

23 **Abstract**

24 Peat fuels representing four biomes of boreal (western Russia and Siberia), temperate 25 (northern Alaska, U.S.A.), subtropical (northern and southern Florida, U.S.A), and tropical 26 (Borneo, Malaysia) regions were burned in a laboratory chamber to determine gas and particle 27 emission factors (EFs). Tests with 25 % fuel moisture were conducted with predominant 28 smoldering combustion conditions (average modified combustion efficiency [MCE] = 0.82 ± 1 29 0.08). Average fuel-based EF_{CO2} (carbon dioxide) are highest (1400 ± 38 g kg⁻¹) and lowest (1073 30 ± 63 g kg⁻¹) for the Alaskan and Russian peats, respectively. EF_{CO} (carbon monoxide) and EF_{CH₄} 31 (methane) are ~12–15 % and ~0.3–0.9 % of E_{CO_2} , in the range of 157–171 g kg⁻¹ and 3–10 g kg⁻¹ 32 ¹, respectively. EFs for nitrogen species are at the same magnitude of $E F_{CH_4}$, with an average of 5.6 \pm 4.8 and 4.7 \pm 3.1 g kg⁻¹ for EF_{NH₃} (ammonia) and EF_{HCN} (hydrogen cyanide); 1.9 \pm 1.1 g kg⁻¹ 1 for EF_{NOx} (nitrogen oxides); as well as 2.4 ± 1.4 and 2.0 ± 0.7 g kg⁻¹ for EF_{NOy} (total reactive 35 nitrogen) and EF_{N_2O} (nitrous oxide).

36 An oxidation flow reactor (OFR) was used to simulate atmospheric aging times of \sim 2 and -7 days to compare fresh (upstream) and aged (downstream) emissions. Filter-based EF_{PM_{2.5}} 38 varied by >4 -fold (14–61 g kg⁻¹) without appreciable changes between fresh and aged emissions. 39 The majority of $E_{PM2,5}$ consists of E_{COC} (organic carbon), with $E_{\text{COC}}/E_{\text{PMA}_2,5}$ ratios in the range 40 of 52–98 % for fresh emissions, and ~15 % degradation after aging. Reductions of E_{DC} (~7–9 g 41 kg⁻¹) after aging are most apparent for boreal peats with the largest degradation in low temperature 42 OC1 that evolves at <140°C, indicating the loss of high vapor pressure semi-volatile organic 43 compounds upon aging. The highest $E_{\text{Levoglucosan}}$ is found for Russian peat (~16 g kg⁻¹), with ~35-44 50 % degradation after aging. EFs for water-soluble OC (EF_{WSOC}) accounts for \sim 20–62 % of fresh 45 EF_{OC}.

46 The majority (>95 %) of the total emitted carbon is in the gas phase with $54-75$ % CO₂, 47 followed by 8-30 % CO. Nitrogen in the measured species explains 24‒52 % of the consumed 48 fuel nitrogen with an average of 35 ± 11 %, consistent with past studies that report ~one- to two-49 thirds of the fuel nitrogen measured in biomass smoke. The majority (>99 %) of the total emitted 50 nitrogen is in the gas phase, with an average of 16.7 % as NH₃ and 9.5 % as HCN. N₂O and NO_v 51 constituted 5.7 % and 2.9 % of consumed fuel nitrogen. EFs from this study can be used to refine 52 current emission inventories.

- Keywords: Peat combustion, modified combustion efficiency, emission factors, oxidation flow
- reactor, carbon balance, nitrogen budget.

1 Introduction

 Globally, peatlands occupy ~3 % of the Earth's land surface, but they store as much as 610 57 gigatonnes (i.e., 610×10^{15} grams) of carbon, representing 20–30 % of the planet's terrestrial carbon (Page et al., 2011;Rein et al., 2009). Peatland fires can persist for weeks to months and are dominated by the smoldering-phase as opposed to the flaming-phase of biomass burning (Stockwell et al., 2016;Hu et al., 2018). This results in lower combustion efficiencies, increased particulate matter (PM) emissions, and larger fractions of brown carbon (BrC) compared to black carbon (BC) or soot (Pokhrel et al., 2016). Peat fires emit reduced nitrogen compounds (e.g., ammonia [NH3] and hydrogen cyanide [HCN]); volatile and semi-volatile organic compounds 64 (VOCs and SVOCs); and PM_{2.5} (PM with aerodynamic diameters $\langle 2.5 \mu m \rangle$ (Akagi et al., 2011;Yokelson et al., 2013). Peat smoke and ash affect ecosystem productivity, soil acidity, biogeochemical cycling, atmospheric chemistry, Earth's radiation balance, and human health. Warmer climates lower the water table in peatlands and change the pattern, frequency, and intensity of the peatland fires causing local- and regional-scale air pollution and visibility impairment (Page et al., 2002;Turetsky et al., 2010;2015a;2015b). For Southeast Asia, fire-related regional air pollution and its effects on atmospheric visibility, ecosystems, and human health have been addressed in many studies (e.g., Behera et al., 2014;Betha et al., 2013;Bin Abas et al., 2004;Engling et al., 2014;Heil and Goldammer, 2001;Kundu et al., 2010;Levine, 1999;Hu et al., 2019;Tham et al., 2019;Fujii et al., 2017;Dall'Osto et al., 2014).

 Nitrogen, one of the most important plant nutrients, affects global carbon and biogeochemical cycles (Crutzen and Andreae, 1990;Gruber and Galloway, 2008). Deposition of oxidized and reduced nitrogen species from biomass burning, such as gaseous nitric oxide (NO), 77 nitrogen dioxide (NO₂), and NH₃ as well as particulate nitrate (NO₃⁻) and ammonium (NH₄⁺), alters 78 terrestrial ecosystems (Chen et al., 2010), while nitric acid (HNO₃) contributes to soil acidification and excessive nitrification that reduce plant resistance to environmental stresses (Goulding et al., 80 1998). Gaseous nitrogen oxides (NO_x) affect atmospheric chemistry through: 1) reactions with 81 hydroxyl (OH) and peroxy $(HO_2 + RO_2)$ radicals; 2) conversion to nitrate radical (NO₃), dinitrogen 82 pentoxide (N_2O_5) , and acyl peroxy nitrates (particularly peroxyacetyl nitrate [PAN]), which are 83 important NO_x reservoirs; and 3) formation of ozone $(O₃)$ and secondary organic aerosols (SOA) 84 (Alvarado et al., 2010;Cubison et al., 2011;Ng et al., 2007). While NH₃ neutralizes HNO₃ to form 85 particulate ammonium nitrate (NH_4NO_3) , it may also react with alkanoic acids to form alkyl

 amides, nitriles, and ammonium salts that can also contribute to SOA formation (Na et al., 87 2007; Simoneit et al., 2003; Zhao et al., 2013). In addition, NH₃ interacts with SOA to form "BrC" 88 that further influence the aerosol radiative forcing (Updyke et al., 2012).

 This study quantifies peat burning emission factors (EFs) for fresh and aged multipollutant mixtures through controlled burns in a laboratory combustion chamber with atmospheric aging simulated by an oxidation flow reactor (OFR). These tests are applied to peat samples from diverse parts of the world.

2 Experiment

2.1 Fuel types

 Peatlands are found all over the world, as illustrated in Fig. 1 (based on Yu et al., 2010) with large deposits found in the northern USA and Canada, northern Europe, Russia/Siberia, and southeast Asia. Eight types of peat fuels from different regions and climates were collected for testing, including: boreal (i.e., Odintsovo, Russia and Pskov, Siberia); temperate (i.e., black spruce forest, northern Alaska, USA); subtropical (i.e., northern [Putnam County Lakebed] and southern [Everglades National Park] Florida, USA and Caohai and Gaopo, Guizhou, southwest China); and tropical (i.e., Borneo, Malaysia) peats.

102 Representative peat samples of 250–1150 g from the upper 20 cm of the peatland surface were excavated for each region indicated in Fig. 1. As peat is a heterogeneous mixture of decomposed plant material, it can be formed in different wetlands under changing climates and nutrient contents (Turetsky et al., 2015a). Supplemental Fig. S1 shows that the appearance of peat fuels varies by region.

 To quantify carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) content, 108 \sim 2–3 g of each peat fuel were dried in a vacuum oven (~105°C) for two hours prior to elemental analysis (Thermo Flash-EA 1112 CHNS/O Analyzer, Waltham, MA, USA).

 Import and export regulations (USDA, 2010) require high temperature heating of soil/peat fuels as part of the sterilization process. Peat fuels were heated to 90°C and weighed every 24 112 hours to achieve a stable dry mass with ~0.16 % moisture by weight content (after ~96 hours of heating). The low heating temperature (i.e., below the water boiling point) minimized VOC losses, although some compounds with high volatilities could have been removed at 90°C. To better simulate the field conditions during peat fires, distilled-deionized water (DDW) was added to 116 rehydrate the dry peat and achieve a fuel moisture of \approx 25 % (by weight) before each experiment (Yatavelli et al., 2017). To examine the effects of fuel moisture on emissions, additional experiments (n=3) were conducted at 60 % fuel moisture content (by weight) for the Putnam (FL) peat.

2.2 Experimental setup

 The laboratory setup shown in Fig. 2 used a biomass combustion chamber with a volume 122 of ~8 m³ (1.8 m[W] x 1.8 m[L] x 2.2 m[H]) (Tian et al., 2015). Instrument specifications and operating principles are shown in Table S1. The chamber is made of 3 mm-thick aluminum to withstand high temperature heating. A blower supplied air filtered by a charcoal bed and a high- efficiency particulate air (HEPA) filter near the bottom of the chamber to remove background gas and particle contaminants. The ventilation rate was controlled by the blower and exhaust fan at $127 \sim 2.65$ m³ min⁻¹, resulting in a smoke residence time of ~ 3 min in the chamber assuming a well-stirred flow model.

129 For each test, \sim 10–30 g of dried peat was placed in an asbestos insulated circular container 130 on top of an induction heater that provided heating during the first \sim 5–10 minutes of combustion (see Fig. S2). This method replaced a propane torch used in initial test burns, thereby minimizing non-peat burning emissions. The smoldering process is usually self-propagating and sustained by heat conduction and radiation with fuel mass continuously monitored by a scale underneath the induction heater (Ohlemiller et al., 1979).

135 Continuous PM_{2.5} mass concentrations were monitored with a DustTrak (TSI Model 8532, 136 Shoreview, MN, USA) (Wang et al., 2009) (Table S1). When PM_{2.5} concentrations reached their maximum and started to decline, the induction heater was turned off. The fuel was consumed with 138 diminished smoke emissions after ~20 minutes. Preliminary tests were conducted using ~10–20 139 g of fuel and a dilution ratio of \sim 3 to 5, yielding sufficient particle loadings on the filters (\sim 150— 140 290 μg per 47 mm filter disc). To achieve higher filter deposits of 300–600 μg per filter that 141 accommodate comprehensive organic speciation, additional fuels $(-15-20 \text{ g})$ were added with the induction heater turned on for another ~10 minutes. Sampling continued until the concentrations returned to background level.

144 Sampling ports for stack concentrations of carbon dioxide (CO₂) and multiple gases by Fourier transform infrared (FTIR; Model DX 4015; Gasmet Technologies Oy, Finland) 146 spectroscopy were located \sim 1 m above the top of the chamber roof in the exhaust duct (Fig. 2). The FTIR spectrometer measured gaseous emissions prior to dilution to obtain enhanced signal-

 to-noise ratios for trace gases (Jaakkola et al., 1998). An exhaust gas sample was drawn into the 149 FTIR where the infrared (IR) absorption spectra in the wave number range of $900-4200$ cm⁻¹ were measured. The instrument software compares the measured absorption spectra with reference gas absorption spectra in the calibration library to identify gas species and calculate concentrations. Examples of reference gas spectra and an Everglades (FL) peat sample spectrum are plotted in Fig. 153 S3.

 Smoke from the chamber was drawn through a dilution sampling manifold where the exhaust was diluted with clean air to achieve cooling that allowed for condensation of SVOCs. A portion of the exhaust was directed through a potential aerosol mass (PAM)-OFR (Aerodyne Research Inc., Billerica, MA, USA) to simulate atmospheric aging prior to quantification by the sampling instruments shown in Fig. 2. The 185 and 254 nm (OFR185) ultraviolet (UV) lamps in 159 the OFR were operated at 2 and 3.5 volts with $10 L \text{ min}^{-1}$ flow rate to simulate intermediate-aged (~2 days) and well-aged (~7 days) emissions assuming an average daily OH concentration of 1.5 161 x 10⁶ molecules cm⁻³. The estimated OH exposures (OH_{exp}) at 2 and 3.5 volts were 2.6 x 10¹¹ and 162 8.8 x 10^{11} molecules-sec cm⁻³ based on the measured decay of sulfur dioxide (SO₂). Due to 163 external OH reactivity from carbon monoxide (CO), NO_x , and other reactants, these OH_{exp} levels represent upper limits of the actual OH exposures inside the OFR (Peng et al., 2015;Li et al., 2015).

165 Oxides of nitrogen were measured as NO_x (the sum of NO and NO₂) and total reactive 166 nitrogen (NO_y, including NO, NO₂, N₂O₅, HNO₃, HNO₄, ClONO₂, HONO, alkyl nitrates, and PAN) 167 by chemiluminescence NO_x and NO_y analyzers (Ballenthin et al., 2003;Allen et al., 2018). The 168 NO_x analyzers placed upstream and downstream of the OFR determined NO_x changes with OH_{exp} 169 in the OFR. There are known interferences for the non-selective catalytic converter in the 170 chemiluminescent NO_x analyzer and for spectroscopic absorption in the FTIR (Allen et al., 171 2018;Prenni et al., 2014;Villena et al., 2012). The chemiluminescence monitor converts most 172 nitrogenous compounds to NO, with HNO₃ and PAN being the most important potential 173 interferents (Winer et al., 1974). However, much of the available HNO₃ and PAN is removed by 174 the tubing leading to the molybdenum converter in the standard NO_x analyzer, which is why the 175 NO_y analyzer locates the converter at the inlet. Allen et al. (2018) found no significant differences 176 between NO_x measurements of biomass burning plumes when comparing a chemiluminescent 177 analyzer with more specific UV absorption measurements.

178 The following analyses are based on: 1) the commercial NO_x analyzers for NO, NO₂, and 179 NO_x (NO + NO₂ as equivalent NO₂); 2) the NO_y analyzer for total reactive nitrogen; and 3) the 180 FTIR spectrometer for trace gas measurements of methane (CH_4) , NH₃, HCN, nitrous oxide (N_2O) , 181 and 13 low molecular-weight VOCs (C2–C6).

 PM2.5 filter packs were sampled upstream and downstream of the OFR to characterize fresh and aged emissions, respectively, with Minivol PM2.5 samplers (Airmetrics, Springfield, OR, 184 USA) operated at 5 L Min⁻¹ flow rate per channel. PM_{2.5} mass, elements, carbon, water-soluble 185 organic carbon (WSOC), ions, carbohydrates, organic acids, as well as gaseous NH₃ and HNO₃ were obtained from the paired upstream and downstream filter samples to examine changes in speciated EFs and source profiles with photochemical aging. Average filter-based EFs are examined by peat types and aging times (i.e., denoted as Fresh 2 vs. Aged 2 and Fresh 7 vs. Aged 7) (Chow et al., 2019).

190 **2.3 Filter pack measurements**

191 PM_{2.5} mass and major chemical species concentrations were obtained from the parallel 192 Teflon-membrane and quartz-fiber filters (Teflo[©], 2 μ m pore size, R2PJ047 and Tissuquartz 2500 193 QAFUP, Pall Life Sciences, Port Washington, NY, USA). Teflon-membrane filters were 194 equilibrated in a temperature (20–23 $^{\circ}$ C) and relative humidity (30–40 %) controlled environment 195 for a minimum of 48 hours prior to gravimetric analysis by a microbalance with ± 1 ug sensitivity 196 (Watson et al., 2017). This was followed by multielemental analysis by x-ray fluorescence 197 (Watson et al., 1999). Quartz-fiber filters were pre-fired at 900° C for four hours to minimize 198 organic artifacts. A portion (0.5 cm^2) of the quartz-fiber filter was submitted for organic, elemental, 199 and brown carbon (OC, EC, and BrC) analysis following the IMPROVE_A thermal/optical 200 reflectance (TOR) protocol (Chow et al., 2007;2015). Half of the quartz-fiber filters was extracted 201 in DDW for ionic speciation (i.e., chloride [Cl⁻], nitrate [NO₃⁻], nitrite [NO₂⁻], sulfate [SO₄⁻], water-202 soluble sodium $[Na^+]$ and potassium $[K^+]$, ammonium $[NH_4^+]$, 17 carbohydrates, and 10 organic 203 acids) by ion chromatography (Chow and Watson, 2017) and for WSOC by combustion and non-204 dispersive infrared detection. Citric acid and sodium chloride impregnated cellulose-fiber filters 205 placed behind the Teflon-membrane and quartz-fiber filters, respectively, acquired NH₃ as NH₄⁺ 206 and HNO₃ as volatilized nitrate, respectively, with analysis by ion chromatography. Details on 207 chemical analyses can be found in Chow et al. (2019).

 The open face sampling manifold allows homogenous particle deposits on 47-mm filters (Watson et al., 2017). To test the uniformity of particle deposits, five individual punches were removed from the center and each quadrant of the 47-mm quartz-fiber filter disc for carbon 211 analyses. Table S2 shows total carbon (TC = $OC + EC$) concentration variations of 1.7 % to 5 % across the filters for the five test burns, within the overall uncertainty of the emission estimates. Standard deviations from the five filter punches for each experiment are low with coefficients of 214 variation of 1.7–5.0 %.

215 **2.4 Modified combustion efficiency and fuel-based emission factors**

216 The modified combustion efficiency (MCE) is defined as the ratio of background-217 subtracted CO_2 to the sum of CO_2 and CO (Ward and Radke, 1993):

$$
218 \t\t\t\tMCE = \frac{\Delta CO_2}{\Delta CO_2 + \Delta CO}
$$
\t(1)

219 where ΔCO₂ and ΔCO are CO₂ and CO concentrations above background. MCE provides a real-220 time indicator of the combustion status (e.g., MCE $>$ ~0.9 for flaming and MCE < ~0.85 for 221 smoldering).

222 Each burn was completed when concentrations of pollutants measured on-line (i.e., CO, 223 NO_x, NO_y, and PM_{2.5}) returned to the baseline/background levels. Dilution ratios ranging from 224 2.7 to 5 were taken into account when calculating EFs. Fuel-based EFs are calculated based on 225 carbon mass balance, expressed as grams of emission per kilogram of dry fuel (g kg⁻¹) (Wang et 226 al., 2012). For gaseous and particle species i , the time-integrated EF_i is:

227

$$
228 \t\t\t EF_{i} = CMF_{fuel} \frac{C_{i}}{C_{CO_{2}}\left(\frac{M_{C}}{M_{CO_{2}}}\right) + C_{CO}\left(\frac{M_{C}}{M_{CO}}\right) + C_{CH_{4}}\left(\frac{M_{C}}{M_{CH_{4}}}\right) + \sum_{j} C_{VOC_{j}}\left(\frac{n_{j} \times M_{C}}{M_{VOC_{j}}}\right) + PM_{c}} \times 1000 \t(2)
$$

229

230 where CMF_{fuel} is the carbon mass fraction of the fuel in kg carbon per kg of fuel; C_i , C_{CO_2} , C_{CO_3} , 231 C_{CH^{4}, and C_{VOC_i} are the background-subtracted concentrations for species *i* (e.g., nitrogen or PM_{2.5})</sub>} 232 species), CO₂, CO, CH₄, and VOC (C₂–C₆) species *j* in mg m⁻³ under standard conditions 233 (temperature = 293K and pressure = 1 atm), respectively; PM_c is the total carbon concentration of 234 PM_{2.5} in mg m⁻³; M_C, M_{CO2}, M_{CO}, M_{CH4}, and M_{VOC_j are the atomic or molecular weights of carbon,} CO2, CO, CH4, and VOC species *j* in mg per mole, respectively; n*^j* is the number of carbon atom in VOC species *j*; and the factor 1000 converts kg to g. All concentrations are converted to stack concentration, i.e., species measured after dilution are adjusted by the dilution ratio. Equation 2 assumes that the carbon mass in unmeasured VOCs and other emissions not listed above is 239 negligible compared to that in $CO₂$, CO, CH₄, measured VOCs (C2–C6), and PM_{2.5} carbon.

2.5 Estimation of wall losses

 Gas and particle wall losses can result in some underestimation of measured EFs, but it is 242 well within the measurement uncertainties of \pm 15 %. Losses can occur inside the combustion chamber, in the exhaust stack, sampling lines, and inside the OFR. Due to the low surface-to-244 volume ratio of the chamber (2.9 m⁻¹) and short residence time (\sim 3 min) in this study, the gas and particle losses are expected to be low in the combustion chamber. Grosjean (1985) estimated an 246 NH₃ loss rate of $4-17 \times 10^{-4}$ min⁻¹ in a small Teflon chamber (3.9 m³) with a surface-to-volume 247 ratio of 3.8 m⁻¹, resulting in < 0.5 % NH₃ wall loss. Even though the NH₃ accommodation coefficient might be higher for aluminum than Teflon (Neuman et al., 1999), the chamber wall 249 loss in this study is expected to be $<$ 5 % for NH₃. To reduce wall losses of sticky gases, the FTIR sampled exhaust gas from the stack without dilution, as shown in Fig. 2. Approximately 9 % NH3 would encounter the stack wall due to turbulent diffusion (Hinds, 1999). The maximum NH3 loss in the stack is <9 % and the maximum overall NH3 loss is <14 %. Losses of less sticky gases would be lower.

 The particle wall loss rates by McMurry and Grosjean (1985) and Wang et al. (2018) 255 indicate \leq 5 % particle number losses for 10 nm–2.5 μ m in a similar chamber. Particle losses by turbulent diffusion in the stack are also low (<0.5 %). For a 2 m-long horizontal heated sampling line in this study (Fig. 2), particle losses by diffusion and gravitational settling are negligible (<0.1 258 %) for 10 nm - 1 µm particles and ~6 % for 2.5 µm particles. Earlier measurements showed that 259 the dilution tunnel had ~100% penetration for 0.5-5 µm particles (Wang et al., 2012). Therefore, 260 maximum particle losses in this study are estimated to be $\lt 5\%$ for 10 nm - 1 µm and $\lt 10\%$ for 2.5 µm. Past studies (Lambe et al., 2011;Bhattarai et al., 2018;Karjalainen et al., 2016) showed 262 that particle number losses through the OFR may be \sim 50 % for 20 nm and \lt 10 % for gt 100 nm particles, with a negligible effect on mass concentration.

3 Results and discussion

3.1 Fuel composition

266 Table 1 shows that peat contains 44–57 % C and 31–39 % O with the exception of the two 267 Guizhou, China peats (20–30 % C and 21–24 % O). The carbon content (50.6 \pm 2.5 % C) in Borneo, Malaysian peat is within the range of carbon fractions reported for Kalimantan and Sumatra, Indonesia peat (44‒60 % C) (Christian et al., 2003;Hatch et al., 2015;Iinuma et al., 2007;May et al., 2014;Setyawati et al., 2017). The low carbon content (20‒30 % C) of Guizhou 271 peats is similar to the 28–30 % C reported for two eastern North Carolina, USA peats (Black et al., 2016).

 Hydrogen contents of 2‒7 % H in Table 1 are consistent with abundances found elsewhere, 274 including: 1) ~6 % H for northern Minnesota, USA peat (Yokelson et al., 1997); 2) ~2–3 % H for 275 the eastern North Carolina peat (Black et al., 2016); and 3) \sim 5–7 % H for Indonesian peats (Iinuma et al., 2007;Christian et al., 2003;Hatch et al., 2015). Sulfur (S) contents are below detection limits 277 (<0.01 %), and nitrogen contents are $1-4$ % N. Ratios of N/C are 0.02–0.08, consistent with the reported N/C ratios of: 1) 0.036 for Neustädter Moor, northern Germany (Iinuma et al., 2007); 2) 279 0.017–0.04 for Ireland and United Kingdom (Wilson et al., 2015); 3) 0.02–0.03 for Alberta and Ontario, Canada (Stockwell et al., 2014); 4) 0.062 for Minnesota, U.S.A. (Yokelson et al., 1997); 281 5) 0.022–0.03 for the eastern coast of North Carolina, U.S.A. (Black et al., 2016); and 6) 0.036– 0.039 for Kalimantan and Sumatra, Indonesia (Christian et al., 2003;Hatch et al., 2015).

283 The sum of elements (i.e., C, H, N, S, and O) accounts for 91–98 % of total mass except 284 for the Guizhou peats (47–56 %). As Guizhou peats appear to be a mixture of peat and soil, these samples may represent degraded peats (Miettinen et al., 2017) or contain additional minerals or high ash contents, similar to North Carolina peats (44‒62 % ash, Black et al., 2016). Therefore, these peats were only used for preliminary testing of sample ignition and heating to optimize burning conditions. Overall, the six other peats in Table 1 represent biomes from different regions of the world.

3.2 Emission factors (EFs)

 Table S3 summarizes the 40 peat combustion tests with the peat masses before and after each burn. The after burn residue may have contained unburned peat as well as non-combustible ash. The residues were not analyzed for carbon and nitrogen contents. A few samples were voided due to sampling abnormalities. The following analyses are based on the 32 paired (Fresh vs Aged) 295 samples at 25 % fuel moisture and 3 paired samples at 60 % fuel moisture. The amount of fuel 296 consumed per test ranged from 21–48 g for all but Russian peat $(14–15 \text{ g})$ due to limited supply.

 $PM_{2.5}$ mass concentrations, in the range of 328–2277 μ g/m³, are one to two orders of 298 magnitude higher than those commonly measured at ambient monitoring sites. Typical sample 299 durations from ignition to completion were ~40–60 minutes, except for the Everglades (FL) peats 300 that took longer (up to 135 minutes). Similar particle loadings (mostly within \pm 20 %) were found 301 for downstream (aged) and upstream (fresh) samples. The exception is Everglades (FL) peat, 302 where prolonged sample durations and 7-days aging times resulted in higher downstream particle 303 loadings with ratios of aged/fresh mass concentrations ranging 1.6–2.0.

304 **3.2.1 Gaseous carbon emission factors**

305 Individual and average carbonaceous gas EFs are summarized in Table S4. As shown in 306 Fig. S4, variations by biome are found among the different peats with relative standard deviations 307 ranging from 2–27 %. The largest EFs are found for CO_2 (EF $_{CO_2}$), ranging from 994–1455 g kg 308 ¹, which are 1–2 orders of magnitude higher than the corresponding $E_{\text{C}\text{O}}$ and E_{CH_4} . Average 309 EF_{CO2} varied by >30 % among biomes, ranging from 1073 ± 61 to 1400 ± 38 g kg⁻¹ for the Russian 310 and Alaskan peats, respectively.

Muraleedharan et al. (2000) reported the first laboratory-combustion EFs of 150–185 g kg⁻ 312 ¹ for EF_{CO_2} , 15–37 g kg⁻¹ for EF_{CO} , and 6–11 g kg⁻¹ for EF_{CH_4} on a wet mass basis for Brunei peat with a 51.4 % moisture content. Table 2 shows studies conducted over the past decade, with more field monitoring during the 2015 ENSO period in Indonesia. Open path (OP)-FTIR was commonly used to acquire gaseous emissions with MCEs ranging 0.77‒0.86, consistent with smoldering combustion. A limited number of burns (n of 1 to 6) were conducted in laboratories using combustion chambers, whereas a larger number of in situ field-burn samples (n of 17 to 35) were acquired for southeast Asian peats (Wooster et al., 2018;Setyawati et al., 2017;Stockwell et al., 319 2016).

320 Table 2 exhibits >2-fold variations in E_{CO_2} among studies. The highest E_{CO_2} with the 321 lowest variability was found for tropical peats (ranges $1331-1831$ g kg⁻¹ for smoldering). Average E_{FCO_2} (1331 \pm 78 g kg⁻¹) for Malaysian peat (n=6) from this study is ~16 % and ~18 % lower than 323 the 1579 \pm 58 and 1615 \pm 184 g kg⁻¹ for Peninsula, Malaysia (Smith et al., 2018) and average 324 boreal/temperate peats (Hu et al., 2018), respectively. Malaysian peat E_{Fco_2} measured in this

325 study is 20 % lower than the 1681 \pm 96 g kg⁻¹, averaged from seven studies of Kalimantan and 326 Sumatra, Indonesia peats (Christian et al., 2003;Stockwell et al., 2014;Huijnen et al., 2016;Nara et 327 al., 2017).

328 Overall average $E_{\text{Fco}_2}(1269 \pm 139 \text{ g kg}^{-1}, \text{ n=32})$ from this study (Table S4) are ~19–25 % 329 lower than the 1563 ± 65 g kg⁻¹ for peatland fires used in atmospheric models (Akagi et al., 2011); 1550 ± 130 g kg⁻¹ in a recent review (Andreae, 2019); and 1703 g kg⁻¹ (Christian et al., 2003) adopted by the 2014 Intergovernmental Panel on Climate Change (IPCC) for organic soil fire inventories (IPCC, 2014). EFs derived from this study cover four biomes which may improve global emission estimates.

334 Average EF_{CO} is typically ~12–15 % of EF_{CO2} in the range of 157–171 g kg⁻¹ for all but the 335 two Florida peats with 394 ± 46 g kg⁻¹ (MCE = 0.65 \pm 0.04) and 93 ± 21 g kg⁻¹ (MCE = 0.90 \pm 336 0.03) for the Putnam and Everglades peats, respectively (Table S4 and Table 2). This is consistent 337 with a higher E_{CO} under lower MCEs reported by Setyawati et al. (2017) –a 45-fold increase from 338 3.1 ± 7.2 g kg⁻¹ for flaming (MCE = 0.998 \pm 0.005) to 138 \pm 72 g kg⁻¹ for smoldering (MCE = 339 0.894 ± 0.055 combustion.

340 Average EF_{CO} of 157–161 g kg⁻¹ for boreal and temperate peats are ~10 % lower than the 341 179 \pm 61 g kg⁻¹ from Hu et al. (2018). The overall average EF_{CO} of 175 \pm 92 g kg⁻¹ from this study 342 is ~4 % lower than the 182 ± 60 g kg⁻¹ in Akagi et al. (2011), ~30 % lower than the 250 ± 23 g kg⁻¹ 343 ¹ in Andreae (2019), and ~15 % lower than the 207–210 g kg⁻¹ used in IPCC (2014).

344 Average E_{CH_4} is ~0.3–0.9 % of E_{CO_2} , lowest for cold climates with 3.2–6.9 g kg⁻¹ for the 345 boreal and temperate peats and $6.7-10.4$ g kg⁻¹ for the subtropical and tropical peats (Table S4). 346 Table 2 shows that E_{CH_4} for Malaysian and Indonesian peats exceed ~10 g kg⁻¹ in five of the eight 347 past studies. These EFs are more in line with the 11.8 ± 7.8 g kg⁻¹ in Akagi et al. (2011), 9.3 ± 1.5 348 g kg⁻¹ in Andreae (2019), and 9–21 g kg⁻¹ in IPCC (2014), but are higher than the average (6.6 \pm 349 2.4 g kg^{-1}) found in this study.

350 Emission factors depends on both fuel composition and combustion conditions. Figure S5a 351 shows that total measured gas and particle carbon increases with fuel carbon content for the six 352 types of peat. EF_{CO₂} increases with fuel carbon content (Fig. S5b) except for the Putnam (FL) peat, 353 which has the highest fuel carbon (56.6 %) but low EF_{CO} . It has high EF_{CO} and EF_{TC} (Figs. S5c-354 d), consistent with its low MCE (0.65 \pm 0.04). EF_{CO} and EF_{TC} do not show a clear trend with fuel

355 carbon content; however, EF_{CH_4} increases with fuel carbon (Fig. S5e) but decreases with fuel 356 oxygen content (Fig. S5f).

357 **3.2.2 Gaseous nitrogen emission factors**

358 Individual and average gaseous nitrogen species EFs are summarized in Table S5. EF_{NO} 359 and EF_{NO_2} (Fig. S6b) are low in the range of 0.2–2.1 g kg⁻¹. For fresh emissions, most of the NO_x 360 (NO + NO₂) is present as NO. After the OFR, NO decreased while NO₂ increased, as shown in 361 Fig. S7. A low correlation coefficient ($r = 0.67$) between the downstream and upstream $E_{N_{\text{O}_x}}$ 362 suggests the changes of NO/NO2 ratios between the fresh and aged emissions as well as 363 variabilities among tests.

 364 Table 3 shows that most studies do not report EF_{NO} or EF_{NO} , partially due to the low 365 concentrations and large variabilities under atmospheric aging. Stockwell et al. (2016;2014) 366 reported 0.31–1.85 g kg⁻¹ EF_{NO} and 2.31–2.36 g kg⁻¹ EF_{NO2} for Indonesia peats. These levels are 367 much higher than the $E\text{F}_{NO_x}$ (as _{NO2}) of 0.75 ± 0.10 g kg⁻¹ for Malaysian peat in this study.

368 Emissions for reactive nitrogen, EF_{NO_V} (as NO_2), ranged 0.61–6.3 g kg⁻¹ with an average 369 of 2.4 \pm 1.4 g kg⁻¹ (Table S5). $EF_{NO_y} > 2.5$ g kg⁻¹ are found for the two Florida peats (Fig S6c) with 370 an average of 4.3 \pm 1.1 g kg⁻¹ for Everglades, which reports the highest nitrogen content (3.93 \pm 371 0.08 %) among peats (Table 1). Figure S5g shows that EF_{NO} increases with fuel nitrogen content, 372 while EF_{NO2} is not dependent on fuel nitrogen content (Fig. S5h). Because EF_{NO} is higher than 373 EF_{NO2}, EF_{NOx} and EF_{NOy} increase with fuel nitrogen content (not shown). Figure S8 shows that 374 \sim 74 % of the NO_y is NO_x with high correlation coefficient (r = 0.93). Nitrogen oxides are typically 375 converted to other oxidized nitrogen species within 24 hours after emission (Seinfeld and Pandis, 376 1998;Prenni et al., 2014). The ratio of NO_x/NO_y has been used to infer photochemical aging 377 (Kleinman et al., 2003;Kleinman et al., 2007;Olszyna et al., 1994;Parrish et al., 1992). The high 378 NO_x/NO_y ratios suggest that NO_x had not converted to other reactive nitrogen species in the diluted 379 peat plume.

 380 Nitrous oxide (N₂O), an inert form of oxide from nitrogen with an atmospheric lifetime of 381 ~110 years, commonly emitted from fossil fuel, solid waste fertilizers, and biomass combustion, 382 is a greenhouse gas defined by U.S. EPA (2016). Table S5 shows that $EF_{N,Q}$ are similar to EF_{NO} 383 except for Everglades (FL) peat with low EF_{N_2O} (1.5 \pm 0.3 g kg⁻¹), in the range of 1.1–4.4 g kg⁻¹

384 and average of 2.0 ± 0.7 g kg⁻¹. The highest average EF_{N_2O} (3.6 \pm 0.6 g kg⁻¹) is found for Putnam 385 (FL) peat (Fig. S6c).

386 Hydrogen cyanide (HCN), a known emission from biomass burning (Li et al., 2000;Stockwell et al., 2014), exhibits >7-fold differences $(1.8-14 \text{ g kg}^{-1})$ in EF_{HCN} (Table S5). 388 The average EF_{HCN} (11.5 \pm 2.3 g kg⁻¹) for Putnam (FL) peat is 2- to 5-fold higher than for the other 389 biomes (Fig. S6a). Table 3 shows large EF_{HCN} variations among studies, from 0.73 ± 0.50 g kg⁻¹ 390 (Ireland, Wilson et al., 2015) to 5.75 ± 1.60 g kg⁻¹ (Indonesia, Stockwell et al., 2016). More 391 consistent EF_{HCN} are found for tropical peats in the range of 3–6 g kg⁻¹. Average EF_{HCN} in this 392 study, 4.7 ± 3.1 g kg⁻¹, are in-line with the 5.0 ± 4.9 and 4.4 ± 1.2 g kg⁻¹ reported by Akagi et al. 393 (2011) and Andreae (2019).

 E_{NH_3} (0.4–8.3 g kg⁻¹) are of the same magnitude as E_{HCN} (Fig. S6a) and independent of 395 fuel nitrogen content (Fig. S5i) except for the Everglades (FL) peat $(9-18 \text{ g kg}^{-1})$ which has the 396 highest fuel nitrogen content. Total reduced nitrogen emissions, EF_{NH_3} + EF_{HCN} , for the two 397 Florida peats (12–25 g kg⁻¹) are \sim 2- to 3-fold higher than those for other regions. Table 3 also 398 shows high variabilities in EF_{NH_3} among studies (1–11 g kg⁻¹). The overall average of 5.6 \pm 4.8 g 399 kg⁻¹ in this study is consistent with the 4.2 \pm 3.2 g kg⁻¹ in Andreae (2019), but ~50 % of the 10.8 ± 12.4 g kg⁻¹ in Akagi et al. (2011). The high standard deviations associated with these averages 401 signify large variabilities among experiments.

402 Figure S9a shows some difference in E_{NH_3} determined by FTIR and the impregnated filter, 403 especially at high concentrations. The regression slope shows that E_{NH_2} by the FTIR was ~22 % 404 lower than that of filters with a correlation coefficient of 0.76. Variable baselines in the FTIR 405 measurements along with some nitrogen content in the diluted air and breath NH3 (Hibbard and 406 Killard, 2011) in the testing laboratory may have contributed to these variations. The impregnated 407 filter collects all of the NH3 over the sampling period, including amounts that are below the FTIR 408 detection limits, so it is probably better representing the time-integrated EF_{NH_2} . Reduction of EF_{NH_2} 409 is most apparent after atmospheric aging in Fig. S9b (slope of 0.11), with $2-14$ g kg⁻¹ in fresh 410 emissions and reduced to \sim 0.5–3 g kg⁻¹ after aging.

411 **3.2.3 PM2.5 mass and carbon emission factors**

412 Continuous PM_{2.5} from the DustTrak with the factory calibration factor yielded PM_{2.5} EFs 413 3- to 5 times higher than of those derived from gravimetric analyses, higher than the 2-fold mass

 differences by Wooster et al. (2018). This discrepancy is well known as the factory calibration uses Arizona road dust with a size distribution that is much coarser than that of biomass burning. 416 Therefore, $EF_{PM_2,5}$ is calculated from the filter samples. Chow et al. (2019) present the species abundances in PM2.5 mass for this study based on the average fresh and aged profiles, separated by 2- and 7-day photochemical aging times simulated with the OFR (Aerodyne, 2019). The same approach is used in Table S6 to compare fresh and aged particle EFs. Comparisons between 420 combined fresh vs. aged EFs for PM_{2.5} mass, carbon (OC, EC, and TC), and levoglucosan for individual tests are shown in Table S7.

422 Figure S10 shows that $E_{PM_2,5}$ varies >4-fold (14–61 g kg⁻¹) for different peats without 423 large differences between fresh and aged emissions. EF_{OC} varied from 9–44 g kg^{-1} while EF_{EC} 424 (0.00–2.2 g kg⁻¹) were low (Table S7). The majority of $EF_{PM_{2.5}}$ consist of EF_{OC} , with average $E_{\text{C}}/E_{\text{FM}_2,5}$ ratios of 52–98 % by peat type in fresh emissions, followed by ~14–23 % reductions 426 after aging, with the exception of Putnam (FL) peats (remained at 69–70 %).

A27 Reductions of EF_{OC} after ~7 days of photochemical aging are most apparent (~7–9 g kg⁻¹) 428 for the boreal peats, with the largest degradation for low temperature OC1 (evolved at 140°C 429 during carbon analysis), indicating losses of high vapor pressure SVOCs upon aging (Table S6). 430 The two Florida peats exhibit an initial E_{OC} decrease of \sim 2 g kg⁻¹ after 2-days aging, but with an 431 increase of 1.8–4.0 g kg⁻¹ after 7 days. However, these changes are less than the standard deviations 432 associated with the averages.

433 EFwsoc varies by 5-fold $(3-16 \text{ g kg}^{-1})$ with over a ~50 % increase for the Putnam (FL) and 434 Malaysian peats after 7 days. Average EF_{WSOC} by peat type accounts for ~16–36 % and ~20–62 % 435 of fresh $EF_{PM_{2.5}}$ and EF_{OC} , respectively. From 2- to 7-day aging, Fig. S11 shows reduced 436 correlation coefficients (*r* from 0.86 to 0.76 for PM2.5, from 0.88 to 0.84 for OC, and 0.94 to 0.68 437 for WSOC).

 As WSOC is part of the OC, the WSOC/OC ratio can be used to illustrate atmospheric 439 aging. Figure S12 shows that WSOC/OC ratios increased by 6–16 % after aging. This is attributed 440 to a combination of oxygenation of the aged organic emissions and the reduction of E_{DC} (Table S7). The increase in WSOC/OC ratios may also be due to photochemical transformation of primary OC to WSOC and/or formation of water-soluble SOA during atmospheric aging (Aggarwal and Kawamura, 2009;Agarwal et al., 2010).

 Table 4 compares filter-based PM mass and carbon from different studies. Since different carbon protocols yield different fractions of OC and EC (Watson et al 2005), the analytical protocols are listed. Most studies follow either IMPROVE_A TOR (Chow et al., 2007) or NIOSH thermal/optical transmittance (TOT) protocols (NIOSH, 1999). As the transmittance pyrolysis correction (i.e., TOT) accounts for charred OC both on the filter surface and organic vapor within 449 the filter substrate, lower EF_{EC} are expected as compared to TOR (Chow et al., 2004). To remove the OC and EC split uncertainty, TC to PM mass ratios are listed for comparison. Two studies reported black carbon (BC) from a micro-aethalometer (Wooster et al., 2018) or a single particle soot photometer (SP2; May et al., 2014). As BC levels are very low, not much differences can be distinguished between BC and EC .

454 Most studies report $E_{PM_{25}}$ with a few exceptions for $E_{PM_{10}}$ (Kuwata et al., 2018;Iinuma 455 et al., 2007) and EF_{PM_1} (May et al., 2014). As most of the PM₁₀ is in the PM_{2.5} fraction for biomass combustion, particle size fractions have a minor effect on PM EFs (Geron and Hays, 2013;Hu et al., 2018).

458 Table 4 shows that the majority of E_{PM_2} lies in the range of ~20–50 g kg⁻¹ with the 459 exception of very low EF_{PM_2} , of 4–8 and 6–7 g kg⁻¹ reported by Bhattarai et al. (2018) and Black et al. (2016). These are probably due to low filter mass loadings and limited testing (n of 1 to 3), which may result in large uncertainties in gravimetric mass.

162 Despite different carbon analysis methods, most E_{C} lies in the range of ~5–30 g kg⁻¹ with 463 the exception of E_{DC} (37 g kg⁻¹) for Putnam (FL) and E_{OA} (organic aerosol, 34.5 g kg⁻¹) for Indonesian peat measured by a time-of-flight/mass spectrometer (May et al., 2014). Most studies 465 show that EF_{TC} accounts for ~60–85 % of the EF_{PM_{2.5}, with low EF_{EC} (0.02–1.3 g kg⁻¹).}

466 EF_{WSOC} of 6–7 and 4–6 g kg⁻¹ for the Alaskan and Malaysian peats from this study are 467 consistent with the 6.7 and 3.1 g kg^{-1} from German and Indonesian peats in Iinuma et al. (2007), respectively. EFLevoglucosan exhibits >2 orders of magnitude variabilities among the biomes with 469 0.24–16 g kg⁻¹ and 0.24–9.6 g kg⁻¹ in fresh and aged emissions, respectively.

- Past studies show that the extent of levoglucosan degradation depends on OH exposure in 471 the OFR, organic aerosol composition, and vapor wall losses (e.g., Bertrand et al.,
- 2018a;2018b;Hennigan et al., 2010;Hoffmann et al., 2010;May et al., 2012;Lai et al.,
- 2014;Pratap et al., 2019). Potential chemical pathways for the formation of organic species in
- 474 biomass combustion emissions were proposed by Gao et al. (2003) that suggested the
- 475 fragmentaion of levoglucosan to C3‒C5 diacids, followed by oxalic acid, acetic acid, and formic
- 476 acid. This is consistent with the increases in EF_{organic acids} after atmospheric aging, as shown in
- 477 Table S6. However, detailed chemical mechanisms need to be further investigated.

478 The highest $EF_{Levoglucosan}$ is found for the fresh Russian peats (15.8 \pm 2.9 g kg⁻¹), and this is 479 diminished by 45 % after 7-day aging $(8.8 \pm 2.1 \text{ g kg}^{-1})$. Few studies report $EF_{Levoglucosan}$ and results 480 are highly variable. The $EF_{Levoglucosan}$ of 0.57 g kg⁻¹ in PM_{2.5} (converted from 46 mg/g OC) by 481 Jayarathne et al. (2018) is \sim 23 % of the 2.5 g kg⁻¹ by Iinuma et al. (2007), both for Indonesia peats. 482 The EF_{Levoglucosan} of 0.5–1.0 g kg⁻¹ from fresh Malaysian peat in this study is comparable to 0.57 g 483 kg⁻¹ by Jayarathne et al. (2018). The 4.6 g kg⁻¹ of $E_{\text{Levoglucosan}}$ for the northern German peat 484 (Iinuma et al., 2007) is higher than the 1.2–4.7 g kg⁻¹ found for the average Siberian and Alaskan 485 peats in this study.

486 EFs for ionic nitrogen species are low $(<0.1 \text{ g kg}^{-1})$ in fresh emissions. Both $EF_{NH_4}{}^+$ and 487 EF_{NO₃} increase with 7-day aging $-$ >0.5 g kg⁻¹ EF_{NH₄⁺ for all peat and >1 g kg⁻¹ EF_{NO₃} for all but} 488 Russian (0.79 \pm 0.08 g kg⁻¹) and Putnam (FL) peats (0.66 \pm 0.08 g kg⁻¹), consistent with the 489 formation of secondary inorganic aerosol.

490 **3.3 Effect of fuel moisture content on emission factors**

 Only a few studies examine the effects of fuel moisture on peat emissions with inconsistent results. An early study by McMahon et al. (1980) reported high emissions for total suspended 493 particle (TSP, \sim 30–60 µm) of 30 \pm 20 g kg⁻¹ for dry (<11 % moisture) as compared to 4.1 \pm 3.8 494 g kg⁻¹ (after the first 24 hours) for wet (53–97 % moisture) organic soil. Rein et al. (2009) found higher CO2 (but not CO) yields while increasing fuel moisture to 600 % for tests of boreal Scotland peats in a cone calorimeter which continuously supplies heat to the fuel. Smoldering combustion is possible with high *in situ* fuel-moisture contents when surrounding peat provides insulation and heat from combustion is available for drying just before the advancing front, but such samples will not burn in the laboratory. Watts (2013) sustained lab-based peat smoldering from a cypress swamp (FL) at ~250 % moisture content, which appears to be a maximum.

501 Table 2 shows that increasing moisture content from ~25 % to ~60 % for the three Putnam 502 (FL) peats resulted in an 11 % increase in E_{CO} , but reductions of 20 % E_{CO} and 12 % E_{CH_4} . 503 No consistent variabilities are found for nitrogen species (Table 3), with negligible changes in

504 EF_{NH₃} and EF_{HCN}; 13–30 % reduction in EF_{NO}, EF_{NO_x}, and EF_{NOy}, as well as 45 % increase in EF_{NO₂} 505 and 9 % increase in $EF_{N,0}$. On the other hand, a reduction of ~30 % $EF_{PM_{2,5}}$ is found (Table 4) as 506 fuel moisture increased from 25 % to 60 %. Higher fuel moisture contents typically result in less 507 efficient burning conditions, thereby increasing CO and reducing MCE (Chen et al., 2010). 508 However, an opposite trend is found with EF_{cO} reduced from 394 ± 46 to 315 ± 10 g kg⁻¹ and 509 MCEs increased from 0.65 ± 0.04 to 0.72 ± 0.01 . It is hypothesized that at higher fuel moisture 510 contents, combustion residence time is slowed enough so that radiant heat transfer from ignited 511 particles to uncombusted areas of peat can be greater, thus increasing the combustion efficiency. 512 It is also possible that the higher water content results in water-gas shift reaction that converts CO 513 and water to $CO₂$ and hydrogen. Overall, the EFs for ~60 % moisture contents are comparable to 514 EFs for the six other peats with ~25 % moisture content.

515 Increased (~25 to 60 %) fuel moisture yields a ~20 % reduction in fresh EF_{OC} , much lower 516 than the 35–43 % reduction (\approx 25 to 50 % moisture) reported by Chakrabarty et al. (2016) for the 517 Siberian and Alaskan peats. By increasing fuel moisture, Chakrabarty et al (2016) also reported an 518 increase in EF_{CO₂} by 20 % but a ~75 % reduction and 35 % increase in EF_{CO} for Siberian and 519 Alaskan peats, respectively, based on a single sample.

520 **3.4 Distribution of carbon and nitrogen species**

 Figure 3 shows the distribution of carbonaceous species. Because the EFs are calculated based on the carbon mass balance method (Eq. (2)), the total emitted carbon is assumed to be the same as total consumed carbon. The majority (>90 %) of total emitted carbon are present in the 524 gas phase with 54–75 % $CO₂$, followed by 8–30 % CO. On average, emitted carbon includes 69.8 \pm 7.5 % CO₂; 14.8 \pm 6.5 % CO; 1.0 \pm 0.3 % CH₄; 9.4 \pm 2.4 % volatile carbon compounds; and 4.8 \pm 1.3 % PM_{2.5} TC. The highest (30 \pm 4 %) and lowest (8.4 \pm 1.9 %) CO abundances for the Putnam (FL) and Everglades (FL) peats are consistent with the lowest and highest average MCEs of 0.65 and 0.90, respectively.

529 The nitrogen budget in Fig. 4 accounts for 24–52 % of nitrogen in the consumed fuel. Since 530 burn temperatures are below those at which NO_x forms from oxygen reactions with $N₂$ in the air, 531 most of the nitrogen in emissions derives from the nitrogen content of the fuels. Kuhlbusch et al. 532 (1991) found N₂ emissions constituted an average of 31 ± 20 % of nitrogen in consumed grass, 533 hay, pine needle, clover, and wood fuels. Since N_2 measurements require combustion in N₂-free

534 atmosphere (e.g., a He-O₂ mixture), N₂ was not quantified here, but it was probably emitted in similar quantities. Isocyanic acid (HNCO) is another important nitrogen-containing compound found in biomass burning emissions (Roberts et al., 2011). Koss et al. (2018) report a 0.16 g/kg nitrogen-equivalent EF (0.5 g/kg for HNCO) for a peat sample, comparable to EFs for several of the measured nitrogen compounds summarized in Table 3. Other nitrogen-containing gases 539 reported by Koss et al. (2018) with EFs >0.1 g/kg include acetonitrile (CH₃CN), acetamide 540 (CH₃CONH₂), benzonitrile (C₆H₅CN), and pyridine + pentadienenitriles (C₅H₅N), which could account for part of the unmeasured nitrogen in emissions. Neff et al. (2002) found that organic 542 nitrogen formed from photochemical reactions of hydrocarbon with NO_x plays an important role 543 in the global nitrogen cycle. Approximately 30 ± 16 % of Neff et al.'s total nitrogen was from organic nitrogen, similar to the 25 % of total nitrogen deposition flux reported by Jickells et al. (2013). Alkaloids, dissolved organic nitrogen, along with nitroaromatic compounds have been reported (e.g., Benitez et al., 2009;Laskin et al., 2009;Kuhlbusch et al., 1991;Koppmann et al., 2005;Kopacek and Posch, 2011;Stockwell et al., 2015).

548 The majority (>99 %) of the measured nitrogen in emissions is in the gas phase. On 549 average, 16.7 % of the fuel nitrogen was emitted as NH₃ and 9.5 % was emitted as HCN. N₂O and 550 NO_y constituted 5.7 % and 2.9 % of nitrogen in the consumed fuel. NH₃ emissions accounted for 551 26–28 % of consumed nitrogen for Everglades (FL) and Malaysian peats while HCN emissions 552 dominated fuel nitrogen(13–17 %) for the Putnam (FL) and Malaysian peats. The fraction of N₂O 553 emissions in Malaysian peat nitrogen (10.3 \pm 1.1 %) was more than twice the fractions found for 554 the other regions with reactive nitrogen (NO_y) only accounting for 2–4 % of the fuel nitrogen. The 555 sum of NH₃ and HCN nitrogen ranged 35–39 % of consumed nitrogen for the Malaysian and 556 Everglades (FL) peats, which is about three times the fraction for Russian peat.

557 Lobert et al. (1990) point out the importance of nitrogen-containing gases in biomass 558 burning for the atmospheric nitrogen balance. On average, the emitted nitrogen includes 17 ± 10 559 % NH₃, 9.5 ± 3.8 % HCN, 5.7 ± 2.5 % N₂O, 2.8 ± 1.0 % NO_y (including NO_x), and 0.14 ± 0.18 % 560 of PM nitrogen (sum of NO₂, NO₃, and NH₄⁺). The average nitrogen budget accounts for 35 ± 11 561 % of the total consumed nitrogen, consistent with past studies showing that ~one- to two-thirds of 562 the fuel nitrogen is accounted for during biomass combustion.

563 **4 Summary and conclusions**

564 This paper reports fuel composition and emission factors (EFs) from laboratory chamber 565 combustion of six types of peat fuels representing boreal (Russia and Siberia), temperate (northern 566 Alaska, USA), subtropical (northern and southern Florida, USA), and tropical (Borneo, Malaysia) 567 climate regions. Dried peat fuel contains $44-57$ % carbon (C), $31-39$ % oxygen (O), $5-6$ % 568 hydrogen (H), 1–4 % nitrogen (N), and <0.01 % Sulfur (S). The nitrogen to carbon ratios are low, 569 in the range of 0.02–0.08, consistent with peat compositions reported in other studies.

570 Thirty-two tests with 25 % fuel moisture were reported with predominant smoldering 571 combustion conditions (MCE = 0.82 ± 0.08). Average fuel-based EFs for CO₂ (EF_{CO₂) are highest} 572 (1400 \pm 38 g kg⁻¹) and lowest (1073 \pm 63 g kg⁻¹) for the Alaskan and Russian peats, respectively. 573 EFco and EFcH₄ are ~12–15 % and ~0.3–0.9 % of EFc_{O2} in the range of ~157–171 g kg-1 and 3– 574 10 g kg⁻¹, respectively. The exception is the two Florida peats, reporting the highest (394 \pm 46 g 575 kg⁻¹) and lowest (93 \pm 21 g kg⁻¹) EF_{CO} for Putnam and Everglades, respectively.

576 Filter-based E_{PM_2} , varied by >4-fold (14–61 g kg⁻¹) without appreciable changes between 577 fresh and aged emissions. The majority of $E_{PM_{2,5}}$ consists of E_{C_2} , with average E_{C_2} $E_{\text{PM}_{2,5}}$ ratios 578 by peat type in the range of 52–98 % in fresh emissions, followed by \sim 14–23 % reduction after aging 579 with the exception of Putnam (FL) peats (retained at 69–70 %). Reduction of E_{DC} (~7–9 g kg⁻¹) are 580 most apparent for boreal peats with the largest decrease in low temperature OC1 (evolved at 581 140°C), suggesting the loss of high vapor pressure semi-volatile organic compounds during aging. 582 EFs for water-soluble OC (EF_{WSOC}) accounts for \sim 20–62 % of EF_{OC} with \sim 6–16 % increase in 583 EF_{WSOC}/EF_{OC} ratios after aging. The highest $EF_{Levoglucosan}$ is found for Russian peat (15.8 \pm 2.9 g 584 kg^{-1}) with a 45 % degradation after aging.

585 The majority (>90 %) of the total emitted carbon is in the gas phases with $54-75$ % CO₂, 586 followed by 8–30 % CO. Nitrogen budget only explains 24–52 % of the consumed nitrogen with 587 an average of 35 ± 11 %, consistent with past studies that ~one- to two-thirds of the total nitrogen 588 are lost upon biomass combustion. The majority (>99 %) of the total emitted nitrogen is in the gas 589 phase, dominated by the two reduced nitrogen species with 16.7 % for NH3 and 9.5 % for HCN. 590 N₂O and NO_y are detectable at 5.7 % and 2.9 % abundance. EFs from this study can be used to 591 refine current emission inventories.

- **5 Author contributions**
- JGW, JCC, JC, L-WAC, and XW jointly designed the study, performed the data analyses, and prepared the manuscript. QW, JT, and SSHH carried out the peat combustion experiments. SG conducted emission factor calculations. ACW acquired peat fuels and provided technical
- advice on peat fuel process.
- **6 Competing interests**
- The authors declare that there are no conflicts of interest.

7 Data availability

The data of this study are available from the authors upon request.

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948 Table 1. Average peat composition^a (dry weight percentage) for total carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O).

						N/C mass	
Peat Location	C(%)	H (%)	N(%	S(%)	O(%)	ratio	Sum (CHNSO; %)
Odintsovo, Russia	44.20 ± 1.01	6.43 ± 0.16	1.50 ± 0.52	< 0.01	38.64 ± 0.78	0.034	90.8
Pskov, Siberia	52.03 ± 0.23	6.30 ± 0.05	2.92 ± 0.12	< 0.01	36.83 ± 0.39	0.056	98.1
Northern Alaska, USA	50.94 ± 0.81	6.05 ± 0.07	1.79 ± 0.09	< 0.01	36.62 ± 0.30	0.035	95.4
Putnam County Lakebed, Florida, USA	56.64 ± 0.37	6.25 ± 0.40	3.53 ± 0.05	< 0.01	31.43 ± 0.36	0.062	97.8
Everglades, Florida, USA	47.22 ± 0.57	5.15 ± 0.16	3.93 ± 0.08	< 0.01	34.18 ± 0.87	0.083	90.5
Caohai, Guizhou, Southeast China	19.74 ± 2.01	2.09 ± 1.26	1.35 ± 0.16	< 0.01	23.95 ± 1.15	0.068	47.1
Gaopo, Guizhou, Southeast China	29.70 ± 2.09	3.13 ± 0.16	2.08 ± 0.22	< 0.01	21.46 ± 1.27	0.070	56.4
Borneo, Malaysia	50.55 ± 2.53	6.46 ± 0.99	1.16 ± 0.08	< 0.01	33.72 ± 0.30	0.023	91.9

^a Elemental analyses were performed using Elemental Analyzer (Flash EA1112 CHNS/O Analyzer, Thermo Fisher Scientific, Waltham, MA, USA). Each dried peat sample (~2–3 g) was submitted for combustion analysis at 900°C for 950 g) was submitted for combustion analysis at 900°C for C, H, N, and S in a helium/oxygen atmosphere and at 1060°C for O in a helium atmosphere. Three to four replicate sample analyses were conducted for each type of pea analyses were conducted for each type of peat to obtain the average and standard deviations.

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953 Table 2. Peat combustion emission factors (EFs) for CO_2 , CO, and CH₄^a.

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955 ^a Data acquired from this study are highlighted in green

956 ^b ^bOnly included number of samples reported

^cFM; Fuel moisture content

958 FTIR: Fourier transform infrared spectroscopy. CH₄ was acquired by FTIR in this study

959 ^e Obtained from Stockwell et al. (2014) as only the ratios of moles compound/total moles carbon detected was reported in Yokelson et al. (1997)

960 ^f NWR: National Wildlife Reserve

^gReviews for atmospheric modeling and emission inventory development

h From Ward and Hardy (1984); Yokelson et al. (1997;2013) i From Christian et al. (2003) for tropical peats

964 ^j Detailed volatile organic gas emission factors for one of these samples are reported by Koss et al. (2018)

966 Table 3. Peat combustion emission factors (EFs) for gaseous nitrogen species^a.

967 ^a Data acquired from this study is highlighted in green

968 ^b Data acquired from Fourier Transport Infrared (FTIR) spectroscopy for this study

- ^c P_{Data} acquired from the NO_x instrument upstream of the oxidation flow reactor for this study
- ^dData acquired from the NO_y instrument for this study
- ^e Reported as NOx
- 972 Free reported NO_x as NO was converted to NO_x as NO₂ for comparison
- **Reviews for atmospheric modeling and emission inventory development**
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977 Table 4. Peat combustion emission factors (EFs) for $PM_{2.5}$ mass and carbon^a.

978 Data acquired from this study are highlighted in green

^bThe IMPROVE_A protocol reports OC and EC by Thermal/Optical reflectance (TOR, Chow et al., 2007); The NIOSH and NIOSH5040 reports OC and EC by Thermal/Optical transmittance

980 (NIOSH, 1999); VDI is German Industrial Standard (VDI, 1999); TOF-MS: time-of-flight mass spectrometer (Drewnick et al., 2005); and Single Particle Soot Photometer (SP2, DMT Inc., Boulder, CO, USA) measures black carbon (BC) by laser-induced incandescence technique (Stephens et al., 2003). ^c 982 Size fraction is PM_{2.5} except where otherwise noted. d^4 FM; Fuel Moisture

eIncludes averages of all fresh and all aged emission factors (EFs) for the 25% fuel moisture (i.e., grouped Fresh 2 and Fresh 7 vs Aged 2 and Aged 7 shown in Table S7)

985 ^f Comparison between 25% and 60% fuel moisture content are only made with Fresh 2 vs. Aged 2 of Putnam (FL) peats.

^gSum of five stages of Berner Impactor with 0.05-0.14, 0.14-0.42, 0.42-1.2, 1.2-3.5, and 3.5-10 µm size ranges.

987 ^h National Wildlife Refuge, eastern NC

ⁱ From Jayarathne et al. (2018)

989 ^j BC by MicroAethalometer (AE 51) (Cheng et al., 2013;Wooster et al., 2018)

k PM₁ and organic aerosol (OA) acquired from Time-of-Flight Mass Spectrometry (TOF-MS) measurements (Drewnick et al., 2005)

 \bigoplus 9991 l Reviews for atmospheric modeling and emission inventory development.

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Figure 1. Global distribution of peatlands (based on Yu et al., 2010). Samples were obtained from Odintsovo, Russia; Pskov, Siberia; black spruce 995 forest, Northern Alaska, USA; Putnam County Lakebed and Everglades National Park, Florida, USA; Caohai and Gaopo, Guizhao, China; and 996 Borneo, Malaysia.

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 Figure 2. Configuration for peat combustion experimental set up. (FTIR: Fourier Transform Infrared Spectrometer; OFR: oxidation flow reactor; 001 OFR lamps were operated at 2 and 3.5 volts to simulate aging of ~2 and 6.79 days, respectively).

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Peat Location

- $005 = OC + EC$). Numbers on top of the bars are average Modified Combustion Efficiencies (MCE) and the number of samples in each average. The 006 Carbon Compounds include hydrogen cyanide (HCN), formaldehyde (CH₂O), methanol (CH₃OH), formic acid (HCOOH), carbonyl sulfide (COS),
- 007 ethylene (C₂H₄), ethane (C₂H₆), acetaldehyde (C₂H₄O), ethanol (C₂H₅OH), acetic acid (CH₃COOH), propane (C₃H₈), acrolein (C₃H₄O), acetone
- 008 (C₃H₆O), 3-butadiene (C₄H₆), benzene (C₆H₆), hexane (C₆H₁₄), phenol (C₆H₅OH), and chlorobenzene (C₆H₅Cl) acquired by Fourier Transfer Infrared
- 009 Spectrometry.

- Figure 4. Ratio of emitted over consumed nitrogen for each type of peat (emitted nitrogen is the sum of nitrogen in HCN, NH₃, NO, NO₂, and NO_z 0.13 [NO_v-NO₃], N₂O, HNO₃, and PM_{2.5} ions [NO₂⁻ + NO₃⁻
- $[NO_y-NO_x], N₂O, HNO₃, and PM_{2.5} ions [NO₂⁻ + NO₃⁻ + NH₄⁺]; and the consumed nitrogen is the product of percent fuel nitrogen content and mass$ of fuel burned).