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Emission Factors from Aerial and Ground Measurements of Field and Laboratory Forest Burns in the Southeastern U.S.: PM_{2.5}, Black and Brown Carbon, VOC, and PCDD/PCDF

Johanna Aurell[†] and Brian K. Gullett*

U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Research Triangle Park, North Carolina 27711, United States

Supporting Information

ABSTRACT: Aerial- and ground-sampled emissions from three prescribed forest burns in the southeastern U.S. were compared to emissions from laboratory open burn tests using biomass from the same locations. A comprehensive array of emissions, including $PM_{2.5}$, black carbon (BC), brown carbon (BrC), carbon dioxide (CO₂), volatile organic compounds (VOCs), and polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were sampled using ground-based and aerostat-lofted platforms for determination of emission factors. The $PM_{2.5}$ emission factors ranged from 14 to 47 g/kg biomass, up to three times higher than previously published studies. The biomass type was the primary determinant of $PM_{2.5}$, rather than whether the emission sample was gathered from the laboratory or the field and from aerial- or ground-based sampling. The BC and BrC emission factors ranged from 1.2 to 2.1 g/kg biomass and 1.0 to 1.4 g/kg biomass, respectively. A decrease in BC and BrC emission factors with decreased combustion efficiency was found from both field and laboratory data. VOC



emission factors increased with decreased combustion efficiency. No apparent differences in averaged emission factors were observed between the field and laboratory for BC, BrC, and VOCs. The average PCDD/PCDF emission factors ranged from 0.06 to 4.6 ng TEQ/kg biomass.

INTRODUCTION

Prescribed forest burns are used to avoid wildfires and keep ecological sustainability to maintain ecosystem habitats for animal and plant species. Wildfires and prescribed forest burns generate a complex mix of emissions, and some of the major pollutants are particulate matter (PM) such as PM_{2.5} (PM with an aerodynamic diameter less than or equal to 2.5 μ m), black carbon (BC), brown carbon (BrC), carbon dioxide (CO₂), volatile organic compounds (VOCs), and semivolatile organic compounds (SVOCs) such as polychlorinated dibenzo-pdioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Measurement of pollutant emission factors allows prediction of exposure and possible harm to human health and the environment, and use in emission inventory calculations. However, obtaining emission factors from wildfires and prescribed forest burns is difficult. Proper distances must be maintained for personnel and equipment safety while at the same time the sampling equipment must be close enough to the source to obtain detectable emission levels. This also raises questions of representativeness, as the less hazardous smoldering phase of the fire may be disproportionately sampled, particularly by close-proximity ground-based sampling. These challenges, together with the relatively high costs for measuring emissions from field forest burns, suggest possible advantages to conducting laboratory burn simulations for emission sampling. However, the laboratory burns may have questions of representativeness, as only a small fraction of biomass can be burned compared to the field burns and the differences in their underlying fuel beds.

Target pollutants from forest burns are selected based on their health, environment, and climate effects. PM_{2.5} is a criteria pollutant regulated by the U.S. EPA due to its health effects. When inhaled, PM_{2.5} can enter the lungs, potentially carrying metals and other toxic pollutants which can cause adverse health effects. PM_{2.5} can also cause decreased visibility in the form of haze. According to the U.S. EPA's National Emissions Inventory (NEI),¹ 12% and 17% of the PM_{2.5} emissions in the U.S.A. (2008) were emitted from prescribed forest burns and wildfires, respectively, making forest burns the largest source of PM_{25} emissions in the U.S.A. This can be compared to 9.2% of $PM_{2.5}^{2.5}$ from transportation sources.¹ The southeastern part of the U.S.A. is responsible for 26% of the $PM_{2.5}$ emissions from forest burns.¹ However, only limited and varied emission factor data are available from this area. A small-scale laboratory forest burn study of mixed biomass species from South Eastern U.S. had an average PM2.5 emission factor of 9.9 g/kg biomass.² While two other small-scale laboratory forest burn with biomass species from North Carolina (NC) and Florida (FL) showed higher emission factors, and average of 20-22 g/kg biomass.^{3,4}

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Та	ble	1.	Ana	lytes,	Instrumentation,	And	Methods
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analytes	instrument/sampling method	mode	period/rate	analyses
black carbon	AE51 ^a	continuous	every second	measures the light attenuation in aerosols accumulated onto a quartz filter at the infrared wavelength of 880 nm
black carbon	AE52 ^a	continuous	every 10 s	see above, IR 880 nm
brown carbon	AE52 ^a	continuous	every 10 s	measures the light attenuation in aerosols accumulated onto a quartz filter at the ultraviolet wavelength of 370 nm
PM_{1} , $PM_{2.5}$, PM_{7} , PM_{10} and TSP'	Aerocet 531 ^b	continuous	every 2 min	light-scattering laser photometer
PM _{2.5} ^{<i>j</i>}	DustTrak 8520 ^c	continuous	every second	light-scattering laser photometer
PM _{2.5}	Impactor ^{<i>d</i>} , 47 mm Teflon filter (pore size 2.0 μ m)	batch	constant 10 L/min ^h	gravimetric, method procedures in 40 CFR part 50^{31}
PCDD/PCDF	Quartz filter/PUF/modified U.S. EPA Method TO-13 ³²	batch	850 L/min	HRGC/HRMS
VOC	Summa Canister/U.S. EPA Method TO-15 ³³	batch	$\sim 2 min$	GC/LRMS, U.S. EPA method TO-15 ³³
CO, CO ₂	Summa Canister/U.S. EPA Method TO-15 ³³	batch	$\sim 2 min$	GC, U.S. EPA method 25C ³⁴
CO ₂	LICOR-820 ^e	continuous	every second	non-dispersive infrared (NDIR)
СО	RC01000F ^f	semicontinuous ^k	every second	electrochemical oxidation of CO, range of 0–1000 ppm
ambient pressure, elevation, and location	MTi-G ^g	continuous	every second	global position system, attitude and heading reference system (AHRS), static pressure sensor
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^{*a*}Aethlabs, U.S. ^{*b*}Met One Instruments Inc., U.S. ^{*c*}TSI Inc., U.S. ^{*d*}SKC Inc. U.S. ^{*e*}LICOR Biosciences, U.S. ^{*f*}Transducer Technology inc., U.S. ^{*g*}Xsens, Netherlands. ^{*h*}Leland Legacy pump, SKC Inc., U.S.). ^{*i*}used in FL and NC. ^{*j*}Used in SC. ^{*k*}Response time: 20–30 s.

These emission factors are higher than the emission factors found from airborne,⁵ tower based,⁶ and ground based⁷ field measurements at prescribed forest burns from South Eastern U.S. (11 g/kg biomass, 14 g/kg biomass and 9–16g kg/ biomass), which in turn is ten times higher than the emission factors found from ground based sampling from prescribed burning in Georgia (0.90 g/kg biomass).⁸

Black carbon is an efficient light-absorbing aerosol in the infrared (IR) spectrum known to be a major contributor to global climate change.9 Brown carbon is defined as lightabsorbing organic matter aerosols from various sources found in the ultraviolet (UV) spectrum,¹⁰ which is starting to get more attention as a possible contributor to global warming.¹⁰⁻¹² Only a few BC emission factors from wildfires and prescribed forest burns have been reported. Kondo et al.¹³ reported values of 180 ng/m³ BC/ppm CO₂ or 0.11 g BC/kg biomass consumed (using a biomass carbon fraction of 0.50) for boreal forest fires while others have reported values of 0.37-0.66 g/kg biomass^{14,15} for savanna and tropical forest burns. In the absence of BC emission factors, elemental carbon (EC) and PM_{25} data are usually used to calculate/estimate BC inventories. Elemental carbon is batch-sampled onto a filter and measured by thermal-optical transmission techniques,⁴ whereas BC is measured continuously with an optical technique such as an aethalometer, which records changes in the optical light attenuation on a disposable filter. A number of studies have reported EC emission factors from wildfires and prescribed forest burns in Brazil,¹⁶ Africa,¹⁷ Georgia (U.S.),⁸ and Portugal¹⁸ as well as laboratory small-scale biomass burns with biomass species from South Eastern U.S..²⁻⁴ These emission factors ranged almost 2 orders of magnitude, from 0.035 to 1.5 g EC/kg biomass consumed, with no difference between field and laboratory emission levels.

The majority of the compounds on the U.S. EPA's list of hazardous air pollutions (HAPs) are VOCs.¹⁹ Some of the VOCs such as benzene, 1,3-butadiene, and acrolein are toxic to

humans, while others such as xylene, toluene, and 1,2,4trimethyl benzene can form fine PM and ground level ozone which is a criteria pollutant tied to respiratory ailments.²⁰ The NEI estimated that 9.6% and 16% of VOC emissions in the U.S.A (2008) were emitted from prescribed forest burns and wildfires, respectively, of which 23% originate from the southeastern U.S.A. Only a limited number of forest burn VOC emission factors from the HAP list are available in the literature. The few VOC emission factors are derived from different biomass sources and vary considerably, i.e., the benzene emission factor was 0.18 g/kg biomass from African²¹ savanna forest burns, 0.65 g/kg biomass from laboratory burns of Brazil tropical forest species,²² 2.2 g/kg biomass from pine dominated forest burns in GA (U.S.),⁸ and 0.28-0.80 g/kg biomass from prescribed burns in SC (U.S.). Yokelson et al.^{22,2} studied VOC emissions from field and laboratory burns of Brazilian tropical forest biomass, finding higher benzene emission factors from the laboratory study than from the field study.

PCDDs/PCDFs are recognized as toxic, bioaccumulative, and persistent in the environment. Combustion sources such as open burning of biomass have been identified as the major source of global PCDDs/PCDFs.²⁴ However, emission factor data, such as from prescribed field forest burning and laboratory forest burns, are limited and of broad range,^{25–27} from 0.55 to 25 ng toxic equivalent (TEQ)/kg biomass. Only one of these studies compared emission factors derived from the field with laboratory measurements, finding no difference.²⁷

This study aimed to obtain emission factors from prescribed forest burns and compare these to emissions obtained from small-scale laboratory burns using the same biomass source. Field measurements were conducted via either aerial-based measurements to achieve proportional emission sampling from both flaming and smoldering phases, or ground-based measurements at three different locations in the southeastern part of the U.S. The same sampling equipment was used for both field and

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laboratory measurements to avoid method differences. A comprehensive list of pollutants was simultaneously collected to allow for intercomparisons.

EXPERIMENTAL SECTION

Three field sampling campaigns of prescribed forest burns were conducted at three different locations of the southeastern part of the U.S.: (1) Eglin Air Force Base (February, 2011), located on the northwestern part of Florida (FL) on the Gulf of Mexico coast; (2) Marine Corps Base Camp Lejeune (February/March, 2011), located on the Atlantic Ocean coast (east coast) of North Carolina (NC); and (3) Fort Jackson (October/ November, 2011), located in the central part of South Carolina (SC) approximately 200 km from the Atlantic Ocean coast. Two to three different areas were burned on separate days for each location. Combustible biomass was collected at each of the locations and brought back to the U.S. EPA's open burn test facility (OBTF) in Research Triangle Park, NC, for small scale burn tests.

Aerial and Ground-Based Sampling Methods. A 4.3 m diameter tethered aerostat (Kingfisher Model, Aerial Products Inc., U.S.) was used as an aerial sampling platform and an all terrain vehicle (ATV) was used as a ground sampling platform (Supporting Information (SI) Figure S1). The helium-filled aerostat and the ATV carried duplicate sampling instrumentation packages, each termed the "Flyer" (SI Figure S2). The ground based platform transported the Flyer on a stand attached on the back of an ATV at an approximate height of 2.5 m above ground level. Emission sampling was not performed while in transport to avoid gasoline fumes from the exhaust. The aerostat sampling method has been described in detail elsewhere.^{28,29} In summary, the aerostat lofts the Flyer into plumes and is maneuvered by a tether attached to a remotecontrolled winch on an ATV. For the NC study, data were recorded every second onto an on-board stand-alone data logger (HOBO U12-013, Onset Computer Corporation, U.S.). For the FL and SC studies, the Flyer was updated with an onboard USB-based data acquisition (DAQ) card (Measurement Computing USB-2537) controlled by an on-board computer running a LabView generated data acquisition and control program. This update also included a ground-based computer used to view data in real time and control the sampling via a wireless remote desktop connection. The computer data were logged at a rate of 10 Hz. Additionally, to avoid dilution of samples when not in the plume, the batch samplers were automatically turned on and off by a carbon dioxide (CO_2) "trigger" at a user-set plume concentration.

Instrumentation. For these sampling efforts, the Flyer was equipped for continuous measurement of CO₂, BC, and particle size distribution, semicontinuous measurement of CO, and batch sampling of PM_{2.5}, VOCs, and PCDD/PCDF (Table 1). The CO_2 was measured at a range set to 0-4500 ppm and underwent three-point calibration for CO2 on a daily basis according to U.S. EPA Method 3A.³⁰ The CO₂ unit (Table 1) had an accuracy of less than 3% of reading, a precision of 1 ppm and a response time of one second. CO was measured using an electrochemical sensor with a response time of 20-30 s. The long response time of the sensor precluded its usefulness in the field, where concentrations could vary significantly in less than 1 s. The CO sensor underwent a three-point calibration before use according to U.S. EPA Method 3A.30 The PCDD/PCDF sampler used a 48 V (DC) Windjammer brushless direct current blower (AMETEK Inc., U.S.) resulting in a nominal

sampling rate of 0.85 m³/min. Flow rate was measured by a 0– 622 Pa pressure differential transducer (Setra, Model 265, U.S.) across a Herschel Standard Venturi tube with a throat and upstream diameter of 31 and 45 mm, respectively. The pressure differential voltage equivalent was recorded on the onboard computer or HOBO data logger and calibrated with a Roots meter (Model 5M, Dresser Measurement, U.S.). The Flyer on the aerostat was run on a 48 V 10 Amp-h Li-ion rechargeable battery, which has a battery capacity for approximately one hour of PCDD/PCDF sampling. The ground-based Flyer was run with four 12 V 75 Amp-h in series deep cycle marine batteries with approximately 4–5 h of sampling. Summa canisters were equipped with an electronic solenoid valve, pressure transducer, and a frit filter. All instruments were timesynchronized each day.

Analyses. The PCDD/PCDF samples were extracted and cleaned up by a modified U.S. EPA Method TO-9A35 and analyzed using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).³⁶ Trip and field blanks were collected and analyzed for PCDD/PCDF. Quantities of raw biomass, 202, 183, and 51 g from NC, FL, and SC, respectively, were Soxhlet-extracted using U.S. EPA Method 3540³⁷ and spiked and analyzed for PCDD/PCDF according to U.S. EPA Method TO-9A.³⁵ The 2005 World Health Organization (WHO) 2005 toxic equivalent factors (TEFs)³⁸ were used to determine the PCDD/PCDF TEQ emission factors. Not all TEF-weighted PCDD/PCDF congeners were detected in all samples. The congeners that were not detected (ND) were set to zero in the text but SI Tables S1-S3 show the PCDD/PCDF values both at ND = 0and ND = limit of detection). All data were normalized to 1 atm and 21.1 °C and background-corrected by subtracting ambient air concentrations. Values of the raw biomass for PCDD/PCDF content were normalized using the raw carbon fraction of each biomass (SI Table S1).

Biomass. The major species in FL and SC were Longleaf Pine (*Pinus palustris*), Turkey Oak (*Quercus laevis*), and Sand Live Oak (*Quercus geminata*), while the NC biomass consisted of Loblolly Pine seedlings (*Pinus taeda*), Red Bay (*Persea borbonia*), Inkberry (*Ilex glabra*), and Red Maple (*Acer rubrum*). The SC burn sites had not been burnt in the last 50 years and were considered "unmanaged" stands with the expectation that their burns would more represent behavior of an uncontrolled fire.

Combustible biomass was collected from a $9.1 \times 9.1 \text{ m}^2$ area at all three locations and transported to the OBTF at U.S. EPA, RTP, NC, for burn testing within seven days. The biomass from each of the locations (approximately 30 to 60 kg) was divided by standard cone and quarter methods for ultimate (SI Table S1) and PCDD/PCDF analyses in the unburnt biomass and for combustion testing in the OBTF. Three replicate OBTF tests were each comprised of multiple, sequential 1.4–1.5 kg biomass charges at the same area density as in the field.

Field Burn Description. Solely the aerostat-based sampling method was used in the FL and NC studies, while only the ground based sampling platform was used in SC due to airspace restrictions. Aerostat sampling was conducted downwind of the prescribed burn areas on the borderline of the burn area along an open field or a road. The average aerostat sampling altitude was higher for the FL burns (115 m, maximum 327 m) than for the NC burns (13 m, maximum 46 m) due to plume rise. The ground-based sampling equipment was approximately 2 m above ground level at all times. Ground-based sampling at SC

Table 2. Results^a

Test	Sampling Matrix	Biomass source	PCDD/PCDF ^b	PCDD/PCDF	Filter PM _{2.5} ^e	Continuous PM _{2.5}	Continuous BC ^e	Continuous BrC ^e	BC/PM _{2.5}
			ng TEQ/kg	Total ng /kg	g/kg	g/kg	g/kg	g/kg	mass ratio
			biomass	biomass	biomass	biomass	biomass	biomass	%
Field	Aerostat	FL	∫ 0 63 [0 71]°	56 °	14	14	2.7	NM	25
Field	Aerostat	FL		50	13	16	1.4	NM	12
Field	Aerostat	NC	0.11 [0.49]	45	35	31	1.6	NM	5.2
Field	Aerostat	NC	1.1 [1.5]	57	13	16	1.9	NM	12
					20				
Field	Ground	SC	0.68~[0.68]	66	80	42	1.6	0.9	3.7
					33				
					39				
Field	Ground	SC	2.2 [2.2]	120	43	70	1.8	1.3	2.5
					73				
					35				
Field	Ground	SC	4.6	495	39	39	1.5	2.1	4.0
					27				
					36				
					60				
OBTF		FL	0.61	53	12 ± 2.6	NM	1.5 ± 0.07	NM	10
OBTF		FL	0.76 [0.76]	63	15 ± 1.2	NM	1.6 ± 0.09	NM	12
OBTF		FL	0.51 [0.51]	39	19 ± 3.6	NM	1.0 ± 0.19	NM	5.3
OBTF		NC	FR	FR	26 ± 13	NM	2.1 ± 0.35	NM	8.1
OBTF		NC	FR	FR	21 ± 15	NM	1.7 ± 0.09	NM	9.0
OBTF		NC	0.060 [0.25]	39	$43\ \pm 0.35$	NM	2.5 ± 0.70	NM	6.0
OBTF ^d		SC	0.26 [0.26]	28	$40\ \pm 6.1$	NM	1.4 ± 0.15	1.1 ± 0.28	3.5
			0.38 [0.38]	44					
OBTF ^d		SC	0.33 [0.34]	39	58 ± 20	NM	1.4 ± 0.11	1.0 ± 0.20	3.2
			0.32 [0.33]	38					

^aOBTF – Open burn test facility, FL – North West Florida, NC – East North Carolina, SC – Central South Carolina, NM – not measured, FR – Failed recovery under method limits). ^bLimit of detection values within parentheses for those samples with not detected congeners. ^cComposite sample from two field days. ^dParallel sampling of PCDD/PCDF - two PCDD/PCDF samples collected during the same time. ^eAll OBTF emission factors shown in SI Table S10.

was performed downwind of the burn area on firebreak roads. Two simultaneous Flyer samples were combined for two of three sampling days in SC to obtain detectable PCDD/PCDF levels. The SC burns were presupposed to be of higher intensity than those in FL and NC since the forest had no history of prescribed burn treatment.

Open Burn Test Facility. A 70 m³ enclosed OBTF, described in detail elsewhere,³⁹ was used for simulating prescribed forest burns (SI Figure S1). The OBTF was equipped with a high-volume blower that pulls ambient air into the OBTF. This blower and small fans located inside the facility ensured complete mixing and oxygen concentrations close to ambient. Burn tests were performed 6-7 days after biomass collection at the same area density as found in the field. Because the small charge sizes used in the OBTF do not necessarily provide sufficient mass of PCDD/PCDF emissions to avoid nondetectable congeners, emissions from multiple charge burns were composited to obtain a single measurement. The biomass charges were burned one after the other; a new charge was loaded when the CO₂ concentration decreased to approximately 500 ppm. The small burn charges were used to mimic the field area density and keep the temperature inside the facility below 50 °C around the sampling equipment to avoid overheating Flyer electronics and the sampling media. The burns were performed on an aluminum-foil-covered steel plate, and the aluminum foil was replaced before each burn test.

The same sampling instrumentation was used in the OBTF as in the field. The Flyer was placed inside the facility near the air exit duct. For the SC biomass burn tests, two PCDD/PCDF samples were collected simultaneously using two Flyers. Two postburn OBTF ambient air background samples were collected for a total of 5-10 h inside the uncleaned OBTF over three separate days.

Calculations. The concentration ratios of the cosampled target analytes and the CO₂ above ambient levels (ΔCO_2) (plus Summa canister ΔCO for VOCs) were used to derive emission factors according to the carbon mass balance approach.⁴⁰ Emission factors are expressed in terms of pollutant mass per mass of biomass, where the latter indicates the mass of biomass consumed by the fire. The carbon mass balance assumes that all combusted carbon in the biomass is emitted to the atmosphere as CO₂, CO, methane, and total hydrocarbons (THCs), and that the carbon and pollutants are completely mixed in the plume. Calculations from a previous forest laboratory burn study show that 90-99.6% of the total carbon emitted (sum of CO and CO_2) was CO_2^4 and that THC concentration was 2-4 times lower than the CO concentration. Thus, carbon concentrations from CO and THC were minimal and only CO₂ measurements were needed to approximate the total mass of carbon emitted. Neglecting CO and trace VOCs could have an approximate 10% effect on the emission factor, a value within the total error of the method and likely the reproducibility of the event. The biomass composition carbon fractions (F_c) in the preburned/raw biomass (SI Table S1) were then used to calculate emission factors (EFs) by multiplying F_c with the mass of analyte per mass of carbon. The semicontinuous CO measurements acquired from the OBTF tests were used only to calculate the modified combustion efficiency (MCE), $(\Delta CO_2/(\Delta CO_2 + \Delta CO))$.

The VOC samples were unique in that the summa canister data provided both CO_2 and measurable CO concentrations, allowing emission factors to be assigned to flaming and smoldering modes by calculating the MCE, where the flaming mode has a MCE > 0.95 and the smoldering mode has a MCE < 0.90.

Custom correction factors for the continuous measured PM were derived as by manufacture instruction to improve the measurement accuracy from prescribed forest burns. These correction factors were conducted by dividing the average continuous $PM_{2.5}$ concentration by the $PM_{2.5}$ by filter concentration during the same collection time (for each collected filter). The average correction factor for the DustTrak 8520 and the Aerocet 531 was 2.0 \pm 0.56 and 6.3 \pm 2.2, respectively.

The black carbon data were postprocessed for noise using an optimized noise-reduction averaging algorithm program.⁴¹ No correction for particle loading on the filters was made since the BC concentration did not change with an increased light attenuation value (ATN) reported from the AE51 and AE52.

RESULTS AND DISCUSSION

Nine prescribed burns were sampled at three separate locations as well as companion laboratory burns with site-gathered biomass. At the field sites, aerial, ground-only, or both aerialand ground-based sampling were conducted as site constraints allowed (Table 2).

Particulate Matter. The continuous $PM_{2.5}$ and CO_2 concentrations were highest for the ground-based field sampling in SC and lowest for the aerostat-based sampling in FL (SI Figure S3) likely due to the comparative proximity of the ground-based sampler to the source. The average $PM_{2.5}$ emission factors from the three different field burn locations and the OBTF, derived from the ratio of the PM mass to the carbon collected as CO_2 , ranged from 14 to 47 g/kg biomass (Figure 1). These emission factors are mostly higher than



Figure 1. $PM_{2.5}$ emission factors from field and OBTF forest burns for three different biomass sources: northwestern Florida (FL), the North Carolina east coast (NC), and Central South Carolina (SC). Error bars denote one standard deviation (NC, SC) or range of data (FL).

previously reported from prescribed and wildfire forest burns in the U.S., Portugal, and Mexico at 0.66–16 g/kg biomass, ^{5–8,42,43} but overlapping those from previous OBTF forest burns of different biomass types, 11–34 g/kg biomass.⁴

A 3-fold difference in average $PM_{2.5}$ emission factors was observed between the three field values. Field and corresponding OBTF $PM_{2.5}$ emission factors were quite similar, also showing a 3-fold range. ANOVA analyses were performed on twenty-one OBTF and fifteen field $PM_{2.5}$ samples from the three field burn locations. No statistical differences ($\alpha = 0.05$) were observed between $PM_{2.5}$ emission factors derived in the field and the OBTF, suggesting the adequacy of the laboratory simulation. A statistical difference between the OBTF-derived emission factors was found between FL and both SC and NC. The field-derived emission factors were only statistically different between the FL and SC biomass sources. These results indicate that it is the biomass composition itself rather than the laboratory-versus field-based sampling distinctions that drive the $PM_{2.5}$ emission factor levels. As none of the testing afforded opportunities for both aerial and ground based sampling, future research should compare emission factors derived from simultaneous use of both of these methods.

Black and Brown Carbon. The field and OBTF average BC and BrC emission factors ranged from 1.2 to 2.1 g/kg biomass and 1.0 to 1.4 g/kg biomass, respectively (Figure 2).



Figure 2. Black and brown carbon emission factors from the three biomass sources, northwestern Florida (FL), North Carolina east coast (NC), and Central South Carolina (SC), sampled in the field and in the OBTF. Error bars denote one standard deviation (SC) or range of data (FL, NC).

These BC emission factors are generally higher than previously reported for forest burn EC and estimated BC emission factors of 0.035–1.3 g/kg biomass^{3,4,8,16–18} and 0.37–0.66 g/kg biomass,^{14,15} respectively. The BC emission factors determined here are in the same range as medium-and high-duty diesel trucks 0.92–2.3^{40,41,44,45} g/kg fuel.^{40,41} ANOVA analysis showed a slight difference (F = 5.33) in BC emission factors between the SC OBTF and its corresponding field data but not for the FL and NC field versus OBTF data. There were statistical differences in OBTF BC emission levels for the NC biomass with those from FL and SC, but no such differences were observed for the field data.

Figures 3A and B show time-resolved BC, BrC, ΔCO_2 , ΔCO , and MCE concentrations and emission factor data, respectively, for a representative OBTF burn of SC biomass. All data reach a rapid peak at the onset of combustion. As the emission factor data are mass-loss-normalized (Figure 3B), the initial peaks indicate that the early onset emissions are proportionately higher than subsequent emissions. The early peak BC and BrC emission factors are more than 2 to 10 times higher, respectively, than their whole-run averages, indicating that fire intensity characteristics have a significant impact on emissions. The BC and BrC concentrations decline exponentially with the MCE and time or as the ΔCO_2 concentration



Figure 3. A: OBTF samples of continuous (10 s average) ΔCO_2 , ΔCO , black carbon (BC), and brown carbon (BrC) concentration traces versus time and modified combustion efficiency (MCE); B: OBTF time- and MCE-resolved BC and BrC emission factors with ΔCO_2 and ΔCO concentrations.



Figure 4. Continuous (10 s average) ΔCO_2 , BC, and BrC concentration traces (A) and BC and BrC emission factors with ΔCO_2 (B) from a representative SC field emission sampling episode. Scatter plots of BC and BrC concentrations vs MCE (D), and average BC and BrC emission factors vs MCE (C) during summa canister sampling in SC.

decreases (Figure 3A). The OBTF laboratory data (Figure 3B) show an exponential decrease in BC and BrC emission factors with a decrease in MCE and also reveal that while the BC and BrC concentrations are low at the start of a burn, the MCE is the highest (Figure 3A).

Figure 4A,B shows the comparable BC, BrC, CO_2 , and CO concentrations and emission factor data, respectively, for the field tests at SC. The concentration data show predictably more fluctuation than the OBTF data (Figure 3A) as the former is subject to turbulent mixing while the latter is a well-stirred scenario. MCE values from the Summa canister CO and CO_2 grab samples were compared to the same-time BC and BrC values (Figure 4C,D). A linear trend between BC and BrC emission factors with MCE is observed, with higher values at

the start of a field burn. The higher BC and BrC emission factors at higher MCE values suggest that more intense forest burns with higher fuel burn rates, such as occur during wildfires, may result in greater releases of BC and BrC than during prescribed burning. Additional scatter plots are available in SI Figure S4.

The paired BC to $PM_{2.5}$ mass percentages for the field and OBTF, respectively, were FL: 18% (±6.6%) and 8.4% (±3.4%); NC: 8.4% (±3.2%) and 7.7% (±2.3%); and SC: 3.4% (±0.71%) and 3.3% (±1.2%). The BrC/PM_{2.5} mass fractions at SC for the field and OBTF were 3.1% (±2.0%) and 2.3% (±0.79%), respectively. These BC/PM_{2.5} mass percentages from NC and FL are higher than the EC/PM_{2.5} mass percentages found in the U.S. EPA SPECIATE version 4.3⁴⁶

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Table

		NC,	field				SC, f	ield			NC	, OBTF			SC, OBTF	
	MCE >	0.95	MCE <	< 0.90	MCE >	0.90	MCE =	: 0.90	MCE <	: 0.90	MCE > 0.95	MCE <	0.90	MCE > 0.95	MCE >0.90 < 0.95	MCE < 0.90
compound	average	AD	average	AD	average	AD	average	AD	average	AD		average	AD			
MCE	0.980	0.004	0.886	0.011	0.928	0.007	0.904	0.004	0.874	0.011	0.951	0.889	0	0.952	0.932	0.855
acrolein ^a	627	599	697	170	385	53	435	183	585	349	312	1023	154	256	381	332
propene	479	522	538	156	323	47	360	80	595	4.1	350	965	197	230	323	307
benzene ^a	370	369	526	262	245	23	276	62	441	92	284	776	102	225	290	199
1,3-butadiene ^a	195	222	246	61	66	23	114	46	195	5.5	121	378	47	97	153	108
vinyl acetate ^a	330	455	363	82	250	29	256	36	QN		166	830	75	183	323	425
acetonitrile	165	188	172	57	115	17	106	16	177	10	54	165	0.13	37	56	83
toluene ^a	271	371	232	107	150	0.62	148	38	277	51	123	369	42	121	171	153
2-butanone (MEK)	128	161	124	39	72	5.8	73	5.4	157	49	51	234	67	52	82	66
xylene ^a	64	74	78	17	62	3.2	73	12.5	131	10	37	126	15	<i>S</i> 7	84	66
naphthalene	64	68	102	68	38	4.0	35	9.2	63	14	44	116	27	42	47	33
styrene ^a	64	67	84	37	40	4.2	40	9.7	82	26	102	286	20	37	53	41
α -pinene	61	29	101	100	56	32	78	28.2	72	55	2.6	24	12	34	59	40
acrylonitrile ^a	54	41	56	11	29	15	24	5.0	43	14	25	49	9.1	16	24	18
ethylbenzene ^a	27	29	32	9.4	22	3.1	20	5.4	42	17	26	76	4.5	19	26	22
D-limonene	35	48	41	6.4	43	1.9	48	5.5	109	83	9.7	68	33	49	06	114
chloromethane ^a	34	29	43	20	9.4	4.7	8.6	0.14	11	3.3	14	54	3.4	9.3	14	16
1,2,4-trimethylbenzene	7.8	7.7	10	2.7	14	0.41	9.4	2.2	16	1.6	3.7	16	3.0	5.4	8.1	12.1
1,3,5-trimethylbenzene	2.2	2.6	2.8	5.5	3.4	0.28	2.4	0.72	4.0	0.62	0.80	3.3	0.87	1.3	1.9	3.0
cumene ^a	2.2	2.3	2.9	5.9	2.3	0.12	2.3	0.84	4.1	0.92	2.2	6.0	0.079	2.1	2.9	2.6
methylene chloride	2.2	3.4	4.0	3.6	0.24	0.42	0.028	0.0079	0.053	0.05	QN	0.079	0.32	ND	ND	ND
bromomethane ^a	2.2	2.3	2.6	5.3	1.5	0.34	1.8	0.12	3.0	1.4	Ŋ	1.5	3.0	1.3	2.3	2.3
^a Included in the EPA list coast of North Carolina.	of hazard SC, centr	lous air p al South	ollutants. Carolina.	^b AD, abs(OBTF, c	olute differ ypen burn	ence (tw test facil	o samples) ity.). МСЕ, п	nodified cc	mbustion	ı efficiency. N]	D, not det	ected, or	not detected <i>i</i>	bove background lev	els. NC, east

database (source category = forest fires) of 1.2-4.5% (ID 4463–4468⁴) which were derived from laboratory (OBTF) tests, while the SC ratios are similar to those in SPECIATE. A similar EC/PM_{2.5} percentage, 3.9%, was found from prescribed burning conducted in Georgia (USA).⁸ The higher ratios found in our work seem to be due to higher BC rather than EC emission factors levels, given the similar PM_{2.5} emission factors discussed above. This difference could be due to the different sampling methods—light-scattering (BC) in this study versus thermal/optical transmission (EC) in Hays et al.⁴ These differences suggest the need for a comparative investigation of parallel BC and EC measurements from combustion sources.

VOC. Ten field and six OBTF summa canister samples were taken for VOC determination for the NC and SC campaigns (canister samples at FL could not be taken due to weight restrictions on the aerostat). Acrolein, benzene, vinyl acetate (on the U.S. EPA's hazardous air pollutant list), and propene had the highest emission factors (425-380 ug/g biomass) of all VOCs analyzed (Table 3). The sixteen VOC samples were divided according to MCE resulting in 1-2 samples in each MCE category (Table 3). The SC field results had no samples with MCE >0.95, likely due more to the limitations of groundonly sampling than distinctions in the combustion characteristics of this unmanaged site. No apparent differences were observed between field and OBTF samples for the different MCE categories, although more replicates would be needed for a robust statistical analysis. A trend in decreased VOC emission factors with increased MCE was found when all of the collected samples were correlated (see SI Figure S5 for four VOCs). The average field emission factor for acrolein was 350 μ g/g biomass, which was in the same range as that for open burning of municipal waste, $310 \ \mu g/g$ biomass,⁴⁷ and prescribed burning in SC 323–472 $\ \mu g/g$ biomass,⁴⁸ but lower than that found from tropical forest fires, 960 $\ \mu g/g$ biomass.²² The 1,3-butadiene had an average emission factor from both field and OBTF of 310 \pm 182 μ g/g biomass, higher than reported from previous prescribed and wild forest burns in the U.S.^{5,8} and Mexico⁴⁹ $(67-100 \ \mu g/g \text{ biomass})$ and from Mexican crop residue fires $(114 \,\mu g/g \, biomass^{43})$ yet similar to open burning of municipal waste (300 μ g/g biomass⁴⁷) and prescribed burning of SC forest (110–240 μ g/kg biomass⁴⁸). Some other individual VOCs, such as benzene and α -pinene, were in the same range as emission factors from prescribed forest burning in Georgia, U.S.⁸ All VOCs analyzed are shown in SI Tables S8-S9.

PCDD/PCDF Emissions. The average PCDD/PCDF emission factors from the three different biomass sources and both field (N = 5) and OBTF (N = 7) testing ranged from 0.06 to 4.6 ng TEQ/kg biomass (ND = 0, Table 2 and SI Tables S2–S4). Emissions exceeded the level anticipated from volatilization of PCDD/PCDF in the raw biomass (Figure 5), which indicates that formation occurs during combustion rather than due to evaporation from the green biomass.

These emission factors are on the lower range of similar OBTF and field studies with U.S. forest biomass at 0.40–25 ng TEQ/kg biomass^{25–27} (the lowest emission factor, 0.06 ng TEQ/kg biomass, was obtained from an OBTF sample burning NC biomass with only 6 of 17 TEF congeners detected). The range of emission factors derived herein overlap those of residential wood heating appliances such as wood heaters (0.39 ng TEQ/kg),⁵⁰ wood stoves (0.25 ng TEQ/kg),⁵¹ and fireplaces (0.88 ng TEQ/kg).⁵¹

To discern potential emission factor differences between aerial- and ground-based field samples, more simultaneous Article



Figure 5. PCDD/PCDF emission factors from three different locations on the eastern part of the USA: northwestern Florida (FL), the North Carolina east coast (NC), and Central South Carolina (SC). ND, not detectable congeners; LOD, limit of detection.

aerial- and ground-based sampling is necessary. The field samples were of limited number and, for the aerial samples, consisted of one single composite (FL) sample from two different burn days with 14 of 17 TEF congeners detected and two replicates (NC) with only 4 and 6 of 17 TEF congeners detected. Further, none of the aerial and ground samples were taken from the same fire.

The PCDD/PCDF emission factors showed similar levels between aerial measurements in the field and OBTF samples for each of the biomass sources (FL and NC), except for the SC ground-based field and OBTF measurements, as shown in Figure 5. The emission factors from the three SC ground field samples showed an increase of up to seven times from the first to last sample (0.68, 2.2, and 4.6 ng TEQ/kg biomass), reflecting the qualitative observations of increasing smoke thickness throughout the campaign (Table 3). In addition, the total PCDD to PCDF and PCDD TEQ to PCDF TEQ mass ratios in these samples increased with increased emission factor levels (SI Tables S4 and S7). A higher emission factor and a greater PCDD TEQ to PCDF TEQ ratio during smoldering versus flaming stages was found in an earlier study by Gullett et al.²⁶ burning standing trees in EPA's OBTF. Thus, the two higher emission factors derived from the SC field study (2.2 TEQ/kg biomass and 4.6 ng TEQ/kg biomass) may be due to sampling a larger portion of the smoldering stage rather than the flaming stage. The SC OBTF emission levels (average 0.32 ng TEQ/kg biomass) and PCDD/PCDF ratios (1.2) are also similar to the initial SC ground-based field sample (0.68 ng TEQ/kg biomass), which suggests the difficulty of collecting a representative PCDD/PCDF sample from ground- rather than aerial-based sampling.

The slight emission level difference between FL and SC biomass from the OBTF could be due to chlorine content in the fuel 645 ppm and 111 ppm, respectively (Table 2 and Figure 5), which is in agreement with a OBTF biomass study showing that increased chlorine content in the fuel increases the PCDD/PCDF emissions.³⁹ The PCDD/PCDF ratio was also higher in the FL OBTF samples (5.7 ± 1.7) than the SC biomass samples (1.2 ± 0.2) , which is in agreement with a laboratory study showing that an increased chlorine content in the fuel enhances the formation of PCDDs over PCDFs.⁵² More definitive conclusions regarding the effect of biomass

chlorine content versus combustion quality on PCDD/PCDF emission levels and ratios requires further study.

Octa-CDD was the most prevalent homologue of the PCDD homologues in all the collected samples, with the exception of the OBTF test of the NC biomass that had several nondetect congeners (SI Tables S5–S7). The PCDD homologue profiles exhibit higher homologue concentrations with increasing chlorination level, similar to previous OBTF results²⁶ from burning standing pine trees. The PCDF homologue profiles followed the opposite trend (SI Tables S5–S7): lower homologue concentrations with increasing chlorination level, consistent with earlier results²⁶ (except for SC day 3 field sample which had Hepta-CDF as the most prevalent congener).

ASSOCIATED CONTENT

S Supporting Information

Additional material noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Phone: (919) 541-1534; e-mail: gullett.brian@epa.gov.

Present Address

[†]University of Dayton Research Institute.

Notes

The authors declare no competing financial interest.

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