



Polycyclic aromatic hydrocarbons in biomass-burning emissions and their contribution to light absorption and aerosol toxicity



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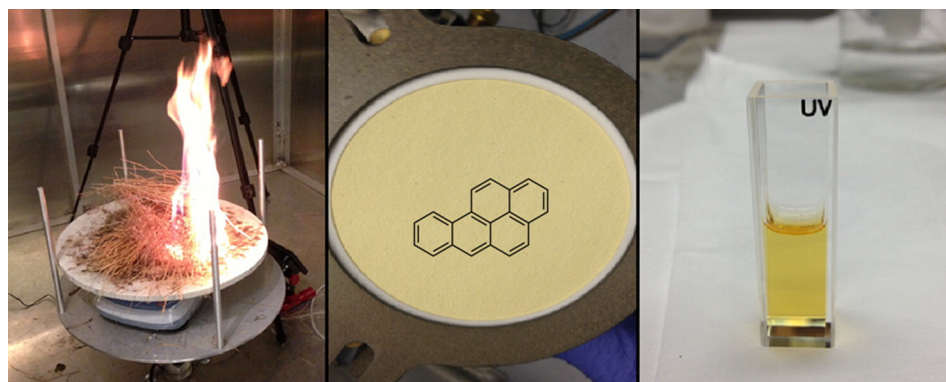
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HIGHLIGHTS

- 113 PAHs and PAH derivatives were analyzed in gas and particle phase combustion emissions of five different biomass fuels.
- Light absorption properties of individual biomass-burning PAHs were analyzed.
- Emission factors of the most effective light absorbing brown carbon PAHs were determined in biomass-emissions.
- Benzo(a)pyrene and naphthalene contributed the most to the PAH carcinogenic potency of biomass-burning emissions.

GRAPHICAL ABSTRACT



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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 $1.9 \pm 0.43.0 \pm 0.6$ and 9.6 ± 1.2 – 42.2 ± 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 the total PAH light absorption with 17.2%, 3.3 to 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

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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.

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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., 2004b), waste (Mastral et al., 1999; Sidhu et al., 2005), crop/agricultural waste (Lu et al., 2009; Oanh et al., 2015), and animal dung (Gadi et al., 2012; Singh et al., 2013; Tiwari et al., 2013). 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 Section 2.1.1): 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) estimate the carcinogenic potency of the emitted PAHs; and iv) determine the contribution of PAHs to the biomass-burning BrC optical properties using spectrophotometric and photoacoustic techniques.

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., 1993; Chow et al., 2004). Teflon-impregnated glass fiber (TIGF) filters ($d = 100$ mm, Fiber Film T60A20, Pall Life Sciences) were used to collect PM for organic analysis.

2.1.1. Fuel selection and preparation

In the present study, all peats combusted had a fuel moisture content of 25% by mass. Chemical and spectrometry analyses of emissions from the combustion of fuels with different moisture contents are a focus of additional studies, e.g., Chakrabarty et al. (2016). Detailed information on fuels selection is presented in Supplementary Material. Briefly, Siberian peat represents large peatlands in Russia (Pskov region), which are particularly vulnerable to long fire seasons (Turetsky et al., 2015) and could emit larger amounts of carbon into the atmosphere close to polar regions (Harden et al., 2000). Alaskan peat from black spruce (*Picea mariana*) forests is another representative of high-latitude regions. 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 also chosen for this study (Watts, 2013; Watts and Kobziar, 2013).

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 were chosen to represent ponderosa pine forests that dominate 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 fires (Dahms and Geils, 1997). Cheatgrass (*Bromus tectorum*) is a grass native to Europe that has become an established invasive species across wide areas of the western USA; it also contributes to fires and fire frequency in the Western USA.

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 (0.01 g 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).

2.2.1. Methods

Pre-cleaned quartz filters collected with a medium flow sampler at a flow rate of 0.11 m³ 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 °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: 80 °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 °C, then filtered with a 0.2-μm 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 N₂ stream and stored at -20 °C until analyses.

Biomass-burning sample extracts were analyzed with electron impact gas chromatography mass spectrometry (GC-MS) (Fujita et al., 2007; Rinehart et al., 2006; Zielinska et al., 2004a; Zielinska et al., 2004b). 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:

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

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). The limit of detection (LOD) for analyzed PAHs varied between 0.02 and 0.05 ng μL⁻¹ (see Table S1 in the Supplemental Material). Recovery rates for 18 standard PAHs were 71–99%.

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 S2, Supplementary Material).

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,

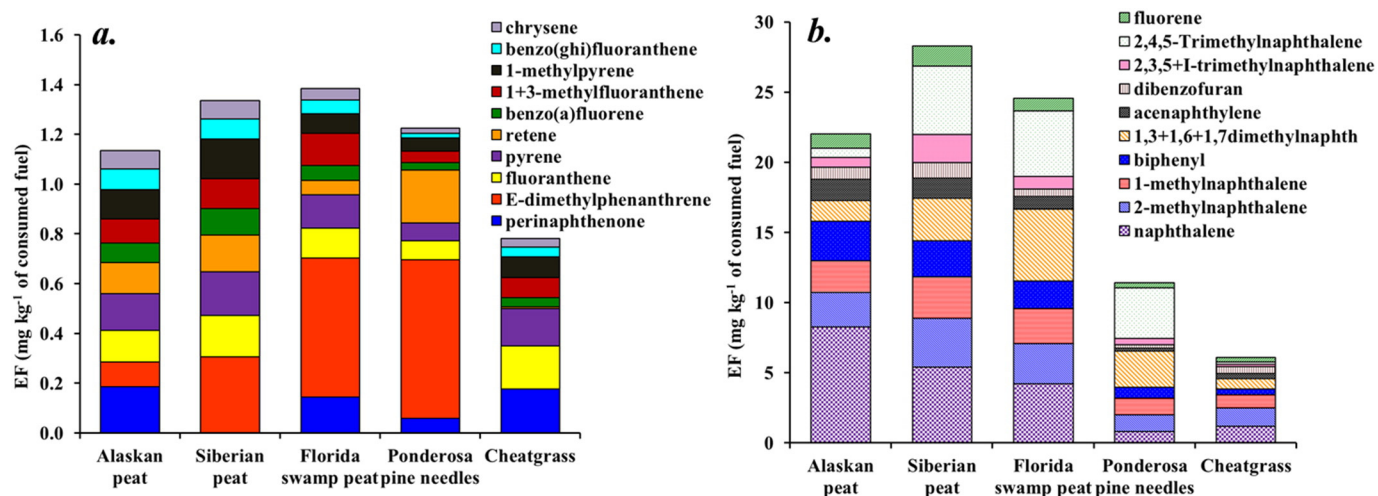


Fig. 1. EFs of the ten most abundant PAHs by mass detected (a) in particle-phase (filter samples) and (b) gas-phase (XAD samples) biomass-burning emissions from five different biomass fuels; the standard deviations were calculated based on three replicate burns of one fuel and accounted on average $20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

benzanthrone, quinolone, dibenzofuran; Table S2). 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.

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 and $3.0 \pm 0.6 \text{ mg kg}^{-1}$ 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 $42.2 \pm 5.4 \text{ mg kg}^{-1}$. 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 leaves) 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; Zaccione 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 CO_2 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)fluorene, 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,

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

Fuel	Particle-phase					Gas-phase		
	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

and Florida swamp peat). The top ten particle-phase PAHs were high molecular weight species with 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 (Figs. 1b and 2b): naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, 1,3 + 1,6 + 1,7-dimethylnaphthalene, acenaphthylene, dibenzofuran, 2,3,5 + 1-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 S3), 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 S3), 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.

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: $0.61 \pm 0.07 \text{ mg kg}^{-1}$, Siberian: $0.69 \pm 0.08 \text{ mg kg}^{-1}$, Florida: $0.51 \pm 0.06 \text{ mg kg}^{-1}$), 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 $1.69 \pm 0.28 \text{ mg kg}^{-1}$ 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).

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 ($0.29 \pm 0.04 \text{ mg kg}^{-1}$) 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 S5–S6 (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.

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 ± 1.6 to $51.8 \pm 8.4 \text{ mg kg}^{-1}$ for gas and 3.3 ± 0.5 to $17.9 \pm 2.7 \text{ mg kg}^{-1}$ 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,

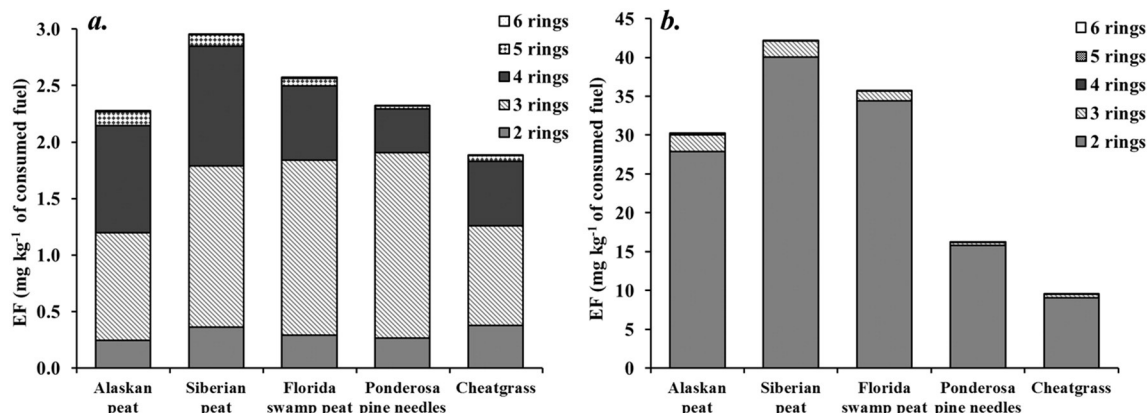


Fig. 2. EFs of two, three, four, five, and six rings PAHs in (a) particle- and (b) gas-phase biomass-burning emissions obtained for five different fuels.

Table 2Concentrations of PAHs obtained in the present study and compared with results reported in the literature. Units: EF PAHs (mg kg^{-1}).

Fuel type	$\sum$ PAHs particle/gas	$\sum_{16}$ 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	$\sum_{113} 2.28/30.27$	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	$\sum_{113} 2.96/42.2$	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	$\sum_{113} 2.57/35.8$	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	$\sum_{19} 20/-$	17.83 ^a /-	ND/-	0.43/-	ND/-	ND/-	ND/-	ND/-	linuma et al. (2007)
German peat	$\sum_{19} 28/-$	25.19 ^a /-	ND/-	0.49/-	ND/-	ND/-	ND/-	ND/-	
NC Peat I	-	$\sum_{g/p} 74.1$	$\sum_{g/p} 0.32$	$\sum_{g/p} 0.66$	$\sum_{g/p} 0.04$	$\sum_{g/p} 0.31$	$\sum_{g/p} 0.23$	$\sum_{g/p} 0.17$	Black et al. (2016)
NC Peat II	-	$\sum_{g/p} 42.9$	$\sum_{g/p} 0.21$	0.49	$\sum_{g/p} 0.04$	$\sum_{g/p} 0.21$	$\sum_{g/p} 0.11$	$\sum_{g/p} 0.09$	
Ponderosa pine needles	$\sum_{113} 2.32/16.2$	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	$\sum_{g/p} 28.96^b$	$\sum_{g/p} 9.73$	$\sum_{g/p} 0.019$	$\sum_{g/p} 0.11$	$\sum_{g/p} \text{ND}$	$\sum_{g/p} 0.037$	$\sum_{g/p} 0.039$	$\sum_{g/p} \text{ND}$	Jenkins et al. (1996)
Pine	$\sum_{19} 1.4/-$	1.252 ^a /-	0.11/-	0.097/-	0.0087/-	0.11/-	0.033/-	0.045/-	linuma et al. (2007)
Cheatgrass	$\sum_{113} 1.88/9.57$	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	$\sum_{19} 5.6/-$	3.44 ^a /-	0.5/-	0.15/-	0.018/-	0.18/-	0.28/-	0.11/-	linuma et al. (2007)

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).

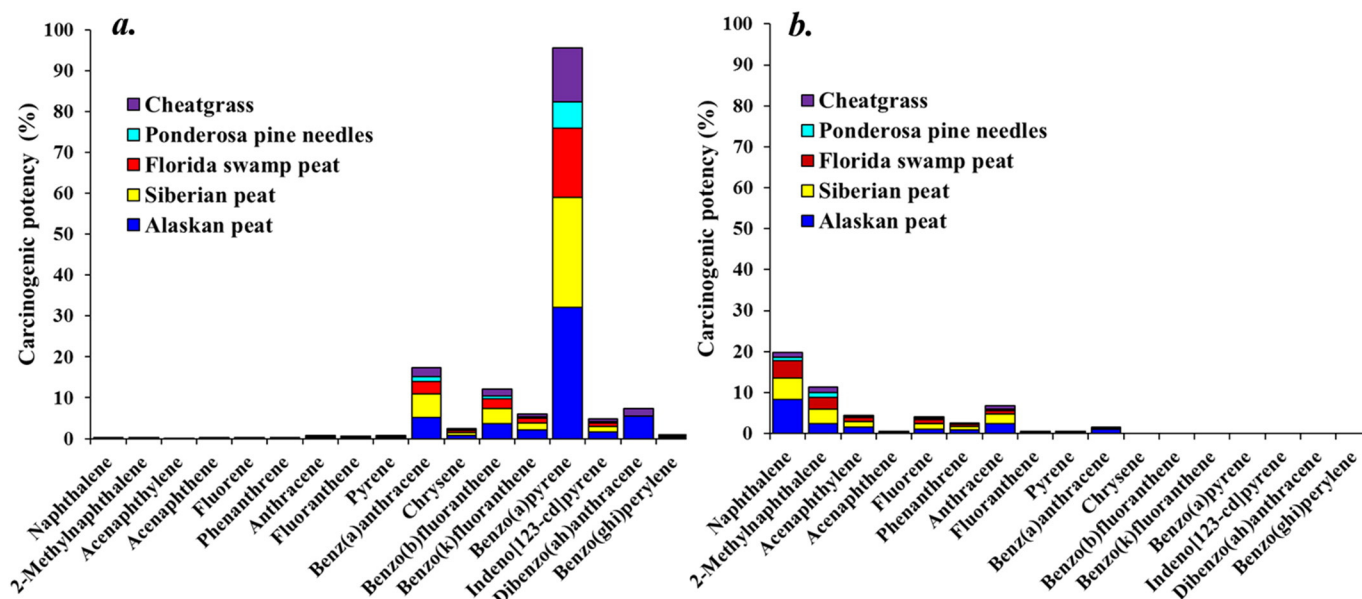
NC Peat I – Alligator River National Wildlife Refuge (Eastern North Carolina, USA), NC Peat II – Pocosin Lakes National Wildlife Refuge (Eastern North Carolina, USA).

^a Concentrations of naphthalene, acenaphthylene, and acenaphthene are not included.^b 16 standard EPA PAHs plus naphthalene and 2-methylnaphthalene.

methylpyrenes, methylfluoranthenes, 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. linuma 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 (linuma 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; Naehar 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).

**Fig. 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.

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.

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 peat, 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).

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 toward 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 ($\lambda < 300 \text{ nm}$) is not be considered. Comparing values of MAE_{bulk} between particle (Fig. 5a) and gas (Fig. 5b) phases at $\lambda > 350 \text{ nm}$, 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 $MAE_{bulk} > 1 \text{ m}^2 \text{ g}^{-1}$. 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 and 600 nm with MAE_{bulk} between 0.001 and $0.1 \text{ m}^2 \text{ g}^{-1}$ 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 $> 400 \text{ nm}$ (Dinar et al., 2008). The spectra obtained for biomass-burning PAHs in the present research (Figs. 5 and 6) display more absorbance at shorter wavelengths (200–400 nm); however, several PAHs showed absorption above 400 nm, such as methylpyrenes ($MAE_{bulk} = 0.137 \text{ m}^2 \text{ g}^{-1}$ at 500 nm), methylfluoranthenes ($MAE_{bulk} = 0.031 \text{ m}^2 \text{ g}^{-1}$ at 500 nm), perinaphthenone ($MAE_{bulk} = 0.075 \text{ m}^2 \text{ g}^{-1}$ at 450 nm), retene ($MAE_{bulk} = 0.138 \text{ m}^2 \text{ g}^{-1}$ at 450 nm), acenaphthalene ($MAE_{bulk} = 0.034 \text{ m}^2 \text{ g}^{-1}$ at 450 nm), and 9-fluorenone ($MAE_{bulk} = 0.019 \text{ m}^2 \text{ g}^{-1}$ 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 3.3). PAHs were apportioned into two groups based on their solar-spectrum-weighted MAE_{bulk} (Fig. 4 and Table S4 in Supplementary Material). The obtained $MAE_{bulk,av}$ ranged from 2×10^{-5} to $2.7 \text{ m}^2 \text{ g}^{-1}$.

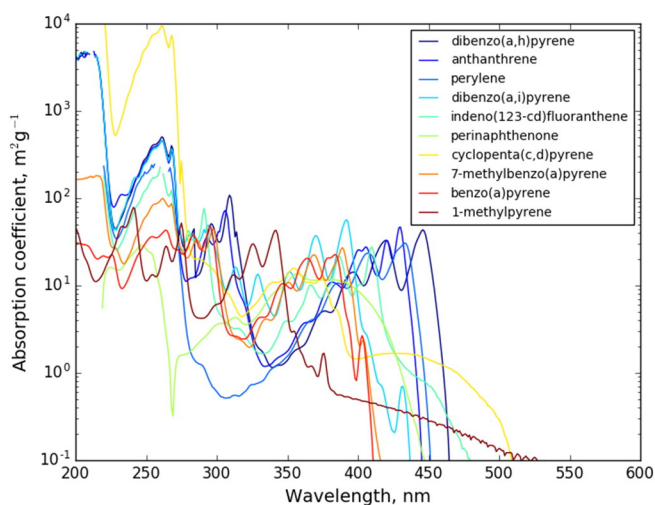


Fig. 4. Bulk mass absorption efficiency MAE_{bulk} for the ten most efficient light-absorbing BrC PAH standards.

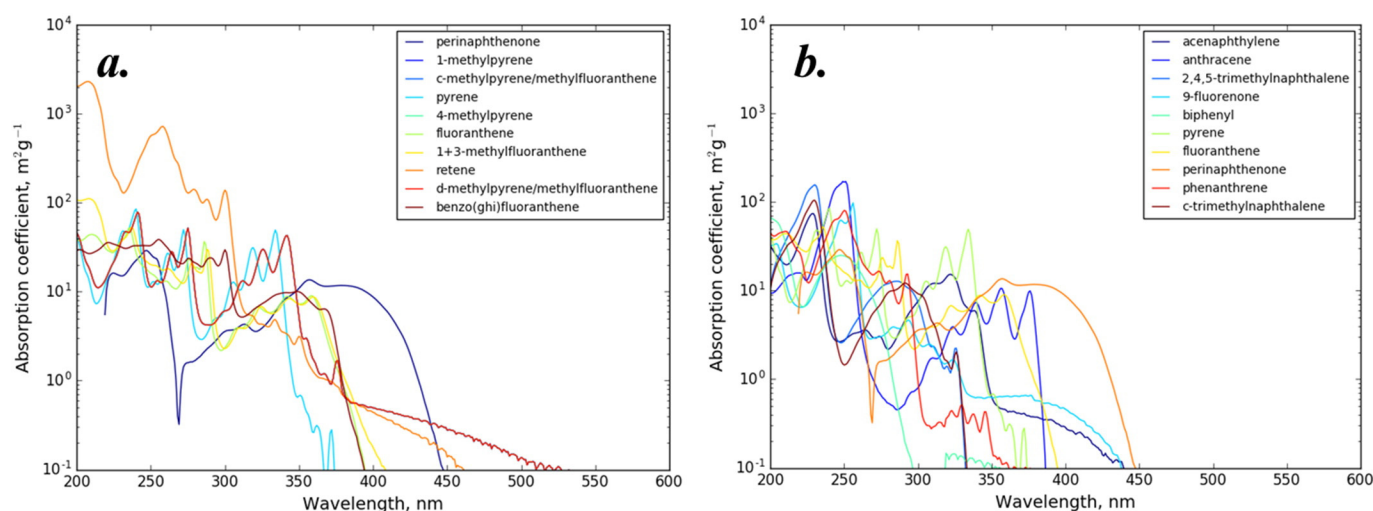


Fig. 5. The most efficient light-absorbing BrC PAHs identified and quantified in (a) particle- and (b) gas-phase of biomass-burning emissions.

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 to $2.33 \pm 0.45 \text{ mg kg}^{-1}$ (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.

Figs. 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 $\text{MAE}_{\text{bulk,av}}$ and relatively high EFs (EFs range: 0.014 ± 0.005 and $0.16 \pm 0.07 \text{ mg kg}^{-1}$). The top ten particle-phase BrC PAHs also include perinaphthenone (EFs: 0.06 ± 0.01 – $0.19 \pm 0.05 \text{ mg kg}^{-1}$, except for Siberian peat fuel emissions that have perinaphthenone concentrations below detection limit), fluoranthene (0.08 ± 0.01 to $0.17 \pm 0.03 \text{ mg kg}^{-1}$), pyrene (0.07 ± 0.01 to $0.18 \pm 0.03 \text{ mg kg}^{-1}$), retene (0.06 ± 0.02 to $0.15 \pm 0.05 \text{ mg kg}^{-1}$), and benzo(ghi)fluoranthene (0.018 ± 0.005 to $0.08 \pm 0.02 \text{ mg kg}^{-1}$) (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 ($4.9 \pm 0.8 \text{ mg kg}^{-1}$), Florida swamp peat ($4.7 \pm 0.7 \text{ mg kg}^{-1}$), and ponderosa pine needles ($3.6 \pm 0.6 \text{ mg kg}^{-1}$), while biphenyl was the most abundant BrC PAH in Alaskan peat and cheatgrass emissions with EFs $2.8 \pm 0.2 \text{ mg kg}^{-1}$.

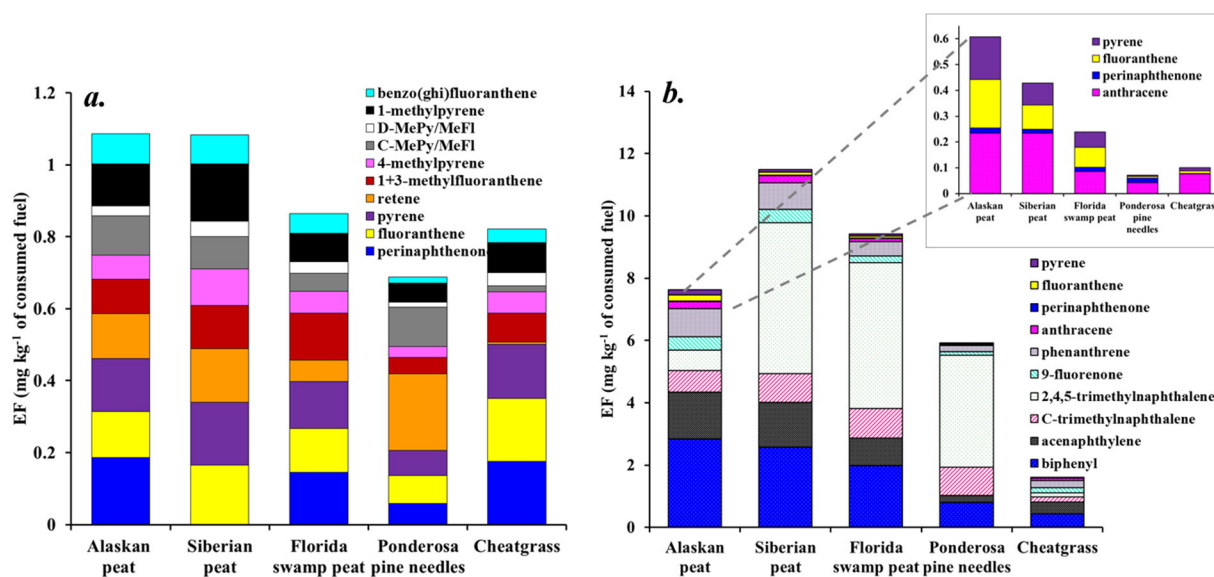


Fig. 6. Emission factors of the ten most abundant light-absorbing BrC PAHs detected (a) in particle-phase (filter samples) and (b) gas-phase (XAD samples) biomass-burning emissions of five different biomass fuels; the standard deviations were calculated based on three replicate burns of one fuel and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

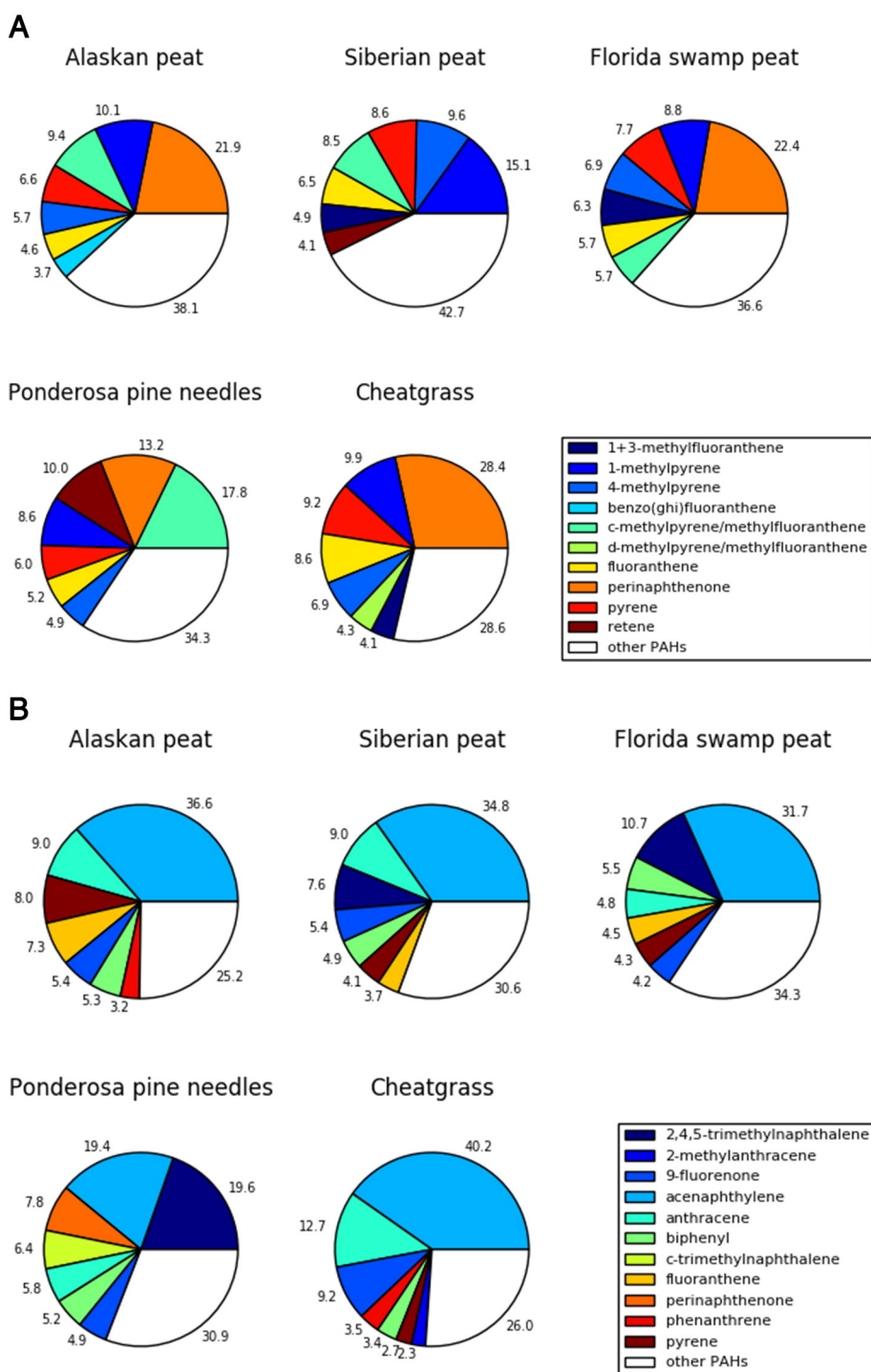


Fig. 7. a. Contribution of top ten BrC PAHs to the total particle phase PAH absorptivity. b. Contribution of top ten BrC PAHs to the total gas phase PAH absorptivity.

and $0.42 \pm 0.03 \text{ mg kg}^{-1}$, 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 to $42.2 \pm 5.4 \text{ mg kg}^{-1}$) than particle phase emissions (1.9 ± 0.4 to $3.0 \pm 0.6 \text{ mg kg}^{-1}$). 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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.06.026>.

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