

Gaseous and Particulate Emissions from Prescribed Burning in Georgia

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Prescribed burning is a significant source of fine particulate matter ($PM_{2.5}$) in the southeastern United States. However, limited data exist on the emission characteristics from this source. Various organic and inorganic compounds both in the gas and particle phase were measured in the emissions of prescribed burnings conducted at two pine-dominated forest areas in Georgia. The measurements of volatile organic compounds (VOCs) and $PM_{2.5}$ allowed the determination of emission factors for the flaming and smoldering stages of prescribed burnings. The VOC emission factors from smoldering were distinctly higher than those from flaming except for ethene, ethyne, and organic nitrate compounds. VOC emission factors show that emissions of certain aromatic compounds and terpenes such as α and β -pinenes, which are important precursors for secondary organic aerosol (SOA), are much higher from active prescribed burnings than from fireplace wood and laboratory open burning studies. Levoglucosan is the major particulate organic compound (POC) emitted for all these studies, though its emission relative to total organic carbon (mg/g OC) differs significantly. Furthermore, cholesterol, an important fingerprint for meat cooking, was observed only in our in situ study indicating a significant release from the soil and soil organisms during open burning. Source apportionment of ambient primary fine

particulate OC measured at two urban receptor locations 20–25 km downwind yields $74 \pm 11\%$ during and immediately after the burns using our new in situ profile. In comparison with the previous source profile from laboratory simulations, however, this OC contribution is on average $27 \pm 5\%$ lower.

Introduction

Forest fires, both wildfire and prescribed burning, are important sources of primary air pollutants and precursors of secondary pollutants. In the southeastern United States, forest fires contribute about 20, 8, and 6% of nonfugitive primary fine particulate matter ($PM_{2.5}$), CO, and volatile organic compound (VOC) emissions, respectively (1), and have been reported as the primary cause of increased $PM_{2.5}$ levels and visibility impairment in the United States (2). Primary air pollutants from forest fires can travel long distances (thousands of km). Canadian forest fires increased CO concentration leading to elevated O_3 levels in the southeastern U.S. (3) and elevated $PM_{2.5}$ levels in an eastern U.S. urban area were observed due to Canadian forest fires (4). While emission factors for major gas-phase species, $PM_{2.5}$ mass, EC, and OC have been calculated in an attempt to improve the emission inventory for forest fires in the United States (5), they are primarily based on measurements and conditions resembling the western U.S. Epidemiological studies show an association between air pollutants emitted by forest fires (e.g., $PM_{2.5}$ and O_3) and adverse health effects (6–9).

Prescribed burning is widely used (e.g., in Georgia >1 million acres annually) for various reasons, including controlling vegetation, enhancing biotic productivity and diversity, controlling disease and insects, reducing fuel accumulation, and habitat management for endangered species in the United States, and especially in the southeast (10). Therefore, it is important to investigate emissions from prescribed burning in order to understand its impact on air quality. Because of its mixed fuel and different combustion condition, prescribed burning likely has a different chemical composition of $PM_{2.5}$ and VOC compared to residential wood burning emissions. Hays and colleagues (11) reported source profiles of $PM_{2.5}$ and VOC from laboratory simulations of different forest fires. However, very limited data exist on emission characteristics from active prescribed burning in the U.S. In our study, emission characterizations of $PM_{2.5}$ and VOC from prescribed burning were determined by directly measuring emissions at prescribed burning sites, providing source profiles of $PM_{2.5}$ and VOC for future source apportionment and information for an improved emission inventory development. In addition, the newly developed source profile was applied for quantifying the primary source contributions to ambient organic carbon (OC) levels by a chemical mass balance model.

Experimental Section

Measurement Sites. Emission and ambient measurements were conducted in Georgia (located in the southeastern U.S.) during April 2004. Emission samples were collected at two pine-dominated forest areas that are managed by prescribed burning (Figure S1, Supporting Information). Fort Benning and Fort Gordon are both military installations that burn approximately 32 000 and 14 000 acres, respectively, every year, primarily to maintain a healthy habitat for endangered species (e.g., the red-cockaded woodpecker), and to sustain

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military operations and training. Fort Benning is situated southeast of Columbus close to the Alabama border, and Fort Gordon is southwest of Augusta near the South Carolina border. Prescribed burnings were conducted on April 15 and 16 (331 and 345 acres, respectively) at Fort Gordon and on April 28 and 29 (204 and 381 acres, respectively) at Fort Benning. During these periods, ambient samples were collected at the state's regulatory monitoring locations of both metropolitan statistical areas (MSA): a residential area in Augusta 21 km downwind, and at a residential area with a few industrial sources in Columbus 26 km downwind, respectively, from the prescribed burning sites.

Emission Measurements. A total of four particle-phase emission samples, two at each site, were collected within a few m away from the downwind edge of the burning area on 4 different days in April 2004. Average ambient temperature during the measurements was $26.5 \pm 2.7^\circ\text{C}$ under mostly clear skies and low to moderate winds, meeting the fundamental requirements for conducting prescribed burns in Georgia (detailed weather conditions are described in the Supporting Information). Custom-designed particulate composition monitors (PCM), federal reference method (FRM), and high-volume samplers (HVS) were operated for about 3 h simultaneously to collect particulate emissions. The PCM is for the determination of gravimetric PM_{2.5} mass, water-soluble ionic species, organic/elemental carbon (OC/EC), and gases (12), the FRM is for determination of gravimetric PM_{2.5} mass and trace elements (13), and the HVS (Tisch Environmental Inc., Cleves, OH, model TE-5070 base with TE-10557 venturi, and TE-6001-2.5 PM_{2.5} impactor) is for OC/EC analysis and particulate organic compound (POC) speciation.

The two-channel PCM was designed to measure particles less than 2.5 micrometers in aerodynamic diameter (PM_{2.5}) and gases by employing denuders (12, 14) and filter packs (Figure S2, Supporting Information). The PM_{2.5} mass concentration was determined gravimetrically from the denuded and desiccated Teflon filter in channel 1, as well as particle-phase sodium, potassium, ammonium, chloride, nitrate, sulfate, formate, acetate, and oxalate by ion chromatography (IC). In addition, 7 gaseous species, NH₃, HCl, SO₂, HNO₃, formic, acetic, and oxalic acids, were measured via IC of the denuder extracts. Channel 2 was for the determination of PM_{2.5} OC and EC, employing a carbon monolith (Novacarb, Mast Carbon Ltd., U.K.) to effectively remove condensable organic vapors, hence minimize semivolatile adsorption artifact prior to particulate OC collection on a 47-mm prebaked quartz fiber filter (Pall-Life Sciences, Ann Arbor, MI), followed by a prebaked back-up filter coated with XAD-4 (15–17). Quartz filters were analyzed by a thermal optical ECOC analyzer (Sunset Laboratory Inc., Tigard, OR) using the NIOSH protocol (18, 19).

A BGI PQ200 portable particulate sampler (BGI Inc., Waltham, MA) equipped with a WINS impactor (FRM) was operated to collect PM_{2.5} on Teflon filters (Teflon ringed membrane, Pall-Life Sciences, Ann Arbor, MI). After gravimetric PM_{2.5} mass determination Teflon filters were analyzed for major trace elements via energy-dispersive X-ray fluorescence spectroscopy (XRF).

The HVS used larger prebaked quartz fiber filters (8 × 10 in., Pall-Life Sciences, Ann Arbor, MI), which were analyzed for POC via gas chromatography/mass spectrometry (GC/MS) at the University of Wisconsin-Madison. The organic analysis method has been described previously (20, 21).

Precision of the IC analysis is ~7% for oxalate and better than 5% for all other ionic species, and the XRF analysis' precision is less than 10%. The precision of the GC/MS analysis is within 25% based on comparing the analysis of blank filters spiked with quantification standards composed of a mix of analytes with historical lab results (22). Uncer-

TABLE 1. Average and Standard Deviation (STD) of the Chemical Composition of Particle-Phase Emissions from Prescribed Burning

	average	STD
PM _{2.5} mass (mg m ⁻³)	1.81	0.68
OC and EC (weight % of PM_{2.5} mass)		
organic carbon	60.25	18.52
elemental carbon	3.92	1.13
Ionic Species (weight % of PM_{2.5} mass)		
acetate	0.548	0.156
formate	0.447	0.114
nitrate	0.440	0.299
chloride	0.527	0.289
potassium	0.649	0.435
sulfate	0.245	0.112
ammonium	0.107	0.108
oxalate	0.069	0.014
sodium	0.016	0.008
X-ray Fluorescence (weight % of PM_{2.5} mass)		
Na	0.0431	0.0175
Mg	0.0001	0.0003
Al	0.0229	0.0426
Si	0.0186	0.0258
P	0.0010	0.0015
S	0.1074	0.0403
Cl	0.4217	0.2295
K	0.5707	0.3711
Ca	0.0006	0.0011
Ti	0.0004	0.0006
V	BL ^a	BL
Cr	BL	BL
Mn	0.0011	0.0010
Fe	0.0082	0.0137
Co	BL	BL
Ni	BL	BL
Cu	0.0010	0.0010
Zn	0.0160	0.0089
Ga	BL	BL
Ge	BL	BL
As	0.0002	0.0003
Se	0.0001	0.0002
Br	0.0141	0.0091
Rb	0.0042	0.0028
Sr	0.0002	0.0003
Pb	0.0001	0.0003

^a BL: below blank level.

tainties for PM_{2.5} mass, OC, and EC were assessed by instrument inter-comparisons. Undenuded FRM mass was $5 \pm 8\%$ higher than the denuded PCM mass at an R^2 of 0.94 based on the linear least-squares regression, indicating the FRM's susceptibility for positive artifacts from condensation and adsorption of less volatile gaseous emissions. For OC/EC inter-comparison, the same samples were analyzed by each thermal optical ECOC analyzer at Georgia Institute of Technology and University of Wisconsin-Madison. Bias between the two instruments was 7% for OC and 3% for EC. The linear least-squares regression for the OC/EC ratios between PCM (x) and HVS (y) yielded a slope of 1.40 ± 0.15 ($R^2 = 0.97$). This slope larger than 1 likely resulted from positive artifacts on HVS rather than small differences in the operating parameters of the analyzers (e.g., temperature program), considering the relatively small instrument biases.

Evacuated stainless steel canisters were used to collect gaseous species including CO, CO₂, CH₄, nonmethane hydrocarbons (NMHCs), halogenated hydrocarbons, and organic nitrates. Several emission samples distinctively separating the flaming from the smoldering stage were collected in February and April 2003 and during the above PM measurements in April 2004. The mobility of the cans allowed the sampling of emissions only a few cm away from

TABLE 2. Average and Standard Deviation (STD) of Normalized POC Emissions from Prescribed Burning in mg per g OC^b

	average	STD		average	STD
Alkanes					
tetracosane	0.1388	0.0705	dotriacontane	DL	DL
pentacosane	0.2501	0.1276	tritriacontane	0.0900	0.0723
hexacosane	0.2282	0.1250	tetratriacontane	DL	DL
heptacosane	0.2499	0.1639	pentatriacontane	DL	DL
octacosane	0.1155	0.0538	hexatriacontane	DL	DL
nonacosane	0.8068	0.3847	tetratetracontane	DL	DL
isononacosane	DL ^a	DL	isohentriaccontane	DL	DL
anteisotriaccontane	DL	DL	anteisodotriaccontane	DL	DL
triacontane	0.1939	0.0937	isotritriaccontane	DL	DL
hentriaccontane	0.2884	0.1375			
Alkenoic Acids					
9-hexadecenoic acid	0.5076	0.3254	9,12-octadecadienoic acid	2.2530	1.2726
9-octadecenoic acid (oleic acid)	2.4382	1.1394			
Alkanoic Acids					
tetradecanoic acid	2.0066	0.9764	tricosanoic acid	0.6541	0.2863
pentadecanoic Acid	0.6372	0.3281	tetracosanoic acid	4.9520	2.2088
hexadecanoic acid	6.7301	2.9428	pentacosanoic acid	0.3832	0.1679
heptadecanoic acid	0.2481	0.1184	hexacosanoic acid	3.6715	1.6200
octadecanoic acid	2.2421	1.0502	heptacosanoic acid	0.1411	0.0652
nonadecanoic acid	0.4882	0.2505	octacosanoic acid	0.9882	0.4472
eicosanoic acid	1.1948	0.5701	nonacosanoic acid	0.1684	0.0868
heneicosanoic acid	0.2886	0.1278	triacontanoic acid	0.8029	0.4244
docosanoic acid	1.7855	0.8199	pinonic acid	DL	DL
Alkanedioic Acids					
butanedioic acid	0.3964	0.2064	octanedioic acid	0.0595	0.0409
pentanedioic acid	0.0813	0.0429	nonanedioic acid	0.2586	0.1358
hexanedioic acid	0.0265	0.0196	decanedioic acid	0.0679	0.0416
heptanedioic acid	0.0300	0.0240			
PAHs					
fluoranthene	0.0895	0.0390	dibenz[<i>a,h</i>]anthracene	0.0017	0.0013
acephenanthrylene	0.0280	0.0140	benzo[<i>ghi</i>]perylene	0.0358	0.0149
pyrene	0.1068	0.0450	cyclopenta[<i>c,d</i>]pyrene	0.2888	0.1381
benz[<i>a</i>]anthracene	0.0800	0.0329	1-methylchrysene	0.0279	0.0159
chrysene/triphenylene	0.0978	0.0411	benzo[<i>ghi</i>]fluoranthene	0.0972	0.0778
coronene	0.0074	0.0044	retene	0.3490	0.1645
benzo[<i>b</i>]fluoranthene	0.0505	0.0210	9,10 anthraquinone	DL	DL
benzo[<i>k</i>]fluoranthene	0.0407	0.0167	1 <i>h</i> -phenalen-1-one	DL	DL
benzo[<i>j,l</i>]fluoranthene	0.0128	0.0067	9-fluorenone	DL	DL
benzo[<i>a,j</i>]pyrene	0.0298	0.0124	benz[<i>a</i>]anthracene-7,12-dione	DL	DL
benzo[<i>e</i>]pyrene	0.0499	0.0208	benz[<i>d,e</i>]anthracene-7-one	DL	DL
perylene	0.0039	0.0022	1,8-naphthalic anhydride	DL	DL
indeno[<i>c,d</i>]pyrene	0.0737	0.0342			
Phthalates					
bis[2-ethylhexyl]phthalate	0.0895	0.0390	dimethyl phthalate	0.0142	0.0095
butyl benzyl phthalate	DL	DL	dibutyl phthalate	0.1031	0.0671
diethyl phthalate	0.0355	0.0322	dioctyl phthalate	DL	DL
Aromatic Carboxylic Acids					
1,2-benzenedicarboxylic acid	0.0147	0.0088	1,3,5 or 1,2,3 benzenetricarboxylic acid	DL	DL
1,3-benzenedicarboxylic acid	DL	DL	1,2,4,5-benzenetetracarboxylic acid	DL	DL
1,4-benzenedicarboxylic acid	0.0090	0.0071	1,2,3,5 or 1,2,3,4 benzenetetracarboxylic acid	DL	DL
1,2,4-benzenetricarboxylic acid	DL	DL	4-methyl-1,2-benzenedicarboxylic acid	DL	DL
Resin Acids					
dehydroabietic acid	33.3164	14.3022	pimaric acid	2.4659	1.0099
isopimaric acid	2.9594	1.2311			
Others					
levoglucosan	94.7506	40.2568	stigmasterol	1.0115	0.4408
cholesterol	0.8071	0.3511	squalene	2.6824	1.2024

^a DL: below detection limit. ^b Steranes and hopanes (16 species) are below detection limit.

the source, whereas the PM sampling equipment was placed a few m away from the downwind edge of the area burnt (see Figure S2 in the Supporting Information). Ambient background levels were measured prior to or upwind of every prescribed burning, and considered in the subsequent determination of the net emissions. Those samples were analyzed by gas chromatography with flame ionization detection (FID), electron capture detection (ECD), and mass spectrometry (MS). The typical analytical precision is 3%

and detection limit is 5 pptv for NMHCs in accordance with the previously described analytical procedure (23).

Ambient Measurements. Two 3-channel PCMs were used to alternately collect gravimetric PM_{2.5} mass, water soluble ionic species, OC/EC, trace elements, and gases following the same denuded filter collection principle from above (Figure S3 in the Supporting Information) and operational details described previously (12). Two HVSs (Thermo Electron Co., Franklin, MA, model GMW PM10-VFC with a 2.5-μm

TABLE 3. Emission Ratios Relative to CO₂ (\pm Standard Error, and Coefficient of Determination R^2) of Gaseous Emissions from Least Squares Linear Regressions between Mixing Ratios of Individual VOCs and CO₂ Measured in 10 Flaming and 12 Smoldering Emission Samples

	Flaming (10)			Smoldering (12)		
	$\Delta X/\Delta \text{CO}_2$	\pm uncertainty	R^2	$\Delta X/\Delta \text{CO}_2$	\pm uncertainty	R^2
CO, ppmv/ppmv	0.0709	\pm 0.0205	0.89	0.2337	\pm 0.0133	0.99
CH ₄ , ppmv/ppmv	0.0030	\pm 0.0016	0.69	0.0107	\pm 0.0016	0.96
chloroform, pptv/ppmv	0.0016	\pm 0.0128	0.01	0.0000	\pm 0.0026	0.00
dichloromethane, pptv/ppmv	-0.1606	\pm 0.5010	0.06	-0.0669	\pm 0.3050	0.02
trichloroethylene, pptv/ppmv	0.0001	\pm 0.0039	0.00	0.0190	\pm 0.0029	0.96
tetrachloroethylene, pptv/ppmv	0.0074	\pm 0.0416	0.02	0.0039	\pm 0.0030	0.47
methyl chloride, pptv/ppmv	8.6976	\pm 3.7600	0.78	32.6700	\pm 3.0600	0.98
methyl bromide, pptv/ppmv	0.2959	\pm 0.1540	0.71	2.0833	\pm 0.2140	0.98
methyl nitrate, pptv/ppmv	0.8219	\pm 0.3510	0.79	0.0113	\pm 0.0113	0.33
ethyl nitrate, pptv/ppmv	0.0579	\pm 0.0253	0.78	0.0044	\pm 0.0011	0.89
i-propyl nitrate, pptv/ppmv	0.1025	\pm 0.0464	0.76	0.0352	\pm 0.0031	0.98
n-propyl nitrate, pptv/ppmv	0.0075	\pm 0.0068	0.45	0.0004	\pm 0.0003	0.49
2-butyl nitrate, pptv/ppmv	0.0531	\pm 0.0207	0.81	0.0095	\pm 0.0028	0.86
ethane, ppbv/ppmv	0.2621	\pm 0.1320	0.72	0.9095	\pm 0.1010	0.98
propane, ppbv/ppmv	0.0525	\pm 0.0284	0.69	0.2445	\pm 0.0275	0.98
i-butane, ppbv/ppmv	0.0029	\pm 0.0019	0.62	0.0177	\pm 0.0019	0.98
n-butane, ppbv/ppmv	0.0091	\pm 0.0053	0.66	0.0651	\pm 0.0071	0.98
i-pentane, ppbv/ppmv	0.0007	\pm 0.0015	0.13	0.0022	\pm 0.0002	0.98
n-pantane, ppbv/ppmv	0.0034	\pm 0.0020	0.66	0.0255	\pm 0.0028	0.98
2-methylpentane, ppbv/ppmv	0.0007	\pm 0.0003	0.74	0.0051	\pm 0.0006	0.98
3-methylpentane, ppbv/ppmv	0.0002	\pm 0.0001	0.60	0.0011	\pm 0.0001	0.98
n-hexane, ppbv/ppmv	0.0023	\pm 0.0013	0.67	0.0162	\pm 0.0018	0.98
n-heptane, ppbv/ppmv	0.0018	\pm 0.0009	0.72	0.0118	\pm 0.0013	0.98
n-octane, ppbv/ppmv	0.0012	\pm 0.0007	0.69	0.0091	\pm 0.0010	0.97
ethene, ppbv/ppmv	1.2414	\pm 0.5550	0.77	0.8568	\pm 0.1680	0.93
ethyne, ppbv/ppmv	0.3888	\pm 0.1780	0.76	0.0969	\pm 0.0566	0.59
propene, ppbv/ppmv	0.2447	\pm 0.0960	0.81	0.3982	\pm 0.0426	0.98
1-butene, ppbv/ppmv	0.0374	\pm 0.0152	0.80	0.0621	\pm 0.0053	0.99
i-butene, ppbv/ppmv	0.0240	\pm 0.0108	0.77	0.0890	\pm 0.0086	0.98
trans-2-butene, ppbv/ppmv	0.0083	\pm 0.0040	0.74	0.0299	\pm 0.0031	0.98
cis-2-butene, ppbv/ppmv	0.0063	\pm 0.0034	0.69	0.0220	\pm 0.0025	0.97
1,3-butadiene, ppbv/ppmv	0.0232	\pm 0.0178	0.53	0.0280	\pm 0.0092	0.82
benzene, ppbv/ppmv	0.0952	\pm 0.0325	0.85	0.1885	\pm 0.0247	0.97
toluene, ppbv/ppmv	0.0431	\pm 0.0151	0.84	0.1044	\pm 0.0219	0.92
ethylbenzene, ppbv/ppmv	0.0053	\pm 0.0021	0.80	0.0133	\pm 0.0033	0.89
m-xylene, ppbv/ppmv	0.0090	\pm 0.0044	0.74	0.0362	\pm 0.0083	0.90
p-xylene, ppbv/ppmv	0.0042	\pm 0.0021	0.74	0.0080	\pm 0.0031	0.77
o-xylene, ppbv/ppmv	0.0035	\pm 0.0017	0.74	0.0127	\pm 0.0019	0.96
isopropylbenzene, ppbv/ppmv	0.0006	\pm 0.0003	0.73	0.0021	\pm 0.0005	0.89
propylbenzene, ppbv/ppmv	0.0008	\pm 0.0005	0.57	0.0047	\pm 0.0013	0.87
3-ethyltoluene, ppbv/ppmv	0.0022	\pm 0.0014	0.62	0.0052	\pm 0.0038	0.48
4-ethyltoluene, ppbv/ppmv	0.0015	\pm 0.0009	0.64	0.0101	\pm 0.0033	0.83
2-ethyltoluene, ppbv/ppmv	0.0007	\pm 0.0005	0.60	0.0031	\pm 0.0004	0.97
isoprene, ppbv/ppmv	0.0010	\pm 0.0106	0.01	0.0250	\pm 0.0102	0.75
a-pinene, ppbv/ppmv	0.0012	\pm 0.0052	0.03	0.0202	\pm 0.0254	0.24
b-pinene, ppbv/ppmv	0.0017	\pm 0.0019	0.35	0.0123	\pm 0.0029	0.90

slotted preseparator SA231) were also deployed for POC collection and speciation following the same procedures as used for the emission samples.

CMB Source Apportionment. Major primary emissions from gasoline-powered motor vehicles, medium-duty diesel trucks, meat cooking, residential wood burning, prescribed fire, and road dust were included in CMB8 to quantify their source contribution to ambient OC concentrations (24, 25). These source profiles were obtained from previous source test studies. The gasoline-powered vehicle source profile was generated by weighted-average of catalyst-equipped gasoline-powered motor vehicles and noncatalyst gasoline-powered motor vehicles (26) based on their emissions in Georgia. The source profile for medium-duty diesel trucks was from Schauer et al. (27), meat cooking was from Schauer et al. (28), prescribed burning was from our study and Hays et al. (11), road dust was from Zheng et al. (29), and vegetative detritus was from Rogge et al. (30). The residential wood burning source profile was generated by averaging 6 source tests from Fine et al. (31).

Results and Discussion

Chemical Composition of PM_{2.5} Emissions. All four PM_{2.5} samples were used to calculate average chemical composition of emissions from active prescribed burnings (Table 1), after subtracting ambient background levels, which were determined at the corresponding burn site up to 1 day prior to the actual conduct of the burn. Fractions of OC and EC in PM_{2.5} emissions were 60.25 \pm 18.5% and 3.92 \pm 1.13%, respectively. Among the water-soluble species, K⁺, acetate, and Cl⁻ are the major ions comprising 0.65 \pm 0.45, 0.55 \pm 0.16, and 0.53 \pm 0.29%, respectively. Total K and Cl are also identified by XRF (0.57 \pm 0.37 and 0.42 \pm 0.23%, respectively). The linear regressions between total and water soluble fraction for K and Cl show that total and water-soluble fractions of the two species are well correlated ($R^2 = 0.97$ and 0.96, respectively). Other trace elements identified by XRF were less than 0.3%.

Organic Compounds of PM_{2.5} Emissions. Emissions of specific POC normalized to OC (mg/g OC) were calculated after subtracting corresponding background levels (Table 2).

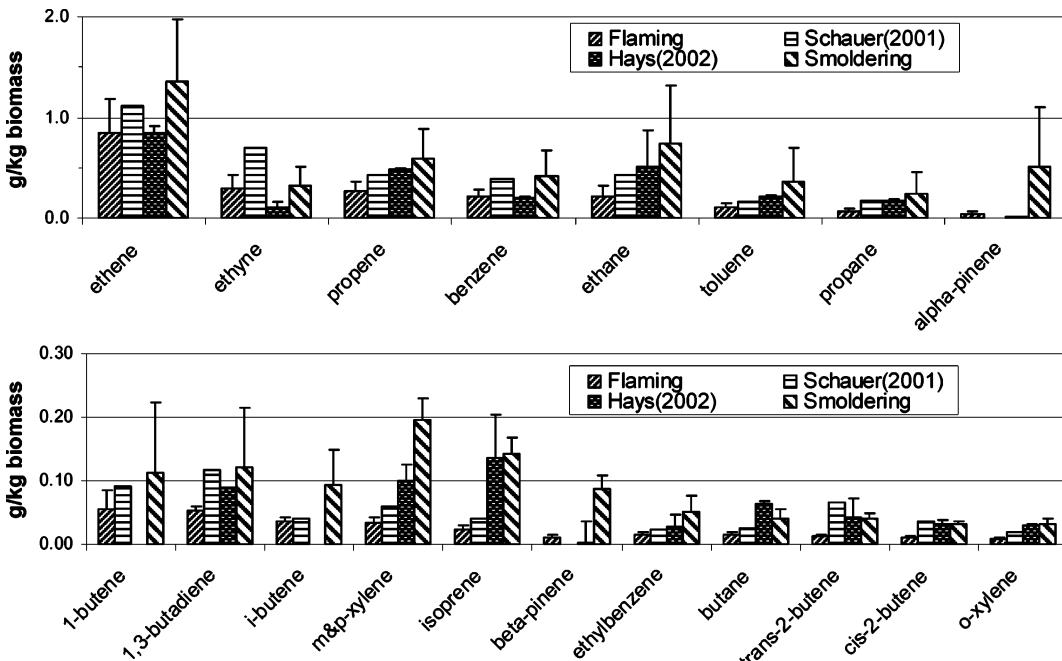


FIGURE 1. Comparisons of VOC emission factors assuming a biomass carbon content of 42.6%; the error bars for our study represent single standard deviations of 10 flaming and 12 smoldering samples.

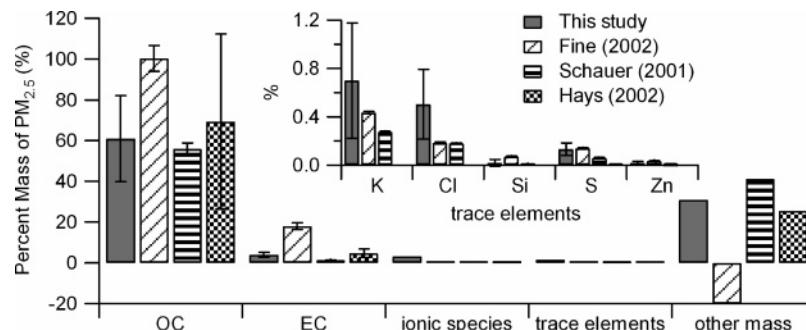


FIGURE 2. Comparison of bulk PM_{2.5} chemical composition of emissions from this in situ study with different laboratory and fireplace wood burning studies (11, 31, 36); the error bars for this study represent single standard deviations of four samples.

The total identified POC mass is 176 ± 54 mg/g OC. Levoglucosan (95 ± 40 mg/g OC), a monosaccharide derivative from the pyrolysis of cellulose, is the most dominant species among the identified POC. It is followed by resin acids, alkanoic acids, and alkenoic acids, 39 ± 15 , 27 ± 12 , and 5 ± 4 mg/g OC, respectively. Resin acids are natural compounds that can be found in plant material, mainly conifers. Two different emission mechanisms, volatilization and pyrolytic alteration, were suggested in a previous study (32). Pimaric, sandaracopimaric, and abietic acid are produced by volatilization and dehydroabietic acid is produced by pyrolytic alteration. In our study, dehydroabietic acid is the major species emitted with 33 ± 14 mg/g OC. It is followed by isopimaric and pimaric acids, 3.0 ± 1.2 and 2.5 ± 1.0 mg/g OC, respectively. In alkanoic acids, hexadecanoic, tetradecanoic, and hexacosanoic acids are the major species emitted (6.7 ± 2.9 , 5.0 ± 2.2 , and 3.7 ± 1.6 mg/g OC, respectively). For alkenoic acids three compounds were identified, with 9-octadecenoic acid and 9,12-octadecadienoic acid being the dominant emissions (2.4 ± 1.1 and 2.2 ± 1.2 mg/g OC, respectively). Small amounts of alkanes were emitted (2.4 ± 1.7 mg/g OC), with nonacosane being the most abundant of the identified alkanes (0.81 ± 0.38 mg/g OC). Polycyclic aromatic hydrocarbons (PAH) emissions were emitted at 1.5 ± 0.7 mg/g OC, with retene as the major species

(0.35 ± 0.16 mg/g OC). Cholesterol, one of the important species identifying meat cooking smoke, was detected in our study (0.81 ± 0.35 mg/g OC).

Gaseous Emissions. Emission ratios were estimated for gaseous emissions from the canister measurements (Table 3). Emission ratio relative to CO₂ is determined by dividing excess mixing ratio above ambient background level by excess mixing ratio of simultaneously measured CO₂ (33). The canister samples were distinguished into flaming (<0.1) and smoldering (>0.1) stages based on $\Delta\text{CO}/\Delta\text{CO}_2$ ratios. In our study, the ratio is higher for smoldering (0.234 ± 0.013) than flaming (0.071 ± 0.021), indicating more incomplete combustion during the smoldering stage. The ratios listed in Table 3 represent the slopes (\pm standard error, SE) of the least squares linear regressions between the mixing ratios of the individual VOC compounds and CO₂ measured absolutely (i.e., nonbackground-corrected) in the flaming and smoldering emissions, respectively. The coefficient of determination (R^2) signifies how closely individual VOC emissions are driven by the combustion intensity and can be explained by the combustion process itself. For example, most species have higher R^2 in the smoldering phase than in the flaming phase, while biogenic compounds (terpenes) and halogenated hydrocarbons show no correlation in either stage except for the methyl chloride and methyl bromide, which are common

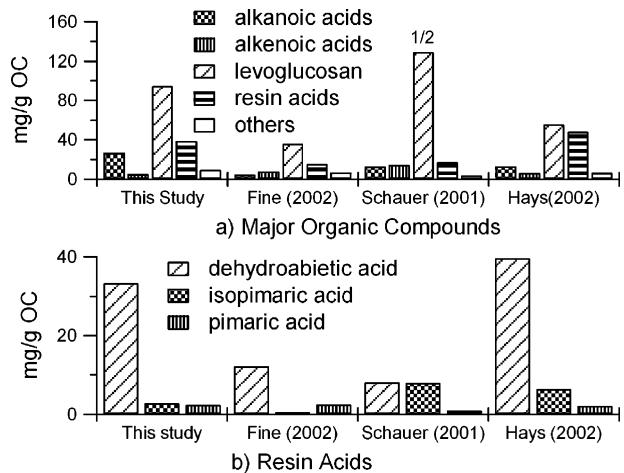


FIGURE 3. Comparisons of normalized POC emissions in mg/g OC of major organic compound groups: (a) levoglucosan $\times \frac{1}{2}$ of Schauer et al. (36), and (b) three resin acids.

atmospheric tracers for biomass burning. In general, emission ratios (i.e., slopes) are higher during smoldering than flaming except for ethene, ethyne, and organic nitrate compounds.

Emission Factors (EFs) and Profiles Comparisons. EFs (g species per kg biomass burned) are estimated using the carbon mass balance method (34, 35) with the carbon content of biomass burned (Table S1, Supporting Information). In this method, it is assumed that all the burned carbon is emitted into the atmosphere as CO₂, CO, CH₄, NMHCs, and particulate carbon species (OC/EC). EF is defined by multiplying the carbon content of biomass to the relative mass ratio of a species (g) to the summation (kg) of all measured carbon mass. Hays and co-workers (11) found that the carbon content for aged needles of loblolly pine, the main fuel here, is 42.6%, which was used in our calculations. Since the discrete nature of the fine PM sample collection

did not allow the distinction between flaming and smoldering, the same particulate carbon mass was applied to the total kg biomass calculations for both flaming and smoldering.

Results from our study were compared with three other biomass burning emission estimates: two from fireplaces and one from an open burning simulation. Fine et al. and Schauer et al. measured emissions from fireplace burning of loblolly pine and pine, respectively (31, 36). Hays et al. measured emissions from open burning simulating the prescribed burning of aged loblolly pine needles (11). Schauer et al. used fuels obtained from the western United States whereas in two other studies fuels from the southern United States were burnt. However, similar dilution sampling systems were used by all investigators to simulate the cooling and dilution effects of the atmosphere.

For the VOC species measured in our study, ethene has the highest EF for all studies (Figure 1). In general, emissions from laboratory burnings are between the flaming and smoldering emissions of our study. Emissions from the smoldering stage are generally higher than those from flaming and also higher than the two laboratory burnings. This trend becomes much stronger for aromatic and biogenic compounds such as benzene, toluene, xylenes, isoprene, and pinenes, which play an important role in the atmospheric formation of ozone and SOA.

OC is the dominant PM_{2.5} component (more than 50%) for all cases (Figure 2). K and Cl are the major trace elements (0.2–0.7%) except for the open burning simulation, in which both were below the detection limit. Water soluble potassium is often used as a tracer for biomass smoke. Note that other studies have reported only total potassium. A very similar amount of water soluble potassium compared to total potassium was found in our study indicating that all potassium from prescribed burnings is likely water soluble. This is also the case for chlorine.

The normalized POC emissions (mg/g OC) from those studies were calculated for the same compounds measured here (Figure 3). Thus, the total identified POC emissions were

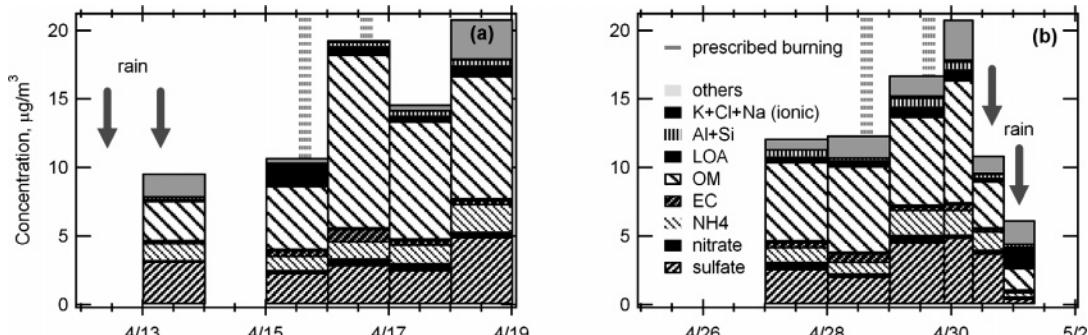


FIGURE 4. Bulk chemical composition of ambient PM_{2.5} measured in April 2004 at Augusta (a), and Columbus (b); LOA is the sum of the three light organic acids.

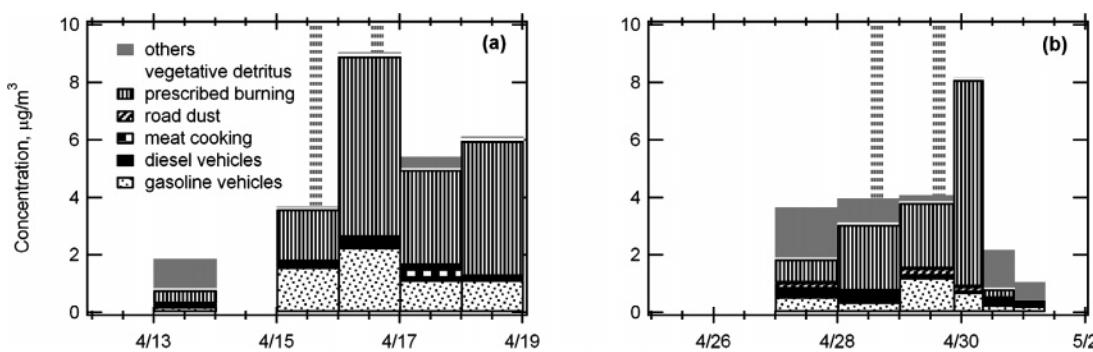


FIGURE 5. Contributions to primary fine particulate OC concentrations measured at Augusta (a) and Columbus (b).

307, 72, and 130 mg/g OC for Schauer et al. (36), Fine et al. (31), and Hays et al. (11), respectively. Our POC emission of 176 mg/g OC is closer to that from Hays et al. than those from the two fireplace wood burnings. Our distribution of major POC emissions is also most similar to that of Hays et al. (Figure 3a). Levoglucosan, a pyrolysis product of cellulose, is the most abundant species and is followed by resin acids for all studies. However, their normalized emissions (mg/g) are very different. While levoglucosan from our study is a factor of 2 or 3 higher than that from Fine et al. (31) and Hays et al. (11), it is a factor of 3 less than that from Schauer et al. (36). Resin acid emissions are similar with those of Hays et al. (11), whereas they are a factor of 2 or 3 higher than the two fireplace burnings. Dehydroabietic acid is the most dominant species for Hays et al. (11) and our study, but abietic acid is the most dominant species for both fireplace burnings (Figure 3b). Note that abietic acid is not included for comparison of total resin acid emissions since it was not measured in our study. Unlike previous wood burning studies, the actual prescribed burning emitted cholesterol, which has been used as an important species for identifying meat cooking. Cholesterol, a common animal steroid, exists in soil due to the presence and activity of soil microorganisms and higher living organisms (37). The cholesterol emission process during prescribed burning could be similar to steam-stripping and vaporization during meat cooking (38).

CMB Source Apportionments. Organic mass (OM), here assumed as $1.6 \times$ OC representing a typical urban environment (12, 39), and sulfate are the major species of the measured ambient PM_{2.5} comprising more than 65% of its mass (Figure 4; Table S2, Supporting Information). Rain events associated with low pressure frontal movements occurred before and after prescribed burning at Augusta and Columbus, respectively. The CMB model was used to quantify the contributions to ambient OC concentrations of the main primary sources (motor vehicles, residential wood burning, meat cooking, road dust, and vegetative detritus) including prescribed burning. Preliminary CMB analysis showed the residential wood burning contribution being statistically equal to zero, therefore, it was excluded. The model was run two times: first with a prescribed burning source profile from our study, and second with one from Hays et al. (11). Both CMB runs used the same selection of fitting species, which is based on a previous study (25). Only the source apportionment results from the first CMB run are reported here (Figure 5; Table S3, Supporting Information). The results show that motor vehicles and prescribed burning are the major sources contributing to the ambient [OC] at both sites during and immediately after the actual prescribed burns with $29 \pm 7\%$ and $74 \pm 11\%$ (\pm SE), respectively. However, before the burns and during the regional rain events, measured [OC] cannot be completely explained by the selected primary sources, leaving a relatively large fraction unapportioned (labeled “others” in Figure 5). Whether this fraction can be considered SOA and to what extent it is related to the local prescribed burning emissions or more regional transport with slower atmospheric processing is highly speculative and subject to future investigation.

CMB sensitivity using different prescribed burning source profiles is evaluated by comparing the two model results via linear least-squares regression (Table S4, Supporting Information). Application of the two different prescribed burning source profiles changes not only the source contribution of prescribed burning itself, but yields also significant differences for both diesel and meat cooking source impacts. Higher levoglucosan (g/g OC) from our study leads to a $27 \pm 5\%$ (\pm SE) lower prescribed burning contribution. A $25 \pm 6\%$ lower meat cooking contribution is largely due to a higher 9-octadecenoic acid (g/g OC) relative to Hays et al. The CMB result yielding lower prescribed burning contribution from

our in situ profile apportions less EC to that source, leading to a $20 \pm 16\%$ higher diesel vehicle contribution.

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Supporting Information Available

Details of site locations, sampler configurations, emission factors, linear least-squares regressions between two CMB results, and tables corresponding to Figures 4 and 5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Barnard, W.; Sabo, E. *Review of 1999 NEI and recommendations for developing the 2002 VISTAS inventory for regional haze modeling*; North Carolina DENR: Asheville, NC, 2003.
- Sandberg, D. V.; Ottmar, R. D.; Peterson, J. L.; Core, J. *Wildland fire on ecosystems: effects of fire on air*; General Technical Report RMRS-GTR-42-5; USDA Forest Service, Rocky Mountain Research Station: Fort Collins, CO, 2002; 79 pp.
- Wotawa, G.; Trainer M. The influence of Canadian forest fires on pollutant concentrations in the United States. *Science* **2000**, *288*, 324–328.
- Sapkota, A.; Symons, J. M.; Kleissl, J.; Wang, L.; Parlange, M. B.; Ondov, J.; Breysse, P. N.; Diette, G. B.; Eggleston, P. A.; Buckley, T. J. Impact of the 2002 Canadian forest fires on particulate matter air quality in Baltimore city. *Environ. Sci. Technol.* **2005**, *39*, 24–32.
- Battye, W.; Battye, R. *Development of Emissions Inventory Methods for Wildland Fire*; final report; EC/R Inc.: Chapel Hill, NC, 2002.
- Samet, J. M.; Dominici, F.; Curreiro, F. C.; Coursac, I.; Zeger, S. L. Fine particulate air pollution and mortality in 20 U. S. cities, 1987–1994. *New Engl. J. Med.* **2000**, *343*, 1742–1749.
- Pope, C. A.; Burnett, R. T.; Thun, M. J.; Calle, E. E.; Krewski, D.; Ito, K.; Thurston, G. D. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *J. Am. Med. Assoc.* **2002**, *287*, 1132–1141.
- Bell, M. L.; McDermott, A.; Zeger, S. L.; Samet, J. M.; Dominici, F. Ozone and short-term mortality in 95 U. S. urban communities, 1987–2000. *J. Am. Med. Assoc.* **2004**, *292*, 2372–2378.
- Fowler, C. T. Human health impacts of forest fires in the Southern United States: a literature review. *J. Ecol. Anthropol.* **2003**, *7*, 39–59.
- Hardy, C. C.; Hermann, S. M.; Mutch, R. E. Overview. In *Smoke Management Guide for Prescribed and Wildland Fire*; Hardy, C. C., et al., Eds.; NFES 1279, National Wildfire Coordination Group: Boise, ID, 2001.
- Hays, M. D.; Geron, C. D.; Linna, K. J.; Smith, N. D. Speciation of gas-phase and fine particle emissions from burning of foliar fuels. *Environ. Sci. Technol.* **2002**, *36*, 2281–2295.
- Baumann, K.; Ift, F.; Zhao, J. Z.; Chameides, W. L. Discrete measurements of reactive gases and fine particle mass and composition during the 1999 Atlanta supersite experiment. *J. Geophys. Res.* **2003**, *108*; (D7), 8416, D001210.
- Air Quality Designations. *Code of Federal Regulations*, Part 50, Title 40, 1997; *Fed. Regist.* July 18, 1997.
- Perrino, C.; Gheradi, M. Optimization of the coating layer for the measurement of ammonia by diffusion denuders. *Atmos. Environ.* **1999**, *39*, 4579–4587.
- Gundel, L. A.; Lee, V. C.; Mahanama, K. R. R.; Stevens, R. K.; Daisey, J. M. Direct determination of the phase distributions of semivolatile polycyclic aromatic-hydrocarbons using annular denuders. *Atmos. Environ.* **1995**, *29*, 1719–1733.

- (16) Gundel, L. A.; Lane, D. A. Direct determination of semi-volatile organic compounds with sorbent-coated diffusion denuders. *J. Aerosol Sci.* **1998**, *29*, s341–s342.
- (17) Lane, D. A. *Advances in Environmental, Industrial and Process Control Technologies, Vol. 2, Gas and Particle Phase Measurements of Atmospheric Organic Compounds*; Gordon and Breach: Amsterdam, 1999; 402 pp.
- (18) Birch, M. E.; Cary, R. A. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci. Technol.* **1996**, *25*, 221–241.
- (19) Schauer, J. J.; Mader, B. T.; DeMinter, J. T.; Heidemann, G.; Bae, M. S.; Seinfeld, J. H.; Flagan, R. C.; Cary, R. A.; Smith, D.; Huebert, B. J.; Bertram, T.; Howell, S.; Quinn, P.; Bates, T.; Turpin, B.; Lim, H. J.; Yu, J. ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon. *Environ. Sci. Technol.* **2003**, *37*, 993–1001.
- (20) Sheesley, R. J.; Schauer, J. J.; Bean, E.; Kenski, D. Trends in secondary organic aerosol at a remote site in Michigan's upper peninsula. *Environ. Sci. Technol.* **2004**, *38*, 6491–6500.
- (21) Sheesley, R. J.; Schauer, J. J.; et al. *Proceedings of the AWMA Annual Meeting*, 2000, Salt Lake City, Utah.
- (22) Manchester-Neesvig, J. B.; Schauer, J. J.; Cass, G. R. The distribution of particle-phase organic compounds in the atmosphere and their use for source apportionment during the southern California children's health study. *J. Air Waste Manage. Assoc.* **2003**, *53*, 1065–1079.
- (23) Colman, J. J.; Swanson, A. L.; Meinardi, S.; Sive, B. C.; Blake, D. R.; Rowland, F. S. Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B. *Anal. Chem.* **2001**, *73*, 3723–3731.
- (24) Watson, J. G.; Robinson, N. F.; Chow, J. C.; Fujita, E. M.; Lowenthal, D. H. *CMB8 User's Manual Draft*; U. S. Environmental Protection Agency: Washington, DC, 2001.
- (25) Schauer, J. J.; Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos. Environ.* **1996**, *30*, 3837–3855.
- (26) Schauer, J. J.; Kleeman, M. J.; Simoneit, B. R. T. Measurement of emissions from air pollution sources. 5. C_1 – C_{32} organic compounds from gasoline-powered motor vehicles. *Environ. Sci. Technol.* **2002**, *36*, 1169–1180.
- (27) Schauer, J. J.; Kleeman, M. J.; Simoneit, B. R. T. Measurement of emissions from air pollution sources. 2. C_1 through C_{30} organic compounds from medium duty diesel trucks. *Environ. Sci. Technol.* **1999**, *33*, 1578–1587.
- (28) Schauer, J. J.; Kleeman, M. J.; Simoneit, B. R. T. Measurement of emissions from air pollution sources. 1. C_1 through C_{29} organic compounds from meat charbroiling. *Environ. Sci. Technol.* **1999**, *33*, 1566–1577.
- (29) Zheng, M.; Cass, G. R.; Schauer, J. J.; Edgerton, E. S. Source apportionment of $PM_{2.5}$ in the southeastern United States using solvent-extractable organic compounds as tracers. *Environ. Sci. Technol.* **2002**, *36*, 2361–2371.
- (30) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. Sources of fine organic aerosol. 4. particulate abrasion products from leaf surfaces of urban plants. *Environ. Sci. Technol.* **1993**, *27*, 2700–2711.
- (31) Fine, P. M.; Cass, G. R.; Simoneit, B. R. T. Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the southern United States. *Environ. Sci. Technol.* **2002**, *36*, 1442–1451.
- (32) Simoneit, B. R. T.; Rogge, W. F.; Mazurek, M. A.; Standley, L. J.; Hildemann, L. M.; Cass, G. R. Lignin pyrolysis products, Lignans, and resin acids as specific tracers of plant classes in emissions from biomass combustion. *Environ. Sci. Technol.* **1993**, *27*, 2533–2541.
- (33) Bongsan, B.; Lambert, G.; Boissard, C. C. Light hydrocarbon emissions from African savanna burnings. In *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*; Levine, J. S., Ed.; MIT Press: Cambridge, MA, 1991; pp 155–161.
- (34) Sinha, P.; Hobbs, P. V.; Yokelson, R. J.; Blake, D. R.; Gao, S.; Kirchstetter, T. W. Emissions from miombo woodland and dambo grassland savanna fires. *J. Geophys. Res.* **2004**, *109*, D11305.
- (35) Radke, L. F.; Hegg, D. A.; Lyons, J. H.; Brock, C. A.; Hobbs, P. V. Airborne measurements on smokes from biomass burning. In *Aerosols and Climate*; Hobbs, P. V., McCormick, M. P., Eds.; A. Deepak: Hampton, VA, 1998; pp 411–422.
- (36) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. Measurement of emissions from air pollution sources. 3. C_1 – C_{29} organic compounds from fireplace combustion of wood. *Environ. Sci. Technol.* **2001**, *35*, 1716–1728.
- (37) Puglisi, E.; Nicelli, M.; Capri, E.; Trevisan, M.; Del Re, A. A. M. Cholesterol, β -sitosterol, ergosterol, and coprostanol in agricultural soils. *J. Environ. Qual.* **2003**, *32*, 466–471.
- (38) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R. Sources of fine organic aerosol. 1. charbroilers and meat cooking operations. *Environ. Sci. Technol.* **1991**, *25*, 1112–1125.
- (39) Turpin, B. J.; Lim, H. J. Species contributions to $PM_{2.5}$ mass concentrations: revisiting common assumptions for estimating organic mass. *Aerosol Sci. Technol.* **2001**, *35*, 602–610.

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