Bruce et al., 2000; W.H.O., 2016).

The burning of biomass fuels is one of the most important sources of gaseous and particulate air pollutants on the global scale (Andreae and Merlet, 2001; Finlayson-Pitts and Pitts, 1999). Of particular interest in terms of organic emissions are polycyclic aromatic hydrocarbons (PAHs), a class of compounds with two or more aromatic rings in their structure. PAHs are mainly formed during natural and anthropogenic combustion processes of fuels like wood (McDonald et al., 2000; Simoneit, 2002),

coal (Chen et al., 2005; Lee et al., 2005; Mastral et al., 1996), peat (Iinuma et al., 2007; Kakareka et al., 2005), oil (Rogge et al., 1997), fossil fuels (Fujita et al., 2007; Zielinska et al., 2004), waste (Mastral et al., 1999; Sidhu et al., 2005), crop/agricultural waste (Lu et al., 2009; Oanh et al., 2015), animal dung (Gadi et al., 2012; Singh et al., 2013; Tiwari et al., 2013), etc. Atmospheric PAHs are of major concern in all environmental compartments due to their mutagenic and carcinogenic properties (IARC, 1983; IARC, 1984; Lewtas, 2007). The most common carcinogenic effect of PAHs on human cells is DNA damage through the formation of adducts in a number of organs, including liver, kidney, lungs, etc. (Vineis and Husgafvel-Pursiainen, 2005; Xue and Warshawsky, 2005). For this reason, for many years research on atmospheric and indoor PAHs has mainly focused on the PAHs that have health implications and thus on quantitative analysis of 16 PAHs prioritized by the United States Environmental Protection Agency (EPA) (Freeman and Cattell, 1990; Kakareka et al., 2005; Tiwari et al., 2013; USEPA, 2013; Yan et al., 2004). Recently, several studies have proposed PAHs as a possible light-absorbing species in atmospheric brown carbon aerosols (Chen and Bond, 2010; Pöschl, 2003; Zhong and Jang, 2014).

It has been demonstrated that OC aerosols contribute to direct absorption of solar radiation due to the presence of so-called brown carbon (BrC) (Andreae and Gelencser, 2006; Moosmüller et al., 2009). BrC is composed of organic compounds that absorb light preferentially in the blue and near-ultraviolet (UV) spectral region giving these aerosols a brownish appearance (Chakrabarty et al., 2010). Several authors showed that the water-soluble OC fraction, in particular humic-like substances (HULIS) (Graber and Rudich, 2006; Samburova et al., 2005; Sun et al., 2007), as well as individual water-soluble OC species (Bones et al., 2010; Nguyen et al., 2012; Updyke et al., 2012; Yu et al., 2014) are partly responsible for light absorption of organic aerosols. The water-soluble aerosol fraction has received the most attention and, to our knowledge, so far no attempt has been made to quantify the contribution of non-water-soluble species, like PAHs, to the light absorption properties of atmospheric pollutants, in particular, biomass-burning emissions. Sun et al. (2007) analyzed UV-Vis spectra of 200 different OC compounds and concluded that more research on light-absorption properties of non-water-soluble BrC material is needed.

In this study, a series of biomass burning experiments were conducted to characterize PAH emissions from different biomass fuels. Globally and regionally significant wildland biomass fuels were reviewed and fuels from five different locations around the world were selected. Selection was based on their relevance and importance for biomass burning emissions (see Experimental Section): Alaskan, Siberian, and Florida swamp peat, cheatgrass (*Bromus tectorum*), and ponderosa pine (*Pinus ponderosa*) needles. The combustion experiments were conducted in a biomass-burning chamber under controlled conditions and gas- and particle phase PAHs were sampled, extracted, and analyzed, with 113 individual PAHs identified. The objectives of this research were to i) obtain emission factors for 113 PAHs emitted from the combustion of five selected fuels; ii) characterize the distribution of PAH species between gas and particle phases; iii) determine the contribution of PAHs to the biomass-burning BrC optical properties using spectrophotometric and photoacoustic techniques; and iv) estimate the carcinogenic potency of the emitted PAHs.

Quantitative chemical and optical analyses of water-soluble OC fractions (including HULIS) were performed for the same biomass-burning samples and will be discussed in a follow-up publication.

2. Experimental

2.1 Reagents and Materials

PAH standards were purchased from Sigma-Aldrich (St. Louis, MO, USA), AccuStandard (New Haven, CT, USA), and Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). High-performance liquid chromatography (HPLC) grade acetonitrile, acetone, and dichloromethane were obtained from Fisher Scientific (Fair Lawn, NJ, USA). A single-channel medium volume sampler preceded by a Bendix 240 cyclone inlet was used to collect particulate matter (PM) on pre-fired 47-mm diameter quartz-fiber filters (2500 Pallflex QAT-UP, Pall Life Sciences) in Nuclepore filter packs for thermal-optical OC and EC analysis (Chow et al., 2004; Chow et al., 1993). Teflon-impregnated glass fiber (TIGF) filters (d=100 mm, Fiber Film T60A20, Pall Life Sciences) were used to collect PM for organic analysis.

Fuel Selection and Preparation

110 In the present study, all peats combusted had a fuel moisture content of 25% by mass. Chemical and
111 spectrometry analyses of emissions from the combustion of fuels with different moisture contents is a
112 focus of additional studies e.g. Chakrabarty et al. (2016).

113 Siberian peat. Peatland ecosystems—generally wetland or mesic ecosystems underlain by soils
114 composed primarily of partially-decomposed biomass, containing mostly organic carbon and >20%
115 mineral content—represent a vast terrestrial C pool, and are potentially vast sources of C flux to the
116 atmosphere during wildfires that consume peat soil (Harden et al., 2000). Peatlands in high-latitude
117 temperate and boreal regions are particularly vulnerable to increased fire-related C emissions due to
118 climatic warming and increases in fire season length (Turetsky et al., 2015). High-latitude and Eurasia are
119 represented in this study by samples from Sphagnum and cotton grass (*Eriophorum spp.*) dominated
120 communities, collected from the Pskov region in Russia

121 Alaskan peat. Also representative of peatlands in high-latitude regions, from which C emissions from
122 smoldering ground fires are anticipated to be an increasing concern, Alaskan peat from black spruce
123 (*Picea mariana*) forests is included in our analysis. Alaskan peat was selected in order to compare
124 smoldering-combustion emissions between two high-latitude peatlands with differing floristic
125 composition.

126 Florida peat. In the southeastern USA, a combination of abundant natural ignition from lightning,
127 fire-dependent ecosystems, and land management make fire particularly important. In this region, land
128 managers burned nearly 2.4×10^6 ha in 2011 (Malone et al., 2011); frequent and regular burning of lands
129 (i.e. every few years) is a strategy employed to reduce the risk of wildfire (Kobziar et al., 2015). Increases
130 in regional human population and associated development activities are expected to place increasing
131 demands on regional water resources, leading to less water available for freshwater wetlands in many
132 areas. As wetlands dry in this fire-prone region, they will become increasingly vulnerable to fires that can
133 spread through this now desiccated land and ignite ground fires in areas with organic soils. Like peat fires
134 in boreal and tropical regions, these fuels contain vast carbon stocks that are released into the atmosphere
135 during fires (Watts, 2013; Watts and Kobziar, 2013). Due to the likely increase in ground fires and

potential for vast carbon emissions, organic soil from a desiccated lakebed in Florida, USA –representing organic muck and swamp soils – was chosen for inclusion in this study.

All peat samples used in this study were prepared for combustion first by drying to constant weight prior to storage in airtight containers; prior to combustion, samples were elevated to 25% moisture content by addition of deionized water. Although peat soils in vivo will undergo ignition and will sustain smoldering combustion at considerably higher moisture contents (Frandsen, 1987; Watts, 2013), laboratory investigations of smoldering in peat soils typically use lower moisture contents due to the difficulty of guaranteeing sustained smoldering combustion at high (>100%) moisture contents. 25% moisture content reflects conditions found at shallow depths during droughts when fires entering peatlands may be expected to contribute ignition sources to soil surfaces (e.g., embers, direct flame contact, or smoldering vectors).

Ponderosa pine (*Pinus ponderosa*) needles. Forests dominated by ponderosa pine occur across large areas of the Western and Southwestern USA, along a wide elevation gradient and near areas with large and dense human populations. Such “warm-dry” mixed-conifer forests are historically adapted to relatively frequent, low-intensity fire, but a combination of land-use changes and policy have disrupted natural fire regimes in many areas, leading to accumulation of abnormally high fuel loads in many areas of mixed-conifer forest (Dahms and Geils, 1997). The eventual wildfires that result can have high severity, and a number of recent very large fires have caused noteworthy impacts on ecosystem services and air quality (e.g., the 104,000 ha 2013 Rim Fire in California, USA). The ongoing historic drought in California and projections for exacerbated climate-change impacts to Western forests manifested as increases in wildfire activity (Westerling et al., 2006) can be expected to have disproportionate impacts on ponderosa pine mortality (Sieg et al., 2006). These factors suggest the inclusion of fuels from mixed-conifer forests, including representative components from ground, understory, and overstory. A related forest type, ponderosa pine-dominated forest, typically occurs at lower elevations; due to ponderosa pine having one of the greatest latitudinal ranges of all pines in North America (Oliver and Ryker, 1990). A focus on this species and its fuel components is warranted.

Cheatgrass. Cheatgrass (*Bromus tectorum*) is a grass native to Europe that has become an established invasive species across wide areas of the western USA. Cheatgrass alters fire risk, behavior, and effects by creating fuel continuity and ignition receptivity early in the fire regime and season of invaded ecosystems, especially sagebrush-steppe ecosystems of the Great Basin. This important fuel component, contributing to increased fire size and frequency in the Western USA, has never been investigated for its contribution to wildland fire emissions, and is included here for a detailed, first-ever assessment of its combustion products.

Samples of ponderosa pine needles were collected from forest floors and represented needle production from the prior two seasons, while cheatgrass samples (leaves, stems, and seedheads) were collected following plant senescence in order to represent cured fuels from the current season's growth. Cheatgrass and pine needle samples were stored at room temperature and low relative humidity (~20%) in order to maintain moisture contents observed when freshly collected; when combusted, samples exhibited moisture contents of ~5%.

2.2 Biomass Burning Experiments

DRI's biomass-burning facility was used to perform combustion of selected biomass fuels. A close replica of the chamber was described by Tian et al. (2015). The facility consists of a sealable laboratory chamber constructed from aluminum panels enclosing a square base (1.83 m × 1.83 m) and is 2.06 m high. Above this height, the chamber tapers to an exhaust pipe that contains multiple sampling ports and exhausts chamber air to a roof outlet with the exhaust flow rate controlled by a fan and a variable opening for the air inlet located at the bottom of the chamber, directly below the burn platform. Small amounts (~40 g) of fuel were burned in this chamber under controlled conditions (relative humidity, combustion efficiency, fuel-moisture content, time of aging, etc.). The fuel weights during the burns were monitored every second with a Veritas L Series Precision balance (0.01g of precision). The resulting smoke was sampled from the chamber through a primary sampling line into a sampling manifold that split the flow to the sample lines. Sample lines, made of non-reactive conductive PolyTetraFluoroEthylene (PTFE) tubing, were connected to real-time instruments and medium volume filter/XAD samplers. Optical

characterization of biomass-burning emissions was performed with a three-wavelength photoacoustic spectrometer and nephelometer (PASS-3, Droplet Measurement Technologies, Boulder, CO, USA; (Arnott et al., 1999; Lewis et al., 2008; Moosmüller et al., 2009).

Methods

Pre-cleaned quartz filters collected with a medium flow sampler at a flow rate of $0.11 \text{ m}^3 \text{ min}^{-1}$ were analyzed for OC by thermal-optical reflectance analysis (Chow et al., 1993). Another medium volume sampler was operated to collect samples on TIGF filters followed by XAD cartridges for analysis of particle and gas phase OC species, respectively. After sampling, filter and XAD samples were stored at a temperature of $-20 \text{ }^\circ\text{C}$ until extraction and analysis.

Collected 100-mm diameter TIGF filters and XAD samplers were spiked with deuterated internal PAH standards and extracted separately using an Accelerated Solvent Extractor (ASE) instrument (DIONEX, ASE-300, Salt Lake City, UT, USA). Naphthalene- d_8 , biphenyl- d_{10} , acenaphthene- d_{10} , phenanthrene- d_{10} , anthracene- d_{10} , pyrene- d_{12} , benz(a)anthracene- d_{12} , chrysene- d_{12} , benzo(k)fluoranthene- d_{12} , benzo(e)pyrene- d_{12} , benzo(a)pyrene- d_{12} , perylene- d_{12} , benzo(ghi)perylene- d_{12} and coronene- d_{12} were used as internal standards. The ASE extraction parameters were: temperature: $70 \text{ }^\circ\text{C}$, solvents: dichloromethane followed by acetone (150 ml each), pressure: 10.3 MPa, extraction time: 15 min. After extraction, the volume of extract solution was reduced to 1 mL with a rotary evaporator (Rotavapor R-124, BÜCHI, New Castle, USA) under a gentle vacuum at $35 \text{ }^\circ\text{C}$, then filtered with a $0.2\text{-}\mu\text{m}$ pore size polytetrafluoroethylene membrane filter (Whatman, Florham Park, NJ, USA), and transferred into a 2-ml volume amber glass vial. The solvent mixture (dichloromethane/acetone) in extracts was exchanged on toluene and then samples were pre-concentrated to 0.5 mL volume under ultra-high purity N_2 stream and stored at $-20 \text{ }^\circ\text{C}$ until analyses.

Biomass-burning sample extracts were analyzed with electron impact Gas Chromatography Mass Spectrometry (GC-MS). A Varian CP-3800 GC equipped with a CP-8400 autosampler and interfaced to a Varian 4000 Ion Trap Mass Spectrometer (Varian, Inc. Walnut Creek, CA, USA) was used to perform splitless injections onto a 30-m length, 5% phenylmethylsilicone fused silica capillary column (DB-5MS,

Agilent Technologies, Palo Alto, CA, USA) with a 10-m length integrated deactivated guard column. All of the analytical results were evaluated in terms of their associated measurement errors according to the following equation:

$$uncertainty = \sqrt{(analyte\ concentration \times replicate\ precision)^2 + (analyte\ detection\ limit)^2}$$

Replicate precision of the GC-MS method was ~10% for all analyzed PAHs. Six-point internal calibration curves were run prior to the GC-MS analyses of biomass-burning samples. Each PAH concentration was calculated based on relative concentration of its deuterated PAH analog (or PAH with similar response factor).

To qualitatively estimate the contribution of the PAHs emitted by biomass-burning, spectrophotometric measurements of non-water-soluble extracts were performed for both gas- and particle phase samples. The extracts from XAD (gas-phase) and filter (particle phase) samples were prepared in acetonitrile and brought to exact volume (i.e., 2 mL) prior to UV-Vis measurements with a spectrophotometer (Lambda 650, PerkinElmer, Waltham, MA, USA). In the “comparison” cell method, blanks were used in order to eliminate/subtract absorption of deuterated internal standards and solvent. The method blanks (XAD and filter separately) were prepared identically to the samples, except that non-sampled media sets were used.

3. Results and discussion

3.1 Emission factors (EF) of Analyzed PAHs

A total of 113 PAHs and PAH derivatives (including PAH isomers and PAH-like compounds), emitted from the combustion of five different biomass fuels (Siberian peat, Alaskan peat, Florida swamp peat, ponderosa pine needles, and cheatgrass) were analyzed and their fuel-based emission factors (EFs) are shown in Fig. 1, (Table S1, Supplementary Material).

Figure 1. EFs of the ten most abundant PAHs by mass detected (a) in particle-phase (filter samples) and (b) gas-phase (XAD samples) biomass-burning emissions from five different biomass fuels; the standard deviations were calculated based on three replicate burns of one fuel and accounted on average $20 \pm 8\%$ for particle and $16 \pm 7\%$ for gas phase PAHs

In the present work “PAH-like” compounds are defined as oxygenated PAHs, PAHs with nitrogen atom in the structure, and the organic species with more than one aromatic ring; which do not share one or more sides of other aromatic ring(s) (e.g., biphenyl, xanthone, anthrone, benzanthrone, quinolone, dibenzofuran; Table S1). EFs were calculated on the basis of the mass of PAH mass (mg) emitted per unit mass of consumed fuel (kg). In the text below “mg kg⁻¹” refers to “mg kg⁻¹ of consumed fuel mass”. The calculated EFs for total PAH mass are given in Table 1.

252 **Table 1.** EFs of PAHs and light absorbing BrC PAHs in particle- and gas-phase biomass-burning emissions collected from five different fuels. *
253 mg kg⁻¹ of consumed fuel, all peat samples had 25% moisture content. The standard deviations were calculated based on three replicate burns of
254 one fuel

	particle-phase					gas-phase		
Fuel	total OC, mg kg ⁻¹ *	total PAH, mg kg ⁻¹ *	% of total PAH mass in OC mass	total BrC PAHs, mg kg ⁻¹ *	% of BrC PAH mass in total PAH mass	total PAH mg kg ⁻¹ *	total BrC PAH mg kg ⁻¹ *	% of BrC PAH mass in total PAH mass
Alaskan peat	874±13	2.3±0.4	0.26	1.7±0.4	75	30.3±3.9	2.3±0.5	7.7
Siberian peat	1464±21	3.0±0.6	0.20	1.7±0.4	59	42.2±5.4	2.1±0.4	4.9
Florida swamp peat	673±10	2.6±0.5	0.38	1.3±0.3	49	35.7±4.6	1.2±0.2	3.4
Ponderosa pine needles	521±8	2.3±0.4	0.44	0.97±0.22	42	16.2±2.1	0.39±0.07	2.4
Cheatgrass	470±7	1.9±0.4	0.40	1.3±0.3	67	9.6±1.2	0.54±0.10	5.6

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The standard deviations were calculated based on three replicate burns of one fuel. Analyzed particle-phase PAH mass collected on filters represented 0.20-0.44 % of total OC mass and their EFs ranged between 1.9 ± 0.4 to 3.0 ± 0.6 mg kg⁻¹ for all analyzed samples. The EFs of gas-phase PAHs were much higher than those of particle-phase PAHs, ranging from 9.6 ± 1.2 to 42.2 ± 5.4 mg kg⁻¹. It should be noted that there is a difference in total PAH concentrations among emissions from tested fuels. Combustion emissions from all peat samples showed higher concentrations of gas- and particle- phase PAHs than those from two other fuels, ponderosa pine needles and cheatgrass (Table 1). A possible reason for this phenomenon could be the presence of PAHs in peat fuels, with these PAHs being released into gas-phase during the combustion process. The presence of PAHs in soil and peat has previously been investigated and reported in the literature (Wilcke, 2000). In contrast, grass and needle fuels do not contain PAHs and thus emitted PAHs most likely form during the combustion process (Iinuma et al., 2007; Jenkins et al., 1996) or are present on fuel surfaces (i.e., needles or leafs) from atmospheric deposition (Wilcke, 2000; Wild et al., 1992). However, the most probable reason for high PAH concentrations in peat combustion emissions is the dominance of smoldering combustion in peat burning (Rein, 2009). Peat smoldering combustion is characterized as low temperature, flameless, surface combustion that produces large amounts of incomplete biomass-burning products (Rein, 2009; Rein, 2013; Zacccone et al., 2014) including aromatic compounds (Kakareka et al., 2005; Olsson, 2006). Combustion of cheatgrass and ponderosa pine needles occurs mainly in the high-temperature, flaming combustion phase (Lobert and Warnatz, 1993), where less organic matter and CO and more CO₂ is emitted (Ferek et al., 1998). The ratio of “total gas-phase PAHs/total particle-phase PAHs” was similar among emissions from the three peat fuels and ranged between 12 and 14. This ratio was approximately two times lower for cheatgrass (i.e., 7) and ponderosa pine needles (i.e., 5), likely due to the partial combustion of gas-phase PAHs in flaming combustion.

PAH emission factors obtained in the present study were compared with previously reported results. Iinuma et al. (2007) performed analysis of 19 particle-phase PAHs in biomass-burning emission from combustion of Indonesian and German peats and reported 20 mg kg⁻¹ and 28 mg kg⁻¹, respectively. Our

analysis showed significantly lower EFs for the same group of particle-phase PAHs (except benzo[b]naphtho[1,2-d]thiophene, cyclopenta[cd]pyrene, triphenylene, and 2,2'-binaphthyl) in Alaskan ($0.73 \pm 0.13 \text{ mg kg}^{-1}$), Siberian ($0.84 \pm 0.15 \text{ mg kg}^{-1}$), and Florida swamp ($0.56 \pm 0.11 \text{ mg kg}^{-1}$) peats. The same author (Iinuma et al., 2007) reported EFs for 19 particle phase PAHs from savanna grass (5.6 mg kg^{-1}) and pine fuel (1.4 mg kg^{-1}) combustion, which are higher comparing to our EFs for combustion of cheatgrass ($0.52 \pm 0.09 \text{ mg kg}^{-1}$) and ponderosa pine needles ($0.49 \pm 0.09 \text{ mg kg}^{-1}$). This variance is most likely caused by differences in combustion conditions and fuels.

The EFs of our top ten high-mass-concentration PAHs emitted from biomass burning are presented in Fig. 1 (a, b); perinaphthenone, e-dimethylphenanthrene, fluoranthene, pyrene, retene, benzo(a)fluorine, 1+3-methylfluoranthene, 1-methylpyrene, benzo(ghi)fluoranthene, and chrysene. These were the most abundant particle phase species, which contributed to 41-54 % of the total mass of the 113 identified PAHs. The top ten emitted PAHs were similar for all our fuels. The only difference is low concentrations (below detection limit) of e-dimethylphenanthrene in Siberian peat and perinaphthenone in cheatgrass emissions. On the other hand, the PAH EFs varied from fuel to fuel even among three peat samples (Alaskan peat, Siberian peat, and Florida swamp peat). The top ten particle-phase PAHs were high molecular weight species with of three or four aromatic rings in their structure. In contrast, top ten high-mass-concentration PAHs in gas-phase were all low-molecular weight species with two aromatic rings (Fig. 1b and 2b): naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, 1,3+1,6+1,7-dimethylnaphthalene, acenaphthylene, dibenzofuran, 2,3,5-I-trimethylnaphthalene, 2,4,5-trimethylnaphthalene, and fluorine. All of these high-concentration gas-phase PAHs were present in the emissions of all our fuels (Fig. 1b) and their contribution to the total gas-phase PAH mass ranged between 67 and 73%. Fig. 2 summarizes the distribution of different size (number of aromatic rings) PAHs between gas- and particle- phases. As expected, light PAHs, like two-ring PAHs, were dominant in the gas-phase fraction and found to contribute 92 – 98% of the total gas-phase PAH mass (Fig. 2b, Table S2), while three- and four-ring PAHs were responsible for only 2.3 – 7.0% and 0.04 – 0.8% of gas-phase PAH mass, respectively. In the particle phase (Fig.2a, Table S2), three-ring PAHs (41.8 – 70.8%) and four-ring

PAHs (16.7 – 41.4%) contributed most to the particle-phase PAH mass emissions, compared to two- (10.9 – 20.2%), five- (0.9 – 5.4%), and six- (0.7 – 0.5%) ring PAH species contributions.

Figure 2. EFs of two, three, four, five, and six rings PAHs in (a) particle- and (b) gas- phase biomass-burning emissions obtained for five different fuels

The total mass EFs of the 16 EPA-prioritized PAHs (USEPA, 2013; Yan et al., 2004) were obtained for gas and particle phase biomass-burning emissions and are presented in Table 2. Comparison between fuels showed that peat emissions have higher concentrations of 16_{EPA} PAHs than those from ponderosa pine needle and cheatgrass combustion. As discussed above, this can likely be explained by the low-temperature smoldering combustion of peat, where PAHs are formed due to incomplete combustion. The EFs (sum of the 16_{EPA} PAHs) were similar for combustion of the three peats (Alaskan: 0.61±0.07 mg kg⁻¹, Siberian: 0.69±0.08 mg kg⁻¹, Florida: 0.51±0.06 mg kg⁻¹), but lower than previously reported EFs for combustion of Indonesian (i.e., 17.83 mg kg⁻¹) and German (i.e., 25.19 mg kg⁻¹) peats presented by Iinuma et al. (2007). Mass EFs of gas- and particle 16_{EPA} PAHs were 0.29±0.04 and 1.69±0.28 mg kg⁻¹ for combustion of ponderosa pine needles. The sum of these EFs for gas- and particle 16_{EPA} PAHs is about a factor of five lower than the 9.73 mg kg⁻¹ EF for the sum of gas and particle phase PAHs emitted from ponderosa pine fuel combustion previously reported (Jenkins et al., 1996).

Table 2. Concentrations of PAHs obtained in the present study and compared with results reported in the literature. Units: EF PAHs (mg kg⁻¹);
 Abbreviations: BaP (benzo[a]pyrene), BaA (benz[a]anthracene), DahA (dibenz[a,h]anthracene), BbF (benzo[b]fluoranthene), BkF
 (benzo[k]fluoranthene), IcdP (Indeno[123-cd]pyrene); * concentrations of naphthalene, acenaphthylene, and acenaphthene are not included, ** 16
 standard EPA PAHs plus naphthalene and 2-methylnaphthalene
 NC Peat I – Alligator River National Wildlife Refuge (Eastern North Carolina, USA), NC Peat II - Pocosin Lakes National Wildlife Refuge
 (Eastern North Carolina, USA)

Fuel type	Σ PAHs particle/gas	Σ_{16} EPA PAHs particle/gas	BaP particle/gas	BaA particle/gas	DahA particle/gas	BbF particle/gas	BkF particle/gas	IcdP particle/gas	Reference
Alaskan peat	Σ_{113} 2.28/30.27	0.61/12.3	0.032/ND	0.051/0.099	0.056/ND	0.037/ND	0.022/ND	0.017/ND	Present study
Siberian peat	Σ_{113} 2.96/42.2	0.69/9.7	0.027/ND	0.058/ND	ND/ND	0.036/ND	0.017/ND	0.013/ND	Present study
Florida swamp peat	Σ_{113} 2.57/35.8	0.51/6.8	0.017/ND	0.03/0.002	ND/ND	0.023/ND	0.011/ND	0.008/ND	Present study
Indonesian peat	Σ_{19} 20/-	17.83*/-	ND/-	0.43/-	ND/-	ND/-	ND/-	ND/-	Iinuma et al., 2007
German peat	Σ_{19} 28/-	25.19*/-	ND/-	0.49/-	ND/-	ND/-	ND/-	ND/-	
NC Peat I	-	$\Sigma_{g/p}$ 74.1	$\Sigma_{g/p}$ 0.32	$\Sigma_{g/p}$ 0.66	$\Sigma_{g/p}$ 0.04	$\Sigma_{g/p}$ 0.31	$\Sigma_{g/p}$ 0.23	$\Sigma_{g/p}$ 0.17	Black et al., 2016
NC Peat II	-	$\Sigma_{g/p}$ 42.9	$\Sigma_{g/p}$ 0.21	0.49	$\Sigma_{g/p}$ 0.04	$\Sigma_{g/p}$ 0.21	$\Sigma_{g/p}$ 0.11	$\Sigma_{g/p}$ 0.09	
Ponderosa pine needles	Σ_{113} 2.32 / 16.2	0.29/1.69	0.006/ND	0.011/0.001	ND / ND	0.008/ND	0.003/ND	0.0002/ND	Present study
Ponderosa pine	$\Sigma_{g/p}$ 28.96**	$\Sigma_{g/p}$ 9.73	$\Sigma_{g/p}$ 0.019	$\Sigma_{g/p}$ 0.11	$\Sigma_{g/p}$ ND	$\Sigma_{g/p}$ 0.037	$\Sigma_{g/p}$ 0.039	$\Sigma_{g/p}$ ND	Jenkins et al., 1996
Pine	Σ_{19} 1.4/-	1.252*/-	0.11/-	0.097/-	0.0087/-	0.11/-	0.033/-	0.045/-	Iinuma et al., 2007
Cheatgrass	Σ_{113} 1.88/9.57	0.53/2.29	0.013/ND	0.022/0.004	0.002/ND	0.016/ND	0.006/ND	0.007/ND	Present study
Savanna grass	Σ_{19} 5.6/-	3.44*/-	0.5/-	0.15/-	0.018/-	0.18/-	0.28/-	0.11/-	Iinuma et al., 2007

Recently, organic analysis of two North Carolina (NC, USA) peat biomass-burning emissions was presented by Black et al. (2016) and EFs of 16_{EPA} PAHs found to be 74.1 mg kg⁻¹ and 42.9 mg kg⁻¹. Iinuma et al. (2007) obtained particle phase PAH EFs from pine combustion 1.25 mg kg⁻¹; this value is about a factor of four higher than our result (0.29±0.04 mg kg⁻¹) given above, which is probably caused by differences in fuels and combustion conditions. It needs to be emphasized that EFs for the total 16_{EPA} PAHs measured in this study were significantly higher in the gas phase than in the particle phase (14 – 20 times higher for peat fuels and 4-5 times higher for ponderosa pine needle and cheatgrass emissions), mostly due to high concentrations of two- and three-ring gas phase PAHs, including naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, and anthracene. This finding suggests that the importance of gas phase PAHs needs to be further assessed in future biomass-burning studies.

3.2 Contribution to Carcinogenic Potency

In order to evaluate the human health risk associated with the 16_{EPA} biomass-burning PAHs, the carcinogenic potency of each PAH was calculated based on the “Toxic Equivalence Factor” (TEF) approach and is shown in Fig. 3 and Tables S4-S5 (Supplementary material). The carcinogenic potency was calculated by multiplying known TEFs (Nisbet and Lagoy, 1992) with the corresponding EFs obtained in the present study. As expected, benzo(a)pyrene, a proven carcinogen (Butler et al., 1993; Nisbet and Lagoy, 1992; Petry et al., 1996), was the major contributor to the PAH toxicity in the particle phase biomass-burning emissions, accounting for 61.8 – 67.4 % of the total adjusted TEF for emissions from our fuels. Benzo(a)pyrene is followed by benz[a]anthracene and benzo[b]fluoranthene with contributions of 10.0 – 14.1 % and 7.2 – 9.2 % to the TEF, respectively. Similarly to our results, benzo(a)pyrene, was found to be one of the major PAH carcinogens in other studies (Jakovljevic et al., 2015; Saxena et al., 2014). For gas phase PAHs, naphthalene had the highest carcinogenic potency for all our fuels with contributions of 35.4 – 46.0 % for emissions from combustion of the three peat fuels.

Figure 3. Carcinogenic potency calculated for the 16 EPA PAHs calculated in (a) particle- and (b) gas-phase biomass-burning emissions obtained for five different fuels

For ponderosa pine needle and cheatgrass combustion, naphthalene contribution to the carcinogenic potency of gas phase emissions was 24.3 % and 25.1 %, respectively, which is lower compared to the peat emissions. 2-Methylnaphthalene and anthracene were second and third most dominant among gas phase PAHs with contribution to the total carcinogenic potency of 13.8 – 35.5 % and 8.1 – 16.5 %, respectively. The total TEF-adjusted values were found to be $9.4 \pm 1.6 - 51.8 \pm 8.4 \text{ mg kg}^{-1}$ for gas and $3.3 \pm 0.5 - 17.9 \pm 2.7 \text{ mg kg}^{-1}$ for particle phases. Comparing gas and particle phases (Fig. 3), it is clear that particle phase plays the major role in the carcinogenicity of analyzed PAHs because of the proven carcinogenic effect of benzo(a)pyrene with a high TEF value of 1.0 (Nisbet and Lagoy, 1992). On the other hand, high EFs of naphthalene into the gas phase of biomass-burning emissions result in a high carcinogenic potency despite its low TEF value of 0.001. In this study, the carcinogenic potency was calculated for the 16_{EPA} PAHs and 2-methylnaphthalene, since TEFs are available only for these PAH species (Nisbet and Lagoy, 1992). Our quantitative analysis of 113 PAHs in biomass-burning emissions showed a number of PAHs with high EFs (Fig. 1), but their carcinogenic effect has not been determined yet. Therefore, the toxicological analysis of PAHs like di-methylnaphthalenes, tri-methylnaphthalenes, benzo(a)fluorine,

methylypyrenes, methylfluroanthenes, is crucial for accurate estimation of their biomass-burning carcinogenic toxicity.

EFs of six PAH compounds (benzo(a)pyrene, benz(a)anthracene, dibenz(a,h)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, Indeno[123-cd]pyrene), which are known as probable/possible carcinogens (Nisbet and Lagoy, 1992; Ramirez et al., 2011) are summarized in Table 2 together with EFs for the total PAHs and data reported in the literature. These PAHs were found almost exclusively in the particle phase and accounted for 7.2 % (Alaskan peat), 5.1 % (Siberian peat), 3.5% (Florida swamp peat and cheatgrass) and 1.3 % (ponderosa pine needles) of the total particulate carcinogenic potency. EFs of the six carcinogens were higher for peat combustion emissions than for ponderosa pine needle and cheatgrass combustion (Table 2). Particle phase benz(a)anthracene had the highest EFs, which ranged from 0.022 ± 0.005 to $0.058 \pm 0.013 \text{ mg kg}^{-1}$ for our fuels. Benzo(a)pyrene, as mentioned above, is known as a highly mutagenic and toxic PAH that causes mutations in cells (Nisbet and Lagoy, 1992; Yu et al., 2011). Its highest EFs were observed for Alaskan ($0.032 \pm 0.006 \text{ mg kg}^{-1}$) and Siberian ($0.027 \pm 0.005 \text{ mg kg}^{-1}$) peat combustion particle emissions, while for ponderosa pine needle ($0.006 \pm 0.001 \text{ mg kg}^{-1}$) and cheatgrass ($0.013 \pm 0.002 \text{ mg kg}^{-1}$) emissions, benzo(a)pyrene EFs were several times lower. The EFs of six probable/possible PAH carcinogens obtained in the present study differ from those reported in the literature (Table 2), most likely due to differences in fuels and combustion conditions. Iinuma et al. (2007) obtained benzo(a)anthracene EFs for Indonesian (0.43 mg kg^{-1}) and German (0.49 mg kg^{-1}) peat combustion emissions and these values are roughly 10 times higher than benzo(a)anthracene EFs for Alaskan, Siberian, and Florida swamp peats presented here (Table 2). On the other hand, the same study showed no presence (below detection limit) of benzo(a)pyrene, dibenz(a,h)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno[123-cd]pyrene from the combustion of the studied peat fuels. For combustion of ponderosa pine needles and grasses, EFs in this study were lower than those reported in the literature (Iinuma et al., 2007; Jenkins et al., 1996; Kakareka et al., 2005). Our results and results from previous studies show the importance of PAH indoor monitoring, where biomass fuels are often burned for domestic cooking and heating (Li et al., 2016;

Naeher et al., 2007; Shen et al., 2013) and in ambient air, especially in populated areas that experience biomass-burning pollution events (Cristale et al., 2012; Robinson et al., 2008; Silva et al., 2010; Wang et al., 2015).

3.3 Spectrophotometric Analysis of PAHs

Light absorption properties of biomass-burning emissions of five selected fuels were analyzed using two techniques: off-line analysis of aerosol extracts with UV-Vis spectrophotometry and in-situ, real-time measurements with multi-wavelength photoacoustic spectrometry (Moosmüller et al., 2009) during the combustion experiments in our biomass combustion chamber (Chakrabarty et al., 2016; Tian et al., 2015).

First, bulk mass absorption efficiency MAE_{bulk} of individual PAHs were obtained for each compound. Standard PAHs with known concentrations were prepared in acetonitrile and spectra between 190 and 900 nm were recorded for each individual PAH with a UV-Vis spectrophotometer. Acetonitrile was used as a blank in the “comparison” cell, thus absorption spectra of standard PAHs were not affected by acetonitrile absorption. MAE_{bulk} was calculated using Lambert-Beer law and obtained values were multiplied by the power distribution of the solar spectrum at the top of the atmosphere and spectrally integrated in order to estimate the contribution of standard PAHs to the aerosol light absorption in real environment. The results showed that majority of standard PAHs absorb light in the wavelength range between ~ 290 and 450 nm and therefore contribute to the light absorption by biomass-burning emissions in the blue and near-UV range of the spectrum (Fig. 4). UV-Vis spectra of all analyzed standards are presented in Supplementary Material (Fig. S1). The top ten standard PAHs with the highest value of MAE_{bulk} (up to $100 \text{ m}^2 \text{ g}^{-1}$) were: dibenzo(a,h)pyrene, anthanthrene, perylene, dibenzo(a,i)pyrene, indeno[123-cd]fluoranthene, perinaphthenone, cyclopenta(c,d)pyrene, 7-methylbenz(a)pyrene, benzo[a]pyrene, and 1-methylpyrene. These PAHs have 4-6 aromatic rings in their structures, except for perinaphthenone, that has 3 rings and one chromophore - ketone group. According to the literature (Pretsch et al., 2000; Sun et al., 2007), the larger number of rings and presence of oxygenated functional groups in aromatic structures enhance the absorption shift from the UV toward the longer wavelengths in the visible.

Figure 4. Bulk mass absorption efficiency MAE_{bulk} for the ten most efficient light-absorbing BrC PAH standards.

However, not all of these standard PAHs were detected in the combustion emissions, e.g., concentrations of dibenzo(a,e)pyrene, and dibenzo(a,i)pyrene were below detection limit for all samples. In order to determine the most effective BrC PAHs, EFs (or concentrations) have to be accounted for together with mass absorption coefficients. Since PAH profiles were similar between fuels, absorption spectra of the PAHs were averaged for combustion emissions from cheatgrass, ponderosa pine needles and the three peat samples (Fig. 5). For particle phase samples, we found that perinaphthenone, methylfluoranthenes, pyrene, fluoranthene, methylpyrenes, retene, pyrene, and benzo(ghi)fluoranthene contribute the most to the light absorption (Fig. 6a). Perinaphthenone had the largest impact on BrC absorptivity for analyzed fuels except for Siberian pet, contributing 13.2 – 28.4% (Fig. 7a) to the total biomass-burning PAH absorption. In the gas phase (Fig. 6b), acenaphthalene (19.4 – 40.2%) was the larger BrC contributor, followed by 2, 4, 5 - trimethylnaphthalene and anthracene, which were responsible for up to 19.6% and 12.7% of PAH absorptivity (Fig. 7b).

Figure 5. The most efficient light-absorbing BrC PAHs identified and quantified in (a) particle- and (b) gas-phase of biomass-burning emissions

Figure 6. Emission factors of the ten most abundant light-absorbing BrC PAHs detected (a) in particle-phase (filter samples) and (b) gas-phase (XAD samples) biomass-burning emissions of five different biomass fuels; the standard deviations were calculated based on three replicate burns of one fuel and accounted on average $22 \pm 8\%$ for particle and $18 \pm 5\%$ for gas phase PAHs

Figure 7a. Contribution of top ten BrC PAHs to the total particle phase PAH absorptivity

Figure 7b. Contribution of top ten BrC PAHs to the total gas phase PAH absorptivity

The comparison of gas-phase and particle-phase PAH absorption coefficients indicates that particulate PAHs absorb more at longer wavelengths (λ : 400 – 500 nm) of the blue and near-UV spectral region, while strong absorption of gaseous PAHs is shifted towards shorter wave lengths (λ : 280 – 400 nm). Since in the present study we focus on the effect of PAHs on light absorption properties of BrC biomass-burning emissions in the troposphere, light absorption of PAHs in the UV region of the spectrum ($\lambda < 300$ nm) is not be considered. Comparing values of MAE_{bulk} between particle (Fig. 5a) and gas (Fig. 5b) phases at $\lambda > 350$ nm, the majority of particulate BrC PAH MAE_{bulk} are above $1 \text{ m}^2 \text{ g}^{-1}$, while only few gas-phase PAHs (fluoranthene, perinaphthenone, anthracene) have MAE_{bulk} greater than $1 \text{ m}^2 \text{ g}^{-1}$. As was discussed above, light-absorbing PAHs in both fractions are different and although absolute concentrations of BrC PAHs in gas phase are higher, particulate phase PAHs dominate BrC aerosol light-absorption. At the same time, analysis of gas phase-PAH is still needed since these compounds, through atmospheric radical reactions may form PAH compounds with higher MW and with different mutagenic and optical properties, e.g., nitrated PAH (Atkinson and Arey, 1994; Finlayson-Pitts and Pitts, 1999; Laskin et al., 2015; Tokiwa et al., 1998). The contribution of identified PAHs to the total absorption of analyzed extracts was 0.087-0.16% (0.13% on average) for particle phase and 0.033-0.15% (0.11% on average) for gas phase. Thus, further quantitative and spectroscopic analyses of other potential BrC species, such as oxygenated PAH species, in biomass-burning emissions are needed.

Comparing MAE_{bulk} obtained in the present study with those in the literature, we found that some PAHs have light absorption properties comparable to those of other potential BrC species. Updyke et al. (2012) showed that laboratory generated secondary organic aerosols (SOA) from certain biogenic precursors (α -pinene, α -cedrine, etc.) react with ammonia and produce BrC compounds, which strongly absorb at wavelengths between 400 - 600 nm with MAE_{bulk} between $0.001 - 0.1 \text{ m}^2 \text{ g}^{-1}$ at 500 nm. Aged limonene with NH_4^+ in aqueous phase was found to be an effective potential BrC SOA with $MAE_{bulk} = 0.3 \text{ m}^2 \text{ g}^{-1}$ at a wavelength of 500 nm (Bones et al., 2010). Several studies have measured UV-Vis spectra of HULIS and demonstrated that HULIS absorb light with wavelength > 400 nm (Dinar et al., 2008). The spectra obtained for biomass-burning PAHs in the present research (Fig. 5 and 6) display more

absorbance at shorter wavelengths (200 – 400 nm); however, several PAHs showed absorption above 400 nm, such as methylpyrenes ($\text{MAE}_{\text{bulk}} = 0.137 \text{ m}^2 \text{ g}^{-1}$ at 500 nm), methylfluoranthenes ($\text{MAE}_{\text{bulk}} = 0.031 \text{ m}^2 \text{ g}^{-1}$ at 500 nm), perinaphthenone ($\text{MAE}_{\text{bulk}} = 0.075 \text{ m}^2 \text{ g}^{-1}$ at 450 nm), retene ($\text{MAE}_{\text{bulk}} = 0.138 \text{ m}^2 \text{ g}^{-1}$ at 450 nm), acenaphthalene ($\text{MAE}_{\text{bulk}} = 0.034 \text{ m}^2 \text{ g}^{-1}$ at 450 nm), and 9-fluorenone ($\text{MAE}_{\text{bulk}} = 0.019 \text{ m}^2 \text{ g}^{-1}$ at 450 nm). Therefore, the significance of these PAHs to BrC light absorption is comparable to other BrC compounds.

3.4 Contribution of Identified PAHs to Light Absorption

The contribution of PAHs to light absorption properties of biomass-burning emissions was determined using the detailed chemical analysis of emissions combined with spectroscopic characterization of individual PAH compounds and extracts of biomass burning samples (see section “*Spectrophotometric Analysis of PAHs*” above). PAHs were apportioned into two groups based on their solar-spectrum-weighted MAE_{bulk} (Fig. 4 and Table S3 in Supplementary Material). The obtained $\text{MAE}_{\text{bulk_av}}$ ranged from 2×10^{-5} to $2.7 \text{ m}^2 \text{ g}^{-1}$. The median and mean values were found to be 0.105 and $0.308 \text{ m}^2 \text{ g}^{-1}$, respectively. PAHs with $\text{MAE}_{\text{bulk_av}}$ above $0.1 \text{ m}^2 \text{ g}^{-1}$ were assigned as BrC PAHs since they strongly absorb light in the blue and near-ultraviolet (UV) spectral region (Fig. 4). PAHs with $\text{MAE}_{\text{bulk_av}}$ below $0.1 \text{ m}^2 \text{ g}^{-1}$ were considered as non-BrC species. The total EFs of particle-phase BrC PAHs are similar for all analyzed fuels and ranged from 0.97 ± 0.22 to $1.7 \pm 0.4 \text{ mg kg}^{-1}$, representing 42 – 75% of the total particle-phase PAH emissions (Table 1). In the gas phase, BrC PAHs were responsible only for 2.4 – 7.7% of the total gas-phase PAH emissions, with the EFs being 0.39 ± 0.07 – $2.33 \pm 0.45 \text{ mg kg}^{-1}$ (Table 1). While EFs of light-absorbing BrC PAHs in gas and particle phases are comparable, the contribution of BrC species to the total PAHs mass emission is considerably higher in the particle phase than in the gas phase biomass-burning emissions due to the higher $\text{MAE}_{\text{bulk_av}}$ of the particle-bound PAHs.

Fig. 5 and 6 show top ten contributors to light absorption among individual gas- and particle-phase BrC PAHs. This contribution was calculated based on two parameters: EF of each PAH and its solar-spectrum-weighted light absorption efficiency $\text{MAE}_{\text{bulk_av}}$ (Fig. 6). We found that BrC PAH profile is very

similar between emissions from tested fuels. However, as was expected, this profile is different between gas and particle phase biomass-burning emissions. The only similarity between the top ten BrC gas- and particle- phase PAHs was the presence of pyrene, fluoranthene, and perinaphthenone. The top ten particle-phase BrC PAHs are dominated by methylpyrenes and methylfluoranthenes, which have high MAE_{bulk_av} and relatively high EFs (EFs range: 0.014 ± 0.005 and 0.16 ± 0.07 mg kg⁻¹). The top ten particle-phase BrC PAHs also include perinaphthenone (EFs: 0.06 ± 0.01 – 0.19 ± 0.05 mg kg⁻¹, except for Siberian peat fuel emissions that have perinaphthenone concentrations below detection limit), fluoranthene (0.08 ± 0.01 – 0.17 ± 0.03 mg kg⁻¹), pyrene (0.07 ± 0.01 – 0.18 ± 0.03 mg kg⁻¹), retene (0.06 ± 0.02 – 0.15 ± 0.05 mg kg⁻¹), and benzo(ghi)fluoranthene (0.018 ± 0.005 – 0.08 ± 0.02 mg kg⁻¹) (Fig. 6a). In general, EFs of the top ten particle-phase BrC PAHs were found to be in the same range for all our fuels (Fig. 6a). In the gas phase, 2,4,5-trimethylnaphthalene was the dominant light absorbing PAH for emissions from the combustion of Siberian peat (4.9 ± 0.8 mg kg⁻¹), Florida swamp peat (4.7 ± 0.7 mg kg⁻¹), and ponderosa pine needles (3.6 ± 0.6 mg kg⁻¹), while biphenyl was the most abundant BrC PAH in Alaskan peat and cheatgrass emissions with EFs 2.8 ± 0.2 mg kg⁻¹ and 0.42 ± 0.03 mg kg⁻¹, respectively. Overall, the BrC PAH profiles for gas phase emissions were similar for all of our fuels, but EFs for the three peats were higher than those for cheatgrass and ponderosa pine needles (Fig. 6).

4. Conclusions

In this study the EFs of 113 gas- and particle phase PAHs emitted from biomass burning of five globally or regionally important fuels were obtained. Gas-phase emissions contained more PAH mass per fuel mass burned (9.6 ± 1.2 – 42.2 ± 5.4 mg kg⁻¹) than particle phase emissions (1.9 ± 0.4 – 3.0 ± 0.6 mg kg⁻¹). Comparing emissions from different fuels, PAH profiles were similar, but peat smoldering emissions contained more PAHs than those from flaming cheatgrass and ponderosa pine needle combustion. The analysis of 16 EPA PAHs for their carcinogenic potency showed, that particle phase PAHs have significantly larger health effects. However, when emitted into the atmosphere, gas-phase PAHs may be transformed into products with stronger carcinogenic and mutagenic potency (i.e. nitro-PAHs) via photo-

chemical reactions (Atkinson and Arey, 1994; Laskin et al., 2015). The analysis of 113 PAHs showed that some PAH species which are not included into the list of 16 EPA PAHs also have high EFs, but their toxicity is still unknown. PAH carcinogenic potency does not vary significantly between combustion emissions from our fuels and this can be used in toxicity evaluation of similar PAH sources. Particle phase PAHs were also found to be more important than those in the gas phase because of their stronger contribution to the light absorption in the visible range of the spectrum (400 – 700 nm), but chemical reactions that may lead to the formation of more atmospheric BrC species, still need to be studied. The most effective light absorbing (400 – 500 nm) biomass-burning PAHs for all analyzed fuels were methylpyrenes, retene, methylfluoranthenes, perinaphthenone, and acenaphthalene. In this research we were able to explain only 0.03% – 0.16% of biomass-burning BrC absorptivity with that of PAHs. Therefore, future detailed quantitative and spectrophotometric analyses of other possible BrC species (e.g. HULIS, polyphenols, nitrophenols) are needed as well as analysis of secondary atmospheric biomass-burning products.

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References

- Aiken AC, Salcedo D, Cubison MJ, Huffman JA, DeCarlo PF, Ulbrich IM, et al. Mexico City aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) - Part 1: Fine particle composition and organic source apportionment. *Atmos. Chem. Phys.* 2009; 9: 6633-6653.
- Andreae MO, Gelencser A. Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. *Atmos. Chem. Phys.* 2006; 6: 3131-3148.
- Andreae MO, Merlet P. Emission of trace gases and aerosols from biomass burning. *Global Biogeochem. Cycles* 2001; 15: 955-966.
- Arnott WP, Moosmuller H, Rogers CF, Jin TF, Bruch R. Photoacoustic spectrometer for measuring light absorption by aerosol: instrument description. *Atmos. Environ.* 1999; 33: 2845-2852.
- Atkinson R, Arey J. Atmospheric chemistry of gas-phase polycyclic aromatic-hydrocarbons - formation of atmospheric mutagens. *Environ. Health Perspect.* 1994; 102: 117-126.
- Black RR, Aurell J, Holder A, George IJ, Gullett BK, Hays MD, et al. Characterization of gas and particle emissions from laboratory burns of peat. *Atmos. Environ.* 2016; 132: 49-57.
- Bones DL, Henricksen DK, Mang SA, Gonsior M, Bateman AP, Nguyen TB, et al. Appearance of strong absorbers and fluorophores in limonene-O-3 secondary organic aerosol due to NH₄⁺-mediated chemical aging over long time scales. *J. Geophys. Res.-Atmos.* 2010; 115.
- Bruce N, R P-P, Albalak R. Indoor air pollution in developing countries: a major environmental and public health challenge. *Bulletin of the World Health Organization*, 2000.
- Butler JP, Post GB, Liroy PJ, Waldman JM, Greenberg A. Assessment of carcinogenic risk from personal exposure to benzo(a)pyrene in the total human environmental exposure study (THEES). *J. Air Waste Manage. Assoc.* 1993; 43: 970-977.
- Chakrabarty RK, Gyawali M, Yatavelli RLN, Pandey A, Watts AC, Knue J, et al. Brown carbon aerosols from burning of boreal peatlands: microphysical properties, emission factors, and implications for direct radiative forcing. *Atmos. Chem. Phys.* 2016; 16: 3033-3040.
- Chakrabarty RK, Moosmueller H, Chen LWA, Lewis K, Arnott WP, Mazzoleni C, et al. Brown carbon in tar balls from smoldering biomass combustion. *Atmos. Chem. Phys.* 2010; 10: 6363-6370.
- Chen Y, Bond TC. Light absorption by organic carbon from wood combustion. *Atmos. Chem. Phys.* 2010; 10: 1773-1787.
- Chen YJ, Sheng GY, Bi XH, Feng YL, Mai BX, Fu JM. Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. *Environmental Science & Technology* 2005; 39: 1861-1867.
- Chow JC, Watson JG, Chen LWA, Arnott WP, Moosmuller H, Fung K. Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols. *Environ. Sci. Technol.* 2004; 38: 4414-4422.
- Chow JC, Watson JG, Pritchett LC, Pierson WR, Frazier CA, Purcell RG. The DRI thermal optical reflectance carbon analysis system: description, evaluation and applications in U.S. air quality studies. *Atmospheric Environment Part A - General Topics* 1993; 27: 1185-1201.
- Cristale J, Silva FS, Zocolo GJ, Rodrigues Marchi MR. Influence of sugarcane burning on indoor/outdoor PAH air pollution in Brazil. *Environ. Pollut.* 2012; 169: 210-216.
- Dahms CW, Geils BW. An assessment of forest ecosystem health in the Southwest. RMGTR-295, USDA Forest Service, Rocky Mountain Forest and Range Experiment Station, Fort Collins, CO. , 1997.
- Dinar E, Riziq AA, Spindler C, Erlick C, Kiss G, Rudich Y. The complex refractive index of atmospheric and model humic-like substances (HULIS) retrieved by a cavity ring down aerosol spectrometer (CRD-AS). *Faraday Discuss.* 2008; 137: 279-295.
- Duan FK, Liu XD, Yu T, Cachier H. Identification and estimate of biomass burning contribution to the urban aerosol organic carbon concentrations in Beijing. *Atmos. Environ.* 2004; 38: 1275-1282.
- Einfeld W, Ward DE, Hardy C. Effects of fire behavior on prescribed fire smoke characteristics: a case study. *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*. MIT Press, Cambridge, MA, pp. 412-419. 1991.

- Ferek RJ, Reid JS, Hobbs PV, Blake DR, Lioussé C. Emission factors of hydrocarbons, halocarbons, trace gases and particles from biomass burning in Brazil. *J. Geophys. Res.-Atmos.* 1998; 103: 32107-32118.
- Finlayson-Pitts BJ, Pitts JN, Jr. Chemistry of the upper and lower atmosphere: theory, experiments and applications. San Diego, CA: Academic Press, 1999.
- Frandsen WH. The influence of moisture and mineral soil on the combustion limits of smoldering forest duff. *Canadian Journal of Forest Research - Revue Canadienne De Recherche Forestiere* 1987; 17: 1540-1544.
- Freeman DJ, Cattell FCR. Wood-Burning as a source of atmospheric polycyclic aromatic-hydrocarbons. *Environ. Sci. Technol.* 1990; 24: 1581-1585.
- Fujita EM, Zielinska B, Campbell DE, Arnott WP, Sagebiel JC, Mazzoleni L, et al. Variations in speciated emissions from spark-ignition and compression-ignition motor vehicles in California's south coast air basin. *J. Air Waste Manage. Assoc.* 2007; 57: 705-720.
- Gadi R, Singh DP, Saud T, Mandal TK, Saxena M. Emission estimates of particulate PAHs from biomass fuels used in Delhi, India. *Human and Ecological Risk Assessment* 2012; 18: 871-887.
- Graber ER, Rudich Y. Atmospheric HULIS: How humic-like are they? A comprehensive and critical review. *Atmos. Chem. Phys.* 2006; 6: 729-753.
- Harden JW, Trumbore SE, Stocks BJ, Hirsch A, Gower ST, O'Neill KP, et al. The role of fire in the boreal carbon budget. *Global Change Biology* 2000; 6: 174-184.
- Hays MD, Fine PM, Geron CD, Kleeman MJ, Gullett BK. Open burning of agricultural biomass: Physical and chemical properties of particle-phase emissions. *Atmos. Environ.* 2005; 39: 6747-6764.
- IARC. Polynuclear Aromatic Compounds, part 1: chemical, environmental, and experimental data. In: monographs on the evaluation of the carcinogenic risk of chemicals to humans, Vol 32. Lyon:International Agency for Research on Cancer, 1983.
- IARC. Polynuclear Aromatic Compounds, part 2: carbon blacks, mineral oils, and some nitroarenes. In: monographs on the evaluation of the carcinogenic risk of chemicals to humans, Vol 33. Lyon:International Agency for Research on Cancer, 1984.
- Iinuma Y, Brueggemann E, Gnauk T, Mueller K, Andreae MO, Helas G, et al. Source characterization of biomass burning particles: The combustion of selected European conifers, African hardwood, savanna grass, and German and Indonesian peat. *J. Geophys. Res.-Atmos.* 2007; 112.
- Jakovljevic I, Pehnec G, Vadjic V, Sisovic A, Davila S, Beslic I. Carcinogenic activity of polycyclic aromatic hydrocarbons bounded on particle fraction. *Environ. Sci. Pollut. Res.* 2015; 22: 15931-15940.
- Jenkins BM, Jones AD, Turn SQ, Williams RB. Emission factors for polycyclic aromatic hydrocarbons from biomass burning. *Environ. Sci. Technol.* 1996; 30: 2462-2469.
- Kakareka SV, Kukharchyk TI, Khomich VS. Study of PAH emission from the solid fuels combustion in residential furnaces. *Environ. Pollut.* 2005; 133: 383-387.
- Kim KH, Jahan SA, Kabir E. A review of diseases associated with household air pollution due to the use of biomass fuels. *J. Hazard. Mater.* 2011; 192: 425-431.
- Kobziar LN, Godwin D, Taylor L, Watts AC. Perspectives on trends, effectiveness, and impediments to prescribed burning in the southern U.S. *Forests* 2015; 6: 561-580.
- Koren I, Kaufman YJ, Remer LA, Martins JV. Measurement of the effect of Amazon smoke on inhibition of cloud formation. *Science* 2004; 303: 1342-1345.
- Laskin A, Laskin J, Nizkorodov SA. Chemistry of atmospheric brown carbon. *Chem. Rev.* 2015; 115: 4335-4382.
- Lee RGM, Coleman P, Jones JL, Jones KC, Lohmann R. Emission factors and importance of PCDD/Fs, PCBs, PCNs, PAHs and PM10 from the domestic burning of coal and wood in the UK. *Environ. Sci. Technol.* 2005; 39: 1436-1447.
- Lewis K, Arnott WP, Moosmueller H, Wold CE. Strong spectral variation of biomass smoke light absorption and single scattering albedo observed with a novel dual-wavelength photoacoustic instrument. *J. Geophys. Res.-Atmos.* 2008; 113.

- Lewtas J. Air pollution combustion emissions: Characterization of causative agents and mechanisms associated with cancer, reproductive, and cardiovascular effects. *Mutation Research-Reviews in Mutation Research* 2007; 636: 95-133.
- Li XZ, Yang Y, Xu X, Xu CQ, Hong JL. Air pollution from polycyclic aromatic hydrocarbons generated by human activities and their health effects in China. *J. Clean Prod.* 2016; 112: 1360-1367.
- Lobert JM, Warnatz J. Emissions from the combustion process in vegetation, *Fire in the Environment: The Ecological, Atmospheric, and Climatic Importance of Vegetation Fires*, P. J. Crutzen, J. G. Goldammer, 15–37, John Wiley. New York, 1993.
- Lu H, Zhu L, Zhu N. Polycyclic aromatic hydrocarbon emission from straw burning and the influence of combustion parameters. *Atmos. Environ.* 2009; 43: 978-983.
- Malone SL, Kobziar LN, Staudhammer CL, Abd-Elrahman A. Modeling Relationships among 217 Fires Using Remote Sensing of Burn Severity in Southern Pine Forests. *Remote Sensing* 2011; 3: 2005-2028.
- Mastral AM, Callen M, Murillo R. Assessment of PAH emissions as a function of coal combustion variables. *Fuel* 1996; 75: 1533-1536.
- Mastral AM, Callen MS, Murillo R, Garcia T. Combustion of high calorific value waste material: Organic atmospheric pollution. *Environ. Sci. Technol.* 1999; 33: 4155-4158.
- McDonald JD, Zielinska B, Fujita EM, Sagebiel JC, Chow JC, Watson JG. Fine particle and gaseous emission rates from residential wood combustion. *Environ. Sci. Technol.* 2000; 34: 2080-2091.
- Moosmüller H, Chakrabarty RK, Arnott WP. Aerosol light absorption and its measurement: A review. *J. Quant. Spectrosc. Radiat. Transf.* 2009; 110: 844-878.
- Naeher LP, Brauer M, Lipsett M, Zelikoff JT, Simpson CD, Koenig JQ, et al. Woodsmoke health effects: A review. *Inhal. Toxicol.* 2007; 19: 67-106.
- Nguyen TB, Lee PB, Updyke KM, Bones DL, Laskin J, Laskin A, et al. Formation of nitrogen- and sulfur-containing light-absorbing compounds accelerated by evaporation of water from secondary organic aerosols. *J. Geophys. Res.-Atmos.* 2012; 117.
- Nisbet ICT, Lagoy PK. Toxic Equivalency Factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul. Toxicol. Pharm.* 1992; 16: 290-300.
- Oanh NTK, Tipayarom A, Bich TL, Tipayarom D, Simpson CD, Hardie D, et al. Characterization of gaseous and semi-volatile organic compounds emitted from field burning of rice straw. *Atmos. Environ.* 2015; 119: 182-191.
- Oliver WW, Ryker RA. *Silvics of North America. Agriculture Handbook 654.* USDA Forest Service, Washington, D.C., 1990.
- Olsson M. Wheat straw and peat for fuel pellets - organic compounds from combustion. *Biomass & Bioenergy* 2006; 30: 555-564.
- Petry T, Schmid P, Schlatter C. The use of toxic equivalency factors in assessing occupational and environmental health risk associated with exposure to airborne mixtures of polycyclic aromatic hydrocarbons (PAHs). *Chemosphere* 1996; 32: 639-648.
- Pöschl U. Aerosol particle analysis: challenges and progress. *Anal. Bioanal. Chem.* 2003; 375: 30-32.
- Pretsch E, Bühlmann P, Affolter C. *Structure determination of organic compounds: tables of spectral data*: Springer, 2000.
- Ramirez N, Cuadras A, Rovira E, Maria Marce R, Borrull F. Risk assessment related to atmospheric polycyclic aromatic hydrocarbons in gas and particle phases near industrial sites. *Environ. Health Perspect.* 2011; 119: 1110-1116.
- Reid JS, Koppmann R, Eck TF, Eleuterio DP. A review of biomass burning emissions part II: intensive physical properties of biomass burning particles. *Atmos. Chem. Phys.* 2005; 5: 799-825.
- Rein G. Smouldering combustion phenomena in science and technology. *International Review of Chemical Engineering* 2009; 1: 3-18. Copy available at <http://www.era.lib.ed.ac.uk/handle/1842/1152>.
- Rein G. Smouldering fires and natural fuels. *Fire Phenomena and the Earth System*. John Wiley & Sons, 2013, pp. 15-33.

- Robinson MS, Anthony TR, Littau SR, Herckes P, Nelson X, Poplin GS, et al. Occupational PAH exposures during prescribed pile burns. *Ann. Occup. Hyg.* 2008; 52: 497-508.
- Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT. Sources of fine organic aerosol .8. Boilers burning No. 2 distillate fuel oil. *Environ. Sci. Technol.* 1997; 31: 2731-2737.
- Samburova V, Zenobi R, Kalberer M. Characterization of high molecular weight compounds in urban atmospheric particles. *Atmos. Chem. Phys.* 2005; 5: 2163-2170.
- Saxena M, Singh DP, Saud T, Gadi R, Singh S, Sharma SK, et al. Study on particulate polycyclic aromatic hydrocarbons over Bay of Bengal in winter season. *Atmospheric Research* 2014; 145: 205-213.
- Shen G, Xue M, Wei S, Chen Y, Wang B, Wang R, et al. Emissions of parent, nitrated, and oxygenated polycyclic aromatic hydrocarbons from indoor corn straw burning in normal and controlled combustion conditions. *J. Environ. Sci.* 2013; 25: 2072-2080.
- Sidhu S, Gullett B, Striebich R, Klosterman J, Contreras J, DeVito M. Endocrine disrupting chemical emissions from combustion sources: diesel particulate emissions and domestic waste open burn emissions. *Atmos. Environ.* 2005; 39: 801-811.
- Sieg CH, McMillin JD, Fowler JF, Allen KK, Negron JF, Wadleigh LL, et al. Best predictors for postfire mortality of ponderosa pine trees in the intermountain west. *Forest Science* 2006; 52: 718-728.
- Silva FS, Cristale J, Andre PA, Saldiva PHN, Marchi MRR. PM_{2.5} and PM₁₀: The influence of sugarcane burning on potential cancer risk. *Atmos. Environ.* 2010; 44: 5133-5138.
- Simoneit BRT. Biomass burning - A review of organic tracers for smoke from incomplete combustion. *Appl. Geochem.* 2002; 17: 129-162.
- Singh DP, Gadi R, Mandal TK, Saud T, Saxena M, Sharma SK. Emissions estimates of PAH from biomass fuels used in rural sector of Indo-Gangetic Plains of India. *Atmos. Environ.* 2013; 68: 120-126.
- Stocker TF, Qin D, Plattner G-K, Tignor M, Allen SK, Boschung J, et al. IPCC, 2013: Climate Change 2013: The physical science basis. Contribution of working group I to the fifth assessment report of the intergovernmental panel on climate change. Chapter 8: Anthropogenic and Natural Radiative Forcing. In: Cambridge University Press C, United Kingdom and New York, NY, USA, editor, 2013.
- Sun H, Biedermann L, Bond TC. Color of brown carbon: A model for ultraviolet and visible light absorption by organic carbon aerosol. *Geophys. Res. Lett.* 2007; 34.
- Tian J, Chow JC, Cao J, Han Y, Ni H, Chen LWA, et al. A biomass combustion chamber: design, evaluation, and a case study of wheat straw combustion emission tests. *Aerosol and Air Quality Research* 2015; 15: 2104-2114.
- Tiwari M, Sahu SK, Bhangare RC, Ajmal PY, Pandit GG. Estimation of polycyclic aromatic hydrocarbons associated with size segregated combustion aerosols generated from household fuels. *Microchem. J.* 2013; 106: 79-86.
- Tokiwa H, Nakanishi Y, Sera N, Hara N, Inuzuka S. Analysis of environmental carcinogens associated with the incidence of lung cancer. *Toxicol. Lett.* 1998; 99: 33-41.
- Turetsky MR, Benscoter B, Page S, Rein G, van der Werf GR, Watts A. Global vulnerability of peatlands to fire and carbon loss. *Nature Geoscience* 2015; 8: 11-14.
- Updyke KM, Nguyen TB, Nizkorodov SA. Formation of brown carbon via reactions of ammonia with secondary organic aerosols from biogenic and anthropogenic precursors. *Atmos. Environ.* 2012; 63: 22-31.
- USEPA. <http://www.epa.gov/north-birmingham-project/polycyclic-aromatic-hydrocarbons-pahs-fact-sheet>, 2013.
- Vineis P, Husgafvel-Pursiainen K. Air pollution and cancer: biomarker studies in human populations. *Carcinogenesis* 2005; 26: 1846-1855.
- W.H.O. Household air pollution and health. World Health Organization. Fact sheet N#292 <http://www.who.int/mediacentre/factsheets/fs292/en/>, 2016.

- Wang J, Li X, Jiang N, Zhang WK, Zhang RQ, Tang XY. Long term observations of PM_{2.5}-associated PAHs: Comparisons between normal and episode days. *Atmos. Environ.* 2015; 104: 228-236.
- Watts AC. Organic soil combustion in cypress swamps: Moisture effects and landscape implications for carbon release. *Forest Ecology and Management* 2013; 294: 178-187.
- Watts AC, Kobziar LN. Smoldering combustion and ground fires: ecological effects and multi-scale significance. *Fire Ecology* 2013; 9: 124-132.
- Westerling AL, Hidalgo HG, Cayan DR, Swetnam TW. Warming and earlier spring increase western US forest wildfire activity. *Science* 2006; 313: 940-943.
- Wilcke W. SYNOPSIS Polycyclic Aromatic Hydrocarbons (PAHs) in Soil — a Review. *Journal of Plant Nutrition and Soil Science* 2000; 163: 229-248.
- Wild SR, Berrow ML, McGrath SP, Jones KC. Polynuclear aromatic hydrocarbons in crops from long-term field experiments amended with sewage sludge. *Environ. Pollut.* 1992; 76: 25-32.
- Xue WL, Warshawsky D. Metabolic activation of polycyclic and heterocyclic aromatic hydrocarbons and DNA damage: A review. *Toxicol. Appl. Pharmacol.* 2005; 206: 73-93.
- Yan J, Wang L, Fu PP, Yu HT. Photomutagenicity of 16 polycyclic aromatic hydrocarbons from the US EPA priority pollutant list. *Mutation Research-Genetic Toxicology and Environmental Mutagenesis* 2004; 557: 99-108.
- Yu L, Smith J, Laskin A, Anastasio C, Laskin J, Zhang Q. Chemical characterization of SOA formed from aqueous-phase reactions of phenols with the triplet excited state of carbonyl and hydroxyl radical. *Atmos. Chem. Phys.* 2014; 14: 13801-13816.
- Yu M-H, Tsunoda H, Tsunoda M. *Environmental toxicology: biological and health effects of pollutants*: CRC Press, 2011.
- Zaccone C, Rein G, D'Orazio V, Hadden RM, Belcher CM, Miano TM. Smouldering fire signatures in peat and their implications for palaeoenvironmental reconstructions. *Geochim. Cosmochim. Acta* 2014; 137: 134-146.
- Zhong M, Jang M. Dynamic light absorption of biomass-burning organic carbon photochemically aged under natural sunlight. *Atmos. Chem. Phys.* 2014; 14: 1517-1525.
- Zielinska B, Sagebiel J, McDonald JD, Whitney K, Lawson DR. Emission rates and comparative chemical composition from selected in-use diesel and gasoline-fueled vehicles. *J. Air Waste Manage. Assoc.* 2004; 54: 1138-1150.