1 Volatile and semivolatile organic compounds in laboratory peat fire emissions

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Abstract

In this study, volatile and semi-volatile organic compound (VOCs and SVOCs) mass emission factors were determined from laboratory peat fire experiments. The peat samples originated from two National Wildlife Refuges on the coastal plain of North Carolina, U.S.A. Gas- and particle-phase organic compounds were quantified by gas chromatography-mass spectrometry and by high pressure liquid chromatography. Hazardous air pollutants (HAPs) accounted for a large fraction (~60 %) of the speciated VOC emissions from peat burning, including large contributions of acetaldehyde, formaldehyde, benzene, toluene, and chloromethane. In the fine particle mass (PM_{2.5}), the following organic compound classes were dominant: organic acids, levoglucosan, *n*-alkanes, and *n*-alkenes. Emission factors for the organic acids in PM_{2.5} including *n*-alkanoic acids, *n*-alkenoic acids, *n*-alkanedioic acids, and aromatic acids were reported for the first time for peat burning, representing the largest fraction of organic carbon (OC) mass (11-12 %) of all speciated compound classes measured in this work. Levoglucosan contributed to 2-3 % of the OC mass, while methoxyphenols represented 0.2-0.3 % of the OC mass on a carbon mass basis. Retene was the most abundant particulate phase polycyclic aromatic hydrocarbon (PAH). Total HAP VOC and particulate PAH emissions from a 2008 peat wildfire in North Carolina were estimated, suggesting that peat fires can contribute a large fraction of state-wide HAP emissions.

Keywords: biomass burning, peat, organic soil, volatile organic compounds, emission factors

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44 **1. Introduction**

45 Peat fires are becoming a greater source of concern due to the immense potential of the
46 resultant carbon emissions to influence climate (Frolking et al., 2011; Sherwood et al., 2013;
47 Turetsky et al., 2011). Peat is an accumulation of partially decayed plant organic matter formed
48 under water saturated wetland conditions over millennial timescales. Peatlands are considered an
49 important global carbon sink, covering ~3 % of the world's land surface yet storing
50 approximately one third of surface terrestrial organic carbon (Joosten and Clark, 2002).

51 Peatlands are expected to become more vulnerable to wildfires due to changing land use
52 activities (i.e. deforestation, drainage, land clearing fires) and exacerbated drought conditions
53 due to climate change. Increased degradation of peat (e.g., from peat fires) and resulting carbon
54 emissions may alter the role of peatlands in the global carbon cycle from a net carbon sink to a
55 source to the atmosphere with potentially significant consequences for climate change. Peat
56 wildfires are characterized as low temperature, smoldering combustion fires that are extremely
57 difficult to extinguish and can continue smoldering for long periods (i.e. weeks to years).
58 Because of these characteristics, they are deemed particularly pernicious environmental
59 disturbances relative to other vegetation fire events. Furthermore, peat fires can propagate
60 laterally and vertically, burning organic matter including underlying organic soil at greater
61 depths and consuming up to 100 times more fuel per unit area than flaming fires (Rein, 2013).

62 Previous studies on peat fires have shown that these events can lead to dramatic negative
63 health impacts. For example, the 1997/1998 Indonesian fire event led to an extreme smoke haze
64 event causing severe deleterious human health effects (Kunii et al., 2002). Another peat fire in
65 2008 occurred in eastern North Carolina over a period of several months, producing a large
66 regional smoke haze pollution event. Rappold et al. (2011) found that this peat fire event led to
67 significant increases in emergency department visits for respiratory and cardiovascular health
68 problems. Furthermore, Kim et al. (2014) has demonstrated that exposure of ambient PM
69 sampled from this 2008 peat wildfire event resulted in significant pulmonary and cardiovascular
70 effects in mice.

71 Biomass burning smoke has been shown to contain a substantial number of hazardous gas-
72 and particle-phase compounds including monoaromatic VOCs, aldehydes, 1,3-butadiene,

polycyclic aromatic hydrocarbons, and chlorinated organics (Naeher et al., 2007). Currently, the research devoted to quantifying emission factors for these hazardous pollutants from peat fires is sparse. However, air quality models require accurate emission factor data for speciated gas and particulate pollutants, particularly those on the U.S. EPA list of hazardous air pollutants (HAPs) (U.S. EPA, 2005), to predict the impact of peat fires on air quality and human health. Detailed speciation of smoke PM also allows for more accurate source apportionment of PM.

The objective of this work is to quantify gas and particulate emission factors for temperate peat fires. Small-scale laboratory burn experiments were conducted with peat samples from North Carolina, U.S., to determine emission factors for a range of trace gas and particulate species. Emission factors for criteria pollutants (i.e. CO₂, CO, total hydrocarbons, NO_x), fine particulate matter (PM_{2.5}) mass, elemental carbon (EC), organic carbon (OC) and semivolatile components will be reported in a companion paper (Black et al., 2015). This paper focuses on the chemical characterization of PM_{2.5} and speciated VOC emissions, with an emphasis on hazardous air pollutants resulting from peat burning.

2. Materials and methods

A detailed description of the experimental methods for the peat sample collection and peat burning experiments used in this study have been provided in a companion paper (Black et al., 2015). Here, a brief summary of general experimental procedures is given along with a detailed account of analytical procedures followed for the speciated gas- and particle-phase organic compounds.

2.1. Peat sampling

Peat core samples were taken from two wildlife refuge sites located on the coastal plains of Eastern North Carolina, U.S: Alligator River National Wildlife Refuge (AR peat) and Pocosin Lakes National Wildlife Refuge (PL peat). Further information regarding prevailing vegetation types at these wetland sites has been provided elsewhere (Geron and Hays, 2013). Peat core samples of 15 cm diameter and 20 to 25 cm depth were taken from each site. The peat samples were dried in an oven for 24 hours at 100 °C and stored intact until used. The carbon content for the two samples was 30 % and 28 %, and chlorine content was 187 ppm and 455 ppm for PL and

AR samples, respectively. Chemical analyses of the peat samples are discussed in greater detail elsewhere (Black et al., 2015).

2.2. *Laboratory burning experiment*

Peat core samples were burned in U.S. Environmental Protection Agency's Open Burn Test Facility (OBTF) at the Research Triangle Park, NC, location described in detail elsewhere (Black et al., 2011). A high volume fan facilitated the introduction of ambient air into the OBTF chamber at a volume exchange time of ~90 s to maintain oxygen levels representative of open burning. Each burn experiment was initiated by placing a peat core (1.5 to 2.5 kg mass) housed inside a stove pipe on a top pan balance and briefly igniting the top center surface by propane torch. Continuous emissions sampling of CO₂, CO, O₂ and total hydrocarbons (THC) and time-integrated sampling of VOCs, and PM_{2.5} commenced approximately one minute after fire ignition. The fires were characterized by a brief flaming phase followed by an extended period of smoldering. Smoke sampling of the peat burns continued for approximately 5 to 7 h. Laboratory burns were carried out in triplicate for both of the two peat sample sites (Pocosin Lakes and Alligator River).

2.3. *Sampling procedures*

A detailed description of the sampling methods for the CEM measurements can be found in Black et al. (2015). The following outlines the sampling procedure for VOC, carbonyl and PM_{2.5} sampling. Smoke emissions were sampled through a heated line (~110 °C) with the inlet placed above the sample inside a metal hood. The sampling line was split to a SUMMA canister and a 2,5-dinitrophenylhydrazine (DNPH)-coated cartridge (Sigma-Aldrich Corp., St. Louis, MO, U.S.) for quantification of VOCs and carbonyls, respectively. A quartz filter (Pall Corp., Port Washington, NY, U.S.) was placed before the canister/cartridge sampling trains to reduce PM contamination of samples. Time-integrated canister and DNPH cartridge samples were taken each hour. A custom-made fitting with a critical orifice controlled sampling flow rate (~70 standard cm³ min⁻¹) to a pre-cleaned and evacuated SUMMA canister. Canisters were filled to below ambient pressure, typically to ~0.6 atm, during one hour of sampling time. The flow through the DNPH cartridge was controlled by a Tylan mass flow controller connected to a pump (Baldor Electric Corp., Fort Smith, AR, U.S.). Flow rates through the cartridge in the range of 0.44 to 0.47 L min⁻¹ were measured every day with a Gilibrator Air Flow Calibration

System (Sensidyne LP, St. Petersburg, FL, U.S.). The remaining pump flow was diverted through a Tylan mass flow controller that was connected directly to the sample line behind the filter to increase the flow rate through the canister/cartridge sampling line by an additional ~3 standard L min⁻¹. Due to sampling issues during the initial tests, carbonyl sampling was conducted for four experiments, and VOC sampling was conducted for five experiments. Background canister and DNPH cartridge samples were taken between experiments. A set of canister and cartridge field blank samples was taken each experiment day.

PM_{2.5} sampling was conducted during the burn experiments for chemical speciation. The PM_{2.5} impactor with quartz filter was collocated with the PM_{2.5} impactor containing polytetrafluoroethylene (PTFE) filter (Pall Corp., Port Washington, NY, U.S.) samples that were used to determine PM_{2.5} mass. A Leland Legacy sample pump (SKC Inc., Eighty Four, PA, U.S.) pulled sample through the impactors at a flow rate of 13 L min⁻¹. Two filter samples were taken for each half of a burn experiment. Filters were stored in a freezer at -50 °C until analysis.

2.4. Sample analysis

A detailed description of the analytical methods for the VOC and carbonyl analysis was reported previously (George et al., 2014). VOC concentrations were determined in the canisters by GC-MS. All canisters were analyzed one day after sample collection. The cartridges were refrigerated (~5 °C) until analysis and were extracted within eight days and analyzed within ten days of sample collection. The cartridges were extracted with Burdick & Jackson carbonyl-free acetonitrile (VWR International, Radnor, PA, U.S.) with final extract volume of 5.0 mL. The derivatized carbonyls were quantified using high performance liquid chromatography (HPLC) with UV detection. The MDLs for VOC analysis ranged from 6 to 50 ppt. For carbonyl analysis, the MDLs were in the range 5.5 to 51.4 ng/cartridge. Acetonitrile was not included in the VOC target analyte list due to high background levels. PM_{2.5} quartz filters were used to quantify organic PM components. Filter samples were solvent extracted and analyzed by GC/MS. Similar analytical procedures for organic compound speciation in PM from previous work (Hays et al., 2002; Hays et al., 2011) were followed with some modifications that are detailed in the Supporting Information.

2.5. Emission factor calculation

Emission factors, defined as mass of compound emitted per mass of dry fuel burned in g/kg, were calculated from the measurements using Equation (1) based on the carbon mass balance approach (Andreae and Merlet, 2001).

$$EF_x = \frac{C_x \times Q \times t}{M_{fb}} \quad (1)$$

The mass of a given compound X emitted was determined from the concentration of compound X, or C_x (g/m³), the dilution flow rate Q (m³/min), and the sampling time t (min). The dry mass of fuel burned M_{fb} (kg) was calculated from the carbon fraction of the fuel and total carbon emitted over the sampling time t calculated as determined from the real-time continuous emission monitor (CEM) measurements of CO₂, CO, and THC. PM_{2.5} carbon emissions were not included because they accounted for less than 0.1 % of the carbon emissions.

3. Results and Discussion

3.1. Volatile organic compounds

Emission factors for 93 VOCs were measured from both peat types, with 49 VOCs above the quantitation level for at least one sample. All VOC emission factor data for both peat fuels are included in Table S3 in the Supporting Information. Figure 1 shows the highest mean emission factors averaged by each peat fuel for noncarbonyl VOCs (Fig. 1A) and carbonyls (Fig. 1B). Major noncarbonyl VOCs with the highest emissions from peat burning included alkenes (e.g. propylene, 1, 3-butadiene), aromatics (e.g. benzene, toluene, ethylbenzene, and xylenes (BTEX)), alkanes (C₆ and C₇), and chloromethane. This work is consistent with measurements of elevated concentrations of chloromethane and BTEX during a peat fire episode in Australia (Blake et al., 2009). Nearly all of the target carbonyls were detected including saturated C₁-C₆ aldehydes, where the highest carbonyl emissions from peat burning were from acetaldehyde, acetone, and formaldehyde. Carbonyls constituted nearly half (47-48 %) of total measured mean VOC emissions for both peat fuels. Compounds marked with an asterisk in Figure 1 and italicized compounds in Table S3 are included in the U.S. EPA list of HAPs (U.S. EPA, 2005). These HAPs represented approximately 60% by mass of the mean speciated VOC emissions, where the major HAP emissions from peat burning include benzene, toluene, chloromethane, acetaldehyde and formaldehyde.

On a carbon mass basis, the VOC emissions from AR and PL peat represented 1.0 % and 1.3 % of total carbon emitted during combustion, respectively. VOC emission profiles including all measured VOCs for the two peat fuels were strongly linearly related ($R^2 = 0.93$), which may be due to similar combustion conditions and similar fuel compositions. Furthermore, the sum of the speciated VOC emissions for PL peat ($\Sigma\text{VOCs EF} = 5 \pm 2$ g/kg) burning was similar to that of AR peat ($\Sigma\text{VOCs EF} = 4 \pm 1$ g/kg). This observation may be linked to the similar carbon fraction for the two peat samples (30 % w/w for PL peat and 28 % w/w for AR peat). As a notable exception, the average chloromethane emission factor and its relative contribution to total VOC emissions for AR was approximately a factor of two higher than for PL. This observation is consistent with the factor of ~ 2.4 higher chlorine content of AR peat, which is likely due to the shorter distance of the location of AR peat from the Atlantic Ocean compared to PL peat (Black et al., 2015).

THC measurements of fire emissions are generally assumed to be a reliable indicator of the measured speciated VOC emissions. Therefore, the sum of VOC emissions were compared with THC measurements to evaluate this assumption. Figure 2 relates EFs of ΣVOCs on a carbon mass basis to EFs from THC carbon mass for both peat fuels for experiments where carbonyl and non-carbonyl VOC emissions data were available. Figure 2 shows that the VOC and THC carbon mass exhibited a strong linear relationship for the first three hours of the peat burn experiments. During the second half of the experiments (4 to 7 h), the VOC to THC carbon mass ratios were much smaller, and the EFs were not linearly related. As noted in Black et al. (2015), the fuel mass consumption rates steadily decreased over time during the peat burns, which has been taken into account in the emission factor calculations. Nevertheless, the decreasing fuel consumption rates with time may be associated with changes in combustion reaction dynamics that control VOC emission factors over time. One possible explanation for this observation is that the speciated VOC emissions in this study may have decreased more quickly than THC emissions during the course of the fire. The THC emissions included methane, which was not measured separately here. Therefore, the influence of variability in methane emissions during the study is unclear.

Figure 2. Comparison of emission factors for sum of speciated VOCs (Σ VOCs) with emission factors for THC, where both sets of data are on a carbon mass basis. Lines represent simple linear regression fits to data for 0-3 h samples and 4-7 h samples.

Many of the major VOCs measured in this work were also detected by Hatch et al. (2015) from Indonesian peat burning emissions. A comparison of EFs from this study with those reported in Hatch et al. (2015) indicated that Hatch et al. measured approximately 4-15 times higher EFs for the compounds shown in Fig. 1A, with the exception of benzene, which was within 20 %. Based on observations noted above regarding the effect of fuel carbon content on VOC emissions, higher VOC EFs from the Indonesian peat (~60 % carbon weight fraction) would be expected. For nearly all of the carbonyls listed in Fig. 1B, however, EFs reported in Hatch et al. (2015) were lower by up to an order of magnitude, likely due to low trapping efficiency for light and oxygenated VOCs during sampling in that work as noted by Hatch et al. (2015). Several FTIR studies of peat burning emissions have also reported VOC emission factors for six out of the seven highest emitted VOCs measured in this work, i.e. propylene, acetaldehyde, benzene, acetone, formaldehyde and toluene (Yokelson et al., 1997; Christian et al., 2003; Stockwell et al., 2014). Christian et al. (2003) reported EFs for five of the six VOCs

mentioned above from Indonesian peat burning, while formaldehyde and propylene EFs were reported in the other two studies for peat from the U.S. (i.e. MN, NC and AL), Canada and Indonesia (Yokelson et al., 1997; Stockwell et al., 2014). This work is the first known to quantify EFs for chloromethane, one of the highest emitted HAP VOCs from this study, as well as a number of other HAPs. Chloromethane EFs from this work are approximately five times higher than compiled EFs for other biomass burning types and similar to the EF reported for pasture maintenance burns (i.e. 0.29 ± 0.13 g/kg) (Akagi et al., 2011). This may be connected to the differences in chlorine content between fuels.

Figure 3. Literature comparison of six VOC emission factors with the following studies:

¹Yokelson et al., 1997; ²Christian et al., 2003; ³Stockwell et al., 2014 and ⁴Hatch et al., 2015.

A comparison of the reported emission factors for peat burning from literature and from this work for the six VOCs is shown in Figure 3. EFs observed in this work were generally lower than EFs from previous peat burning. There was better agreement for propylene emission factors,

particularly for those reported by Stockwell et al. (2014), than for other VOCs. Differences in peat emission factors between these studies may be related to differences in peat fuel characteristics such as carbon content, ash content, fuel moisture and the chemical structure of peat. Given the differences in measurement methods, fuel composition and experimental conditions between these studies, it is not possible to determine the causes of the variability in VOC EFs between the few studies involved. Further study is required to investigate the influence of various factors, such as fuel moisture and carbon and ash content, on peat fire emissions in a more systematic fashion.

3.2. Chemical Speciation of $PM_{2.5}$ emissions

The chemical composition of the organic content of $PM_{2.5}$ emissions from peat burning was characterized by GC-MS, which included 152 compounds from the following compound classes: *n*-alkanes, *n*-alkenes, PAHs, *n*-alkanoic acids, *n*-alkenoic acids, aromatic acids, resin acids, methoxyphenols, anhydrosugars, sterols and other branched and cyclic alkanes. A detailed list of emission factor data for all organic species that were detected can be found in Table S4 in the Supporting Information. Emission factors in mg/kg fuel burned for speciated $PM_{2.5}$ were grouped by organic compound class in Figure 4 for the two peat sources averaged over first (0–3 h) and second (4–7 h) parts of the burn experiments. For comparison, Figure 4 also shows the mass emission factors of PM_{10} organics in similar compound groupings for German and Indonesian peat from the only known published study on speciated organic PM emissions from peat fires (Iinuma et al., 2007). The four most abundant compound groups in this work (i.e., *n*-alkanes, *n*-alkenes, organic acids, and anhydrosugars) comprised 89–98 % of the sum of the speciated $PM_{2.5}$ organic mass emitted in this work. Here, the organic acid group included *n*-alkanoic, *n*-alkanedioic, *n*-alkenoic and aromatic acid compounds, which have not been quantified previously in peat burning smoke to our knowledge.

Figure 4. Sum of speciated organic PM_{2.5} emission factors by compound class compared to Iinuma et al. (2007).

Several other organic compound classes were detected in the PM_{2.5} emissions but made up a relatively small weight fraction of identified organic species, i.e. the “other” group comprised of PAHs, resin acids, sterols, various branched alkanes and cycloalkanes. In this work, the sum of the speciated PM_{2.5} organic emissions was reduced overall by ~60 % in the latter half of the burn tests compared to the first half. This observation is consistent with observed reductions in OC mass and PM_{2.5} emissions with elapsed time from ignition of the peat samples (Black et al., 2015). The predominance of anhydrosugars, *n*-alkanes and *n*-alkenes over the other compound

groups (i.e. PAHs, resin acids) in peat burning PM emissions was also observed by Iinuma et al. (2007).

Figure 5. OC mass fraction of speciated $PM_{2.5}$ emissions by compound class on a carbon mass basis compared to Iinuma et al. (2007).

The peat burning carbon mass emissions from the speciated $PM_{2.5}$ are shown as fractions of OC mass by compound class in Figure 5 for each peat source. The relative contributions of each organic compound group to total OC mass were similar for the two peat sources in this work, as evidenced by Figure 5. Similar to the VOC emission profiles, this suggests that the combustion conditions or peat composition were similar between sites leading to similar speciated organic $PM_{2.5}$ emissions. The total carbon mass from the identified organic compounds comprised approximately a quarter of the total OC mass emissions for both AR and PL peat sources, indicating that three quarters of the carbon mass is unidentified as observed previously for peat burning PM (Iinuma et al., 2007).

3.2.1. *n*-Alkanes, *n*-alkenes and other alkanes

The homologous series of *n*-alkanes with carbon numbers in the range of C₁₃ to C₃₅ were quantified in the PM_{2.5} samples. Samples exhibited an odd over even Carbon Preference Index (CPI) with average odd:even CPI values of $\text{CPI} = 1.4 \pm 0.2$ and 1.5 ± 0.2 for AR and PL peat sources, respectively. These values are within the range of CPI values for alkanes measured for biomass burning PM (Alves et al., 2010; Balachandrian et al., 2013; Hays et al., 2002; Iinuma et al., 2007). Total *n*-alkane emissions were approximately 510 and 320 mg kg⁻¹ representing on average ~7 % and 6 % of PM_{2.5} OC mass on a carbon basis for AR and PL peat, respectively. The particulate alkane emissions factors are greatly enhanced in peat burning PM compared to other biomass types (Alves et al., 2010; Hays et al., 2002; Iinuma et al., 2007; Vincente et al., 2011), where alkanes represented in most cases <1 % of OC mass but were variable with fuel type. This is likely due to the higher lipid content in peat fuel compared to other biomass types as suggested previously by Iinuma et al. (2007).

Emission factors for the sum of C₁₅ to C₂₅ *n*-alkenes were ~120 and 170 mg kg⁻¹ for PL and AR peat sources respectively, accounting for ~2 % of the particulate OC mass. The average CPI values for the *n*-alkenes, $\text{CPI} = 0.6 \pm 0.1$ and 0.5 ± 0.1 for AR and PL peat, respectively, indicate an even over odd carbon number predominance. The emission rates of alkenes and alkanes were reasonably well related linearly ($R^2 = 0.93$), suggesting that thermal cracking of alkanes could partly explain alkene formation from peat burning or that they have similar modes of formation. A minor fraction of particulate OC mass (~0.3 %) consisted of a few branched and cyclic alkanes, including hopanoids.

3.2.2. *Organic acids*

Of the speciated compound classes, organic acids represented the largest fraction of OC mass from peat emissions in this work (i.e., 11 % and 12 % for AR and PL peat, respectively). The homologous series of *n*-alkanoic acids (C₆ to C₃₀) dominated the organic acid emissions, comprising between 75 to 99 % of speciated organic acids by OC mass. The even:odd CPI values for the *n*-alkanoic acids ranged from 3.1 to 5.3 in this work, exhibiting an even over odd carbon preference typical of plant oils, which has previously been observed in particulate emissions from biomass burning (Alves et al., 2010; Balachandrian et al., 2013; Hays et al.,

2002; Oros and Simoneit, 2001; Vincente et al., 2011). Unsaturated fatty acids, or *n*-alkenoic acids, contributed up to 26 % w/w of the organic acid fraction, which consisted of palmitoleic acid, oleic acid, linoleic acid and a minor contribution from linolenic acid.

Aliphatic dicarboxylic acids, or *n*-alkanedioic acids, from C₄ to C₁₀ were 0.4 to 7 % of the speciated organic acid OC mass emissions, with maximum emissions observed for heptanedioic acid. Aromatic acids were detected as a minor fraction <1 % of the speciated organic acid mass, which included several aromatic di-, tri-, and tetra-carboxylic acid isomers. Resin acids (included in the “Other” group) that were observed (0.1 % of OC mass) in peat burning included abietic acid, dehydroabietic acid and isopimaric acid.

3.2.3. Lignin and cellulose pyrolysis products

Both lignin and cellulose pyrolysis products, including methoxyphenols and levoglucosan, have been classified as biomass burning chemical tracers in ambient PM (Robinson et al., 2006; Schauer and Cass, 2000; Simoneit et al., 1993; Simpson et al., 2005). In this work, a number of methoxyphenol compounds were quantified in the peat burning smoke PM, constituting 0.4 % of observed OC mass for both AR and PL peat fuels. The majority of the methoxyphenol mass was represented by a few compounds: syringaldehyde, acetovanillone, vanillin, isoeugenol, and acetosyringone. The lack of clear predominance of either syringyl or guaiacyl compounds may reflect the mixed biomass sources of the peat.

Levoglucosan is an important organic tracer from pyrolysis of cellulose and is often the largest contributor to the identified organic mass in PM from biomass burning for any individual compound (Simoneit, 2002). Levoglucosan contributed on average ~2 and ~3 % of the smoke OC mass. Other anhydrosugars (galactosan and mannosan) were a minor fraction (~4 %) of the total observed anhydrosugar PM emissions. As noted previously, the levoglucosan fraction of PM is highly variable (Balachandrian et al., 2013; Mazzoleni et al., 2007; Rada et al., 2012; Zhang et al., 2013). The average levoglucosan fractions were within the ranges with OC fractions observed previously (Zhang et al., 2013). However, a comparison of levoglucosan with OC mass EFs did not exhibit a strong linear relationship ($R^2 = 0.31$) as was observed previously for a wide range of fuels during FLAME I and II studies ($R^2 = 0.68$) (Sullivan et al., 2008). Interestingly, Sullivan et al. (2008) observed the weakest levoglucosan to OC correlations for duff fuels (Figure 4b, $R^2 = 0.18$) of all fuel types burned in that study, which is more in line with

the results from this study. The weak linear relationship between levoglucosan and OC emissions may be linked to the variable cellulosic content in the peat samples (Sullivan et al., 2008).

3.2.4. Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons are produced during incomplete combustion and are a toxicological concern. The gas + particle emissions of 16 U.S. EPA priority PAHs (ATSDR, 2005) in the peat fire emissions from this study will be reported elsewhere. In this work, 27 particulate PAHs (including the 16 U.S. EPA priority PAHs) were quantified in peat smoke PM_{2.5} samples, making up approximately 0.1 % of OC mass for both peat sources on a carbon basis. The particulate PAH emissions profiles for the two peat samples were highly correlated ($R^2 = 0.99$), suggesting that differences in peat fuel composition between sites did not influence the PAH emission profiles. Retene was the most abundant PAH, contributing approximately two-thirds of the sum of speciated particulate PAH emissions in peat smoke. Other important PAHs detected in this work were methylfluorene and phenanthrene. Retene is considered a biomarker of softwood combustion (Simoneit, 2002). Several studies have also observed retene as the major PAH in smoke PM influenced by conifer biomass burning (Fine et al., 2002; Hays et al., 2002, 2011; Schauer and Cass, 2000; Vincente et al., 2011), whereas Iinuma et al. (2007) observed fluorene as the major PAH compound in peat smoke samples. See et al. (2007) characterized ambient particles during a peat fire and detected phenanthrene as the most abundant PAH, but did not quantify retene in that work.

3.3. Estimated HAP emissions from the 2008 NC Evans Road wildfire

The Evans Road Wildfire at the Pocosin Lakes National Wildlife Refuge in North Carolina resulted in significantly increased hospital visits (Rappold et al., 2011). Geron and Hays (2013) estimated the relative importance of peat burning PM_{2.5} emissions using PM_{2.5} EFs measured from that wildfire event. A similar estimation approach was followed here to assess the relative importance of emissions of hazardous air pollutant VOCs and particulate PAHs (also considered a HAP) produced from the ERW event.

The total carbon released to the atmosphere from the Evans Road Wildfire was previously estimated as 9.4 Tg carbon, with 98 % originating from below-ground fuel consumption (Geron and Hays, 2013). Based on previous studies of peat, a carbon content of 50 % w/w was used for this calculation (Geron and Hays, 2013; Ingram, 1987; Stockwell et al., 2014). The emission

factors for HAP VOCs (italicized compounds in Table S3 in the supporting information) and particulate PAHs (Table S4) for PL peat from this work were used to calculate total speciated HAP emissions for these compounds from burning peat during the Evans Road Wildfire. Results shown in Table 1 were compared to estimated emissions for HAP VOCs and PAHs from all pollution sources and for wildfires specifically both on national and state-wide scales in 2008 from the U.S. EPA National Emissions Inventory (NEI) (U.S. EPA, 2008). For wildfire HAP VOC emissions, NEI included the following HAPs: 1,3-butadiene, acetaldehyde, acrolein, benzene, carbonyl sulfide, chloromethane, formaldehyde, *n*-hexane, toluene, and xylenes. The EFs for these VOCs measured in this work were within an order of magnitude of emission factors used in the NEI to calculate wildfire emissions. However, particulate PAH EFs were over an order of magnitude smaller than the EF values used in the NEI, likely due to the nature of peat combustion resulting in lower PAH emissions.

Table 1. Comparisons of total estimated emissions for U.S. EPA HAP VOCs and particulate PAHs (in units of 10^9 g) from all sources and from wildfires, both nationwide and for North Carolina (NC) as reported in National Emissions Inventory (U.S. EPA, 2008). Evans Road Wildfire (ERW) emissions were estimated from this work.

	National	NC	NC/National
HAP VOCs			
All Sources	6806	176	2.6 %
All Wildfires	191	22.0	12 %
ERW		52.1	
WildFires/All sources	2.8 %	12 %	
ERW/All Sources	0.8 %	30 %	
ERW/Wildfires	27 %	236 %	
Particulate PAHs			
All Sources	9.04	0.472	5.2 %
All Wildfires	2.54	0.293	12 %
ERW		0.134	
All Wildfires/All sources	28 %	62 %	
ERW/All Sources	1.5 %	28 %	
ERW/All Wildfires	5.3 %	46 %	

According to the NEI, HAP VOC emissions from wildfires comprised 2.8 % of all pollution sources nationally, while NC wildfires made up 12 % of emissions from all sources in NC during 2008. The estimated HAP VOC emissions for the Evans Road Wildfire represented 27 % of all wildfire emissions nationally and over twice the estimated NC wildfire emissions for 2008. Notably, total estimated Evans Road Wildfire emissions of acetaldehyde, hexane, and chloromethane were all over an order of magnitude greater than for all NC wildfires in 2008. Furthermore, estimated Evans Road Wildfire chloromethane emissions represent nearly half (48 %) of the chloromethane emissions from all pollution sources nationally in 2008, greater than the chloromethane contributions from all national wildfires combined (45 %). This observation suggests that chloromethane may be an important indicator of peat wildfires. Wildfires represented a larger portion of total particulate PAH emissions than VOCs, contributing 28 % of the particulate PAHs from all sources nationally and 62 % in NC. PAH emissions from the Evans Road Wildfire were estimated to represent ~5 % of these emissions from all wildfires nationally and approximately half of the particulate PAH emissions from all NC wildfires.

4. Conclusions

In this work, speciated gas and particle phase organic emissions were quantified from laboratory peat fires for two peat sources originating from coastal North Carolina, U.S. The highest emitted VOCs from the peat burning included a number of HAPs, including monoaromatics (i.e. BTEX) and carbonyls (e.g. formaldehyde and acetaldehyde). Chloromethane emission factors were reported for the first time for peat fires, and these EFs were ~5 times higher than for most other biomass burning types and likely connected to the chlorine content of the peat sources. EFs of other important VOCs from this work were compared to literature values for peat burning from various locations, and the EFs from this work were on the low end of the ranges of the literature values. Further work is needed to determine the causes of the differences in emissions between studies, which can be due to a number of factors linked to fuel composition and experimental conditions.

A wide range of particulate organic compounds was identified in PM_{2.5} samples of smoke from burning peat. The sum of *n*-alkanes, *n*-alkenes, levoglucosan, and organic acids was responsible for over 90 % of the speciated organics from PM_{2.5}. Minor contributions of PAHs,

resin acids, methoxyphenols and other branched and cyclic alkanes were observed in peat smoke. The organic species in the particulate phase in this study contributed ~24 % by carbon mass to total OC mass emissions. Organic acids were the most abundant compound class in PM_{2.5}, and predominated by the homologous series of *n*-alkanoic acids. The relatively high *n*-alkane mass contributions to PM_{2.5} in peat smoke compared to biomass types from previous studies is a unique feature of peat smoke organic composition that is likely linked to the lipid content in the peat fuel. This feature has been shown to have significant effects on the hygroscopic properties of fresh peat smoke, i.e. reduced ability to form cloud droplets compared to other biomass burning aerosols (Dusek et al., 2005). The implications of the reduced hygroscopicity of fresh peat burning aerosols on climate, however, are not clear. Estimated emissions of hazardous air pollutants (VOCs and particulate PAHs) from a previous peat wildfire in North Carolina in 2008 were found to represent a sizable fraction of total emissions from the state for that year. This study indicates that HAP emissions and particle properties of aerosols from peat burning should be considered when assessing health and climate impacts of wildfires.

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Disclaimer

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