

PCDD/F, PCB, HxCBz, PAH, and PM Emission Factors for Fireplace and Woodstove Combustion in the San Francisco Bay Region

BRIAN K. GULLETT*

Office of Research and Development,
National Risk Management Research Laboratory (E305-01),
U.S. Environmental Protection Agency,
Research Triangle Park, North Carolina 27711

ABDERRAHMANE TOUATI

ARCADIS Geraghty & Miller, Inc., 4915F Prospectus Drive,
Durham, North Carolina 27713

MICHAEL D. HAYS

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

Emissions from residential fireplace and woodstove appliances burning fuels available from the San Francisco Bay area were sampled for polychlorinated dibenzodioxins and dibenzofurans (PCDDs/Fs), polychlorinated biphenyls (PCBs), hexachlorobenzene (HxCBz), particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs), oxygenated PAHs, and the monosaccharide levoglucosan. Emission factors for these pollutants were determined, the first known characterization of this extent. Common California natural firewoods and manufactured artificial logs were tested under operating conditions intended to reflect domestic use patterns in the Bay area, which are primarily episodic burning for aesthetic reasons. Emission factors were determined by fuel type, fuel weight, mass emission rates, and energy output, highlighting differences between fuel and combustion facility type. Average PCDD/F emissions factors ranged from 0.25 to 1.4 ng toxic equivalency (TEQ)/kg of wood burned for natural wood fuels and 2.4 ng TEQ/kg for artificial logs. The natural wood emission factors are slightly lower than those which had been estimated for the U.S. inventory. Background-corrected PCBs emitted from woodstove/oak combustion (8370 ng/kg) are 3 orders of magnitude higher in mass than total PCDDs/Fs; however, their toxicity (0.014 ng TEQ/kg) is significantly lower. HxCBz emission factors varied from 13 to 990 ng/kg and were likely fuel- and appliance-specific. Relative PAH concentrations of particle-phase compounds and emission factors were consistent with others' findings. A total of 32 PAH compounds, ranging in concentration from 0.06 to 7 mg/kg, amounted to between 0.12 and 0.38% of the PM mass, depending on the wood and facility type. Preliminary analyses suggest relationships between wood combustion markers and PCDD/F levels.

* Corresponding author phone: (919) 541-1534; fax: (919) 541-0554; e-mail: gullett.brian@epa.gov.

Introduction

Residential wood combustion (RWC) in woodstoves and fireplaces is estimated to account for 2% of polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/F) emissions in the U.S. inventory (1). In the San Francisco Bay region, where industrial sources are limited, emissions from woodstoves and fireplaces may be on the order of 40% of the PCDDs/PCDFs emitted into the air (2). These estimates are subject to large uncertainty: the U.S. inventory emission factor of 2 ng toxic equivalency (TEQ)/kg burned was derived from only two measurement studies conducted in Europe (3, 4) and has been characterized as of "low" certainty (1). The data are likely of limited use in accurately representing San Francisco Bay area emissions due to wood and facility type differences as well as the inferential assumptions made. To more fully understand the contribution of RWC as a source of PCDDs/PCDFs in the environment and, more specifically, the San Francisco Bay area, this effort intended to more accurately quantify emissions from this source.

Meaningful efforts to determine RWC contributions to regional PCDD/PCDF emissions require use of representative wood fuels, woodstove and fireplace types ("facilities"), and use modes. For the San Francisco Bay area, common fuel types include western pine and California oak, as well as manufactured artificial "logs". The most common RWC facility in the West Coast region is the fireplace (66% of the homes built in the West Coast in 1999 have one or more fireplaces (5, 6)). Because of the temperate climate of the area, fireplaces are most commonly used on an infrequent basis: almost 69% of the usage is less than once per week (7) with an annual average of about 43.4 h (5, 6). Because fireplaces are used more for their aesthetic appeal than for a source of heat, the most common use mode is an evening fire that is not maintained throughout the night. Artificial logs, consisting of wax and sawdust, are commonly used; of a survey population that used artificial logs, 46% said they used them several times a month or more (7) either as a sole or supplementary fuel, but more for aesthetics than heat. Woodstoves are used primarily for heating purposes and, hence, are operated more continuously with natural wood fuels, but these sources are less common in the area.

Limited efforts have been made to determine the effect of wood types on PCDD/F emissions. Differences in wood heating value could have an effect on emissions; recent woodstove tests (8) with black spruce (*Picea mariana*) and hard maple (*Acer saccharum*) showed species-specific distinctions in emissions. Additional effects on emission factors are likely to be caused by changes in fuel combustion conditions resulting from variation in fuel loading, orientation, air draft conditions, fuel charge rate, and other operating parameters. An accurate assessment of RWC emissions requires sampling a population representative of these combustion factors. To minimize the large sampling effort necessary to fully characterize emissions over a broad range of conditions representative of those in the United States, it is important to understand what conditions have an effect on emissions so that efforts can be prioritized.

Other pollutants of interest from fireplaces and woodstoves include particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs), hexachlorobenzene (HxCBz), and polychlorinated biphenyls (PCBs). Similarly to PCDD/Fs, emission factors for these pollutants are a function of fuel-, facility-, and condition-specific variables. PM and PAH emission factors for woodstoves and, to a lesser extent, fireplaces have been determined (9), although the quality of

the PAH values suffers from a high degree of variability in the data. PCBs are of interest because of the PCDD/F-like toxicity in 14 of the 209 congeners. HxCBz is of interest because of its characterization as a persistent organic pollutant (10) and its dioxin-like activity (11). HxCBz emissions have been detected from open burning of household waste (12), but currently the major sources are believed to be industrial. PAHs are of interest due to their known carcinogenic behavior (13); in particular, oxygenated and hydroxylated PAHs have been linked to endocrine disruption effects (14). PM has been implicated as a major cause of respiratory disease and adverse health effects (15).

Characterization of the U.S. inventory of PCDD/F emissions, particularly for diffuse, hard-to-characterize sources such as woodstoves and fireplaces, and prediction of source-to-receptor pathways requires an ability to attribute ambient sampling pollutant concentrations to specific sources. PAH compounds such as retene (16) (1-methyl-7-isopropylphenanthrene, C₁₄H₁₀) and monosaccharide compounds such as levoglucosan (17) (1,6-anhydro-β-D-glucopyranose, C₆H₁₀O₅) have been suggested as unique markers of biomass combustion. Source-specific indicators such as dehydroabietic acid for conifers, levoglucosan from cellulose, and methoxyphenols (18, 19) were suggested. These relationships remain to be strengthened through additional testing, and the correlation between these biomass combustion markers and PCDD/F emissions remains untested. As this occurs, source attribution and transport/distribution of PCDD/F pollutants may be better resolved.

To more fully characterize residential wood combustion sources of PCDDs/Fs, and enable efforts to estimate their contribution to the San Francisco Bay area environment, a series of tests were conducted to determine and propose initial PCDD/F emission factors (as well as those for PCBs, HxCBz, PM, and PAHs) from fireplaces and woodstoves burning typical local fuels. Burn procedures were intended to be representative of typical residential use, to more closely reflect actual emission potential.

Experimental Section

Thirteen combustion tests were conducted in an enclosed, wood-fired facility with a conventional fireplace (10 tests) and a woodstove (3 tests) using three types of fuels common to the San Francisco Bay area. The woodstove (termed "WS") was a free-standing, EPA-certified, noncatalytic woodstove (Quadrafire 3100 model) with a glass window in the front door. The woodstove is made from steel and is lined with cinderblock firebrick. An auxiliary air damper is opened during ignition of the kindling charge and a main air damper controls the burn rate during normal operation. The fireplace (termed "FP") used in this test program is a zero-clearance, factory-built fireplace (Majestic MRC42A) with a log grate and a glass door. The fireplace has an auxiliary air supply plumbed to an external source of makeup air for combustion, and a heat exchanger fan that pulls in room air below the glass door and blows out heated air just above the glass.

The woodstove and fireplace were tested within a wood-fired testing facility (described more fully in ref 20) built to comply with the U.S. EPA woodstove certification standards (21), but subsequently modified to allow for energy balances. This facility consists of: a residential wood combustion appliance (either a woodstove or fireplace) set on a continuous, weigh-scale platform located inside a calorimeter chamber; a chimney system exhausting to a dilution tunnel hood; and a dilution tunnel system. The test facility allows the products of combustion to cool and mix with the indoor air in the dilution channel upstream of the extractive gas sampling locations, allowing collection of samples in their ambient atmosphere form. Gas velocities in the stack and in the dilution tunnel were measured with a multimeter (AirData

TABLE 1. Fuel Properties

fuel properties	oak	pine	artificial logs
Ultimate Analysis (Moisture Free)			
carbon (%)	48.09	49.73	70.37
hydrogen (%)	6.16	6.39	10.88
nitrogen (%)	<0.5	<0.5	0.55
sulfur (%)	<0.05	<0.05	0.13
chlorine (ppm)	<50	<50	437
ash (%)	0.66	0.27	0.44
oxygen (% by differ.)	45.09	43.61	17.63
heat of combustion (MJ/kg)	19.0	19.7	34.0
Proximate Analysis (Moisture Free) (%)			
volatile matter	84.36	90.7	92.44
ash	0.66	0.27	0.44
fixed carbon (by difference)	14.98	9.03	7.12
Average Moisture Content (%)			
oven drying method	16.2	8.7	1.0
moisture meter	17.3	8.8	1.0

Multimeter ADM-860) via a pitot tube, and ranged from 0.127 to 152 m/h. The calorimeter chamber is built of dimensional lumber, drywall, and plywood with insulating fiberglass panels. The chamber has a thermal resistance that meets the ISO 13336 criterion (22) of not less than 2.5 m² K/W. Two centrifugal fans connected to ducts at either end of the chamber provide dilution air for the dilution tunnel. The supply and return air temperatures are recorded using precision thermocouple transmitters connected to a data acquisition system. The calorimeter chamber is calibrated using a 30 kWe resistance heater over three power levels. An amp meter is used to monitor the heater power consumption in order to compute the heat load being delivered to the calorimeter chamber.

Two natural wood types, from among those most commonly used in the San Francisco Bay area, and a commercial, artificial log were tested. The wood types included a California oak mixture (black oak, *Quercus kelloggii*; and live oak, *Quercus agrifolia*) termed "oak" and Western pine (*Pinus lambertiana*) termed "pine." The oak and pine woods were harvested from a mountain area near Cazadero, CA, and consisted of logs approximately 40 cm long and 18 cm in diameter. The artificial logs were from a single manufacturer and were made of wax and sawdust; considerable variation in composition is expected across manufacturers, as this is a formulated product with different constituents and regional sources of materials. Fuel properties are shown in Table 1.

At the start of each new-wood test sequence, a pre-burn test was performed to condition the wood burning facility with the test fuel and to determine the timing for fuel additions that would allow for a 5-h test cycle. Each burn test consisted of: (1) ignition/kindling, (2) addition of the main fuel charge, (3) one or more supplementary fuel charges to maintain a sustainable fire for a prescribed time, and (4) a burn-down phase with no wood addition. The starting fuel for the woodstove ignition/kindling phase consisted of 3.5 kg of 3-cm-wide pieces (or smaller) of the test wood and 0.25 kg of paper, lit with a propane torch through the open door. The door was kept open for about 9 min during the ignition/kindling phase, shut, then reopened after 14 min (air damper fully open) and then again after an additional 70 min (air damper at the minimum setting) for addition of 5.76 ± 0.05 kg charges for a total mass loading of 15.0 ± 0.1 kg. In this manner, wood fuel was added throughout the burn/sampling period so as to maintain an approximate burn rate of 2.5 kg/hr, consistent with a similar Canadian study (8).

The fireplace procedures started with a similar ignition/kindling charge as the woodstove (3.5 kg of wood and 0.25 kg of newspaper). This was followed by five subsequent charge

additions (6.5 ± 0.2 kg) at intervals sufficient to maintain a sustainable fire in the fireplace for an operational cycle of 5 h. The total fireplace loading was 36.2 ± 1.2 kg of wood, leading to an average burning rate (absent the ignition/kindling phase) of 7.0 ± 0.3 kg/hr.

Artificial logs made for use in fireplaces require no kindling because of their wax content. We followed the manufacturer's burning procedure for igniting the logs, which included lighting the paper bag wrapper. Two 2.3-kg logs produced 5 h of quality flames each day. Emission sampling combined two 5-h operational cycles in a single, cumulative sampling train/adsorbent to more fully ensure exceeding the detection limits of the target compounds.

The mild climate in the San Francisco Bay area lends itself to only episodic fireplace and woodstove use. Therefore, a cold-to-cold cycle, in which the fireplace or woodstove is used discontinuously, is most representative of use patterns, and was used throughout this testing program. As the intent of this work was to determine a representative emission factor, the flue or chimney stack was not cleaned between tests, despite the potential influence of deposits on emissions (the average homeowner is assumed to clean the flue less frequently than once each year). Residual contamination could influence subsequent tests, but would result in a more representative emission factor. The unburned residues, composed of unburned wood and inorganic ash, were removed from the wood-burning appliance at the end of each burn run.

Characterization of trace emissions from combustion tests is made more difficult by the high variability caused by random factors such as fuel and air orientation. In anticipation of this variability, three replicate tests were conducted to provide more robust emission data. Although true replicate tests at identical burn rates were not possible, the burn procedures and wood burning rates were set to provide consistent burn procedures for each test. Emission factors were calculated in units of nanograms/hour (ng/h), nanograms/kilogram dry fuel (ng/kg), and nanograms/kilowatt-hour (ng/kWh).

The sampling duration covered the full period of the flaming combustion through the active smoldering phase until more than 90% of the wood mass was consumed. PCDDs/Fs, PCBs, and HxCBz were sampled via separate, simultaneous method 23 trains from the dilution tunnel and analyzed via method 23-8290 (23) for PCDDs/Fs, modified method 1668A (24) for PCBs, and New York State Department of Environmental Conservation HRMS method (25) for HxCBz. The respective XAD-2 resins were prespiked with five PCDD/F surrogate compounds and three PCB surrogate compounds. PCDD/F emissions are reported as total congener concentrations (sum of tetra- to octa-Cl-substituted), and as calculated emission factors based on the product of the seventeen 2,3,7,8-Cl-substituted PCDD/F isomer concentrations and their respective World Health Organization (WHO) toxic equivalency factors (TEFs) (26).

Organic chemical speciation (PAHs, oxy-PAHs, and levoglucosan concentrations) on the PM fraction was performed by applying previously detailed methods (27 and references therein). Briefly, the quartz fiber sample filters were spiked with two internal standard suites (prepared and certified at the Wisconsin State Laboratory of Hygiene, University of Wisconsin, Madison, WI) composed of isotopically labeled, target organic compounds which included PAHs (acenaphthene- d_{10} , chrysene- d_{12} , and dibenz[*a,h*]anthracene- d_{14}), an oxy-PAH (4,4'-dimethoxybenzophenone- d_8), and a monosaccharide (levoglucosan- $^{13}C_6$). Hexane and benzene/isopropyl alcohol extractions were split into two fractions, one of which remained neutral and the other of which was derivatized with bis-(trimethylsilyl)trifluoroacetamide-*N,O*-bis(trimethylsilyl) acetamide (BSTFA, Supelco, Bellefonte, PA) reagent

(30 min, 70 °C) to allow polar alcohols to be successfully chromatographed. Both the neutral and derivatized extracts were analyzed by gas chromatography/mass spectrometry (GC/MS, HP6890/5973, Agilent, Palo Alto, CA). Automated splitless mode injections (1 μ L) of extract into a heated (300 °C) split/splitless inlet were made. The GC was outfitted with an ultralow bleed capillary column (30-m length, 0.25-mm i.d., and 0.25- μ m film thickness; HP-5MS, Agilent) with a diphenyl (5%)–dimethoxysiloxane (95%) copolymer stationary phase heated at 65 °C for 10 min, ramped at 10 °C/min to 300 °C, and held for 41.5 min. The MS detector was operated in scan mode (50 to 500 amu, 3 scans/s).

Target analytes were quantified using a multi-level calibration of concentration and response ratios for the authentic and isotopically labeled standards. Of the over 300 compounds commonly identified by this analysis, 29 PAHs, 3 oxy-PAH compounds, and the monosaccharide levoglucosan were targeted based on availability of standards. Identification of these compounds in the sample extracts was confirmed using retention times and mass fragmentation patterns of the authentic standards or, when an authentic standard was unavailable, published retention times (28) and National Institute of Standards and Technology (NIST) spectral matches. Concentrations of the latter compounds were estimated using response factors from their nearest structural match.

The analytical uncertainty for individual PAHs and oxy-PAHs was determined by extracting, in triplicate, NIST standard reference material 1649a for airborne particulate matter. Twenty-seven of the 32 target PAHs and oxy-PAHs were quantified in the NIST reference material. A mean analytical method precision of 17% (values ranged from 4 to 36%) for these analytes was calculated on a weight percent basis. Twenty-two of the 32 target compounds had precisions $\leq 25\%$. Method precisions below 1% are achievable for analysis of levoglucosan in biomass extracts (27).

To relate PAH and other organic emissions to PCDD/F emissions as a potential source apportionment tool, optimal multiple linear regression models were fit to predict TEQ and total for PCDD, PCDF, and PCDDs/Fs with measured PAH/organic concentrations. Sixteen of the thirty-three measured compounds were used (those with molecular weights > 228) to provide assurance that sampling losses due to volatility were minimized. All possible models using subsets of one or two predictors were considered, with principal model selection criteria consisting of maximization of the model's squared correlation coefficient (R^2), minimization of each selected predictor's p value (e.g., $p \leq 0.05$), and maximization of each predictor's squared semipartial correlation, R^2_{sp} (this term reflects the influence of each particular predictor on modeling the observed dependent variable values).

Total PM was collected using a 47-mm filter and a sampling flow rate of 1.1 L/min via dilution tunnel sampling [modified EPA method 5G (29)]. PM emissions are reported here using EPA method 5H (30) equivalents for stack sampling (31) in order to compare them with EPA's AP-42 (9) values on the same basis. The size distribution of the airborne particles was determined with an electrical low-pressure impactor (ELPI) resulting in 12 size classes ranging from 0.03 to 10 μ m. In all the sampling trains, isokineticity was not maintained and deemed not necessary due to the relatively fine size distribution of the particles collected and to enhance the sampling rate of the target organic compounds of interest. Continuous measurements of oxygen (O_2) and carbon dioxide (CO_2) were performed in the dilution tunnel, while carbon monoxide (CO) was measured in both the stack and the dilution tunnel (since CO may still be reacting in the stack). Flow measurements were taken in both the stack and the dilution tunnel.

TABLE 2. Test Matrix and Operating Conditions

fuel	appliance	run	fuel mass (kg, dry)	fuel moist. (%)	run time (min)	sample vol. (m ³)	power (kWh)	O ₂ (dry)	CO (ppm dry, 7% O ₂)	CO ₂ (% dry, 7% O ₂)
oak	woodstove	1	11.45	23.02	300	11.6	42.1	19.9	4847	6.55
		2	10.97	26.03	300	8.9	41.4	20.1	6212	7.39
		3	12.24	18.22	300	8.4	37.1	19.6	4803	4.84
oak	fireplace	1	28.78	19.88	300	8.9	16.9	19.9	881	3.37
		2	30.21	20.5	300	9.6	17.6	19.4	685	2.34
		3	28.72	28.72	300	9.3	17.4	20.1	1182	4.18
pine	fireplace	1	32.27	11.18	300	9.4	20.5	19.9	735	3.93
		2	32.49	11.01	300	7.6	20.6	20.4	1454	7.44
		3	31.83	11.16	300	8.9	NA ^a	19.9	441	2.81
oak	fireplace	1	28.63	28.72	330	10.1	17.1	19.9	887	2.95
artifi. log	fireplace	1	8.98	1.01	600	18.2	7.7	20	266	2.14
		2	11.22	1.06	720	21.7	10.7	20.3	394	3.18
		3	11.22	1.06	720	20.1	10.1	19.9	308	2.81
QA blank	woodstove	1	NA	NA	300	12.0	NA	NA	NA	NA
QA blank	fireplace	1	NA	NA	300	9.2	NA	NA	NA	NA
QA blank	room	1	NA	NA	300	9.2	NA	NA	NA	NA

^a NA = not applicable.

TABLE 3. PCDD/F Total Emission Factor^a Results

wood	appliance	ng/kg _{FUEL}		ng/m ³		ng/h		ng/kWh	
		avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)
oak	woodstove	7.44	35.6	0.053	30.0	17.3	37.2	2.16	37.3
QA blank		NA ^{1 b}		0.006	NA ^{2 c}	2.06	NA ²	NA ¹	
oak	fireplace	9.62	38.8	0.016	43.7	55.7	43.3	16.3	39.9
pine		54.4	124	0.100	125	346	127	118	106
artif. log		75.8	11.5	0.018	13.5	68.9	11.5	83.8	10.0
QA blank		NA ¹		0.010	NA ²	38.5	NA ²	NA ¹	

^a Tetra- to octa-CDD/F only, NDs = 0, EMPCs = values, corrected for background. ^b NA¹ = not applicable, blank (no fuel burned). ^c NA² = not applicable, only one run.

TABLE 4. PCDD/F Toxic Equivalency Emission Factor^a Results

wood	appliance	ng TEQ/kg _{FUEL}		ng TEQ/m ³		ng TEQ/h		ng TEQ/kWh	
		avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)
oak	woodstove	0.25	102	0.0021	66.9	0.58	100	0.071	96
QA blank		NA ^{1 b}		0.0004	NA ^{2 c}	0.13	NA ²	NA ¹	
oak	fireplace	0.35	21.5	0.0009	2.26	2.0	14.7	0.59	1.6
pine		1.4	120	0.0025	121	8.9	121	3.0	106
artif. log		2.4	11.9	0.0006	16.1	2.3	9.27	2.8	16.6
QA blank		NA ¹		0.0004	NA ²	1.4	NA ²	NA ¹	

^a NDs = 0, EMPCs = values, corrected for background. ^b NA¹ = not applicable, blank (no fuel burned). ^c NA² = not applicable, only one run.

The PCDD/F, PCB, and HxCBz data were corrected for the contribution of target analytes in the background dilution air because the sampled flow consisted of over 80% dilution air. Three sample blanks were collected: one from the room air and one from air through each of the woodstove and fireplace appliances (without combustion). The appliance-specific blanks were used to determine the concentration of the target analytes in the dilution air and to correct, by congener-specific subtraction, analyte concentrations due to background levels. Congeners that were nondetects (NDs) were reported as zeros. Analytes that met the mass/time/elution order criteria but not the isotopic ratio criterion for PCDD/F compounds, or estimated maximum possible concentration compounds (EMPCs), were treated as values where their presence could be confirmed in other samples. Data are reported with their percent precision values, or 100 × SD/average. A summary test matrix with operating conditions is included in Table 2.

Results and Discussion

PCDD/F Emission Factors. Run-type-specific average emission factors are shown in Table 3 for PCDD/F Total and Table

4 for PCDD/F TEQ results. On average, the seven oak runs, three pine wood runs, and three firelogs runs had average emission factors of 0.28 (0.17 SD), 1.4 (1.7 SD), and 2.4 (0.29 SD) ng TEQ/kg, respectively. The emission factors between runs vary by a maximum of about a factor of 5; intra-run type variability, however, is low, except for FP-Pine, where a precision of over 120% was recorded for the three runs (the source of high variability is unknown, although high variability in emission factors from other marginally controlled combustion practices has been observed previously (32)). The emission factors for the four run-types show that FP-Logs have the highest PCDD/F Total and TEQ emission factors at 75.8 ng/kg and 2.4 ng TEQ/kg, respectively. However, this ranking is primarily due to the high energy density of artificial logs (Table 1). On a nonmass-specific basis, FP-Pine has the highest emission factor at, for example, 0.0025 ng TEQ/m³ and 346 Total ng/h. High values for FP-Pine are due primarily to one run in which emission factors were about 5 times higher than those in the other two trials.

Comparison of the WS-oak and the FP-oak total and TEQ values shows no statistical distinction in emission factors based on appliance type alone (primarily due to the wide

TABLE 5. PCB Emission Factor^a Results

wood	appliance	ng/kg _{FUEL}		ng/m ³		ng/h		ng/kWh	
		avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)
oak	woodstove	8370	21.1	54.8	17.2	19200	16.9	2398	16.7
QA blank		NA ^{1 a}		11.1	NA ^{2 b}	7400	NA ²	NA ¹	
wood	appliance	ng TEQ/kg _{FUEL}		ng TEQ/m ³		ng TEQ/h		ng TEQ/kWh	
		avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)
oak	woodstove	0.0014	59.0	0.0001	56.1	0.032	55.9	0.0041	55.1
QA blank		NA ¹		0.0001	NA ²	0.0504	NA ²	NA ¹	

^a NDs = 0, EMPCs = values, corrected for background. ^b NA¹ = not applicable, blank (no fuel burned). ^c NA² = not applicable, only one run.

TABLE 6. HxCBz Emission Factor^a Results

wood	appliance	ng/kg _{FUEL}		ng/m ³		ng/h		ng/kWh	
		avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)
oak	woodstove	13	33.3	0.085	34.4	30	34.3	3.7	33.7
QA blank		NA ^{1 b}		0.10	NA ^{2 c}	36	NA ²	NA ¹	
oak	fireplace	310	27.7	0.50	30.1	1900	28.9	5500	31.1
pine		380	26.0	0.68	26.8	2400	26.4	600	31.3
artif. log		990	27.5	0.23	24.9	910	24.9	1100	32.6
QA blank		NA ¹		0.33	NA ²	1200	NA ²	NA ¹	

^a NDs = 0, EMPCs = values, corrected for background. ^b NA¹ = not applicable, blank (no fuel burned). ^c NA² = not applicable, only one run.

variance in the WS-oak tests). The mass-, hourly-, and energy-specific emission factors were higher for the FP-Oak than for the WS-oak, although emissions were more concentrated (e.g., ng/m³) in the WS due to lower flowrates. Neither the pine wood nor the artificial logs were run in both facilities due to project duration limitations, so it is not possible to determine whether emissions are partly determined by facility type.

In general, run-to-run replicates among run types were fairly consistent, resulting in median precision values of <40%. The one exception was the FP-pine runs, where one run was extremely distinctive, resulting in a precision around 120%. Of the 13 runs with 17 TEF-weighted isomers per run, only 4 isomers were NDs. Consequently, treatment of NDs as zeros had little effect on the emission factor estimates. Background concentration levels of target analytes were low for PCDDs/Fs, where the minimum sample (corrected)-to-background ratio was 2.5:1 and the maximum was 12:1. A repeatability test, in which FP-oak was rerun after three FP-pine tests, showed little distinction in the prior three results: total PCDD/F had decreased while TEQ had increased, both about 25–30%. This suggests little change in emissions between appliance “aging,” but the limited duration of the tests suggests that these results are tentative. PCDD/F isomer patterns and homologue profiles by run type are presented in the Supplemental Information, part 1.

Polychlorinated Biphenyls (PCBs). PCB emission factor results (Table 5) are limited to the WS-oak experiments (results from the fireplace experiments were not usable because of sample contamination from the contracted analytical laboratory). PCB emission factors, corrected for background levels, averaged 0.014 ng TEQ/kg and 8370 ng/kg. There are scant published data with which to compare these levels; recent results from forest litter burns resulted in 0.007 ng TEQ/kg and 390 ng/kg (33). The total PCB emitted from the woodstove is 3 orders of magnitude greater than the total PCDD/F emissions. The contribution of PCB TEQ to the total TEQ (PCB + PCDD/F) is 0.5%. The coplanar PCBs accounted for 6.6% of the total 209 PCB congeners, which compares well with 5.6% found in post-burn forest-fire soil samples (34).

PCB homologue profiles and TEF-weighted PCB isomer patterns for both WS-oak (not shown) indicate that the high background concentrations require sufficient conditions and controls from which to discern combustion source analytes from those of the background. The mono-CB homologue is the most distinctive homologue from that of the background, increasing from about 0.2 ng/dscm (1% of the PCB total) for the background level to 9.5 ng/dscm (18% of the PCB total) during combustion. In contrast, the TEF-weighted PCB isomer pattern (not shown) shows little distinction from that of the background. The mass-weighted average degree of chlorination of the PCB is 3.5 ± 0.5 (unitless) for a total Cl mass composition of 44%. The PCB distributions (209 congeners) are included in the Supplemental Information, part 2.

Precision values on the PCB totals were less than 22%, indicating a high degree of reproducibility. The PCB TEQ values had higher relative standard deviations, around 55%. The sample (corrected) to background ratio of PCB total was about 5:1, indicating a high degree of confidence in the emission measurements.

Hexachlorobenzene (HxCBz). Emission factors for HxCBz are summarized in Table 6 for all wood- and facility-specific run types. Considerable differences are noted between appliance and fuel type. HxCBz emissions for WS-oak average 13 ng/kg, the lowest of the four run type emission factors. The emission factor for FP-oak was about 310 ng/kg, considerably higher than that for the woodstove, suggesting that the difference in combustion conditions (affected by facility type) has a significant effect on emissions. FP-pine resulted in emission factors similar to those of FP-oak. The FP-log run type had the highest HxCBz emissions with an emission factor of about 990 ng/kg. However, as with PCDD/F, the higher energy density of the artificial logs inflates the mass-specific emission factors: emission-factors-based rates of emissions (ng/h), show that artificial logs have a lower emission factor (910 ng/h) than the FP-oak (1900 ng/h) and FP-pine (2400 ng/h) conditions.

The precision of the HxCBz measurements across all run type averages was <35%, indicating good reproducibility. The average ratio of the sampled HxCBz concentration

TABLE 7. Particle Emission Factor^a Results

wood	appliance	g/kg _{FUEL}		mg/m ³		g/h		g/kWh	
		avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)
oak	woodstove	9.58	21.8	53.5	28.3	20.7	29.3	3.25	36.6
QA blank		NA ^{1 b}		0.00	NA ^{2 c}	0.00	NA ²	NA ¹	
oak	fireplace	5.56	11.3	8.38	7.32	27.3	10.12	8.91	11.3
pine		2.80	17.6	4.78	17.4	15.1	17.9	4.43	19.7
artif. log		16.6	4.41	4.52	3.11	32.3	9.83	18.2	7.93
QA blank		NA ¹		0.02	NA ²	0.07	NA ²	NA ¹	

^a Method 5H (30) equivalent. ^b NA¹ = not applicable, blank (no fuel burned). ^c NA² = not applicable, only one run.

TABLE 8. PAH and Other Related Compound Emission Factor Results (mg/kg)

target compounds	WS and oak		FP and oak		FP and pine		FP and logs	
	avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)	avg.	prec. (%)
benzo[a]anthracene ^a	0.73	73.6	0.68	41.9	0.34	15.0	0.79	2.4
chrysene & triphenylene ^a	0.78	54.0	0.72	35.0	0.33	18.3	1.48	3.8
benzo[b&j]fluoranthene ^a	0.36	72.9	0.37	46.2	0.23	17.7	0.42	8.7
benzo[k]fluoranthene ^a	0.44	88.3	0.42	41.5	0.27	15.7	0.49	9.3
benzo[a]pyrene ^a	0.56	92.8	0.58	40.7	0.31	12.8	0.54	9.9
benzo[e]pyrene ^a	0.34	75.7	0.32	42.6	0.18	14.9	0.88	10.4
benzo[ghi]perylene ^a	0.19	95.5	0.23	41.9	0.15	11.5	0.41	44.8
indeno[1,2,3-cd]pyrene ^a	0.13	64.2	0.29	42.4	0.19	14.6	0.38	30.0
PAH MW 276 (anthanthrene) ^a	0.06	122.6	0.08	51.4	0.03	17.2	0.19	40.6
Dibenzo[a,h]anthracene ^a	0.04	69.2	0.05	35.2	0.03	17.1	0.08	22.2
PAH MW 278 (pentaphene) ^a	0.01	105.1	0.01	46.8	0.01	13.1	0.01	86.6
PAH MW 278 (benzo[b]chrysene) ^a	0.03	79.8	0.04	35.6	0.03	17.0	0.05	26.1
PAH MW 278 (picene) ^a	0.06	61.9	0.08	27.9	0.03	19.2	0.06	17.8
coronene ^a	0.07	99.7	0.10	47.5	0.06	8.3	0.26	53.2
retene	ND		ND		0.49	26.2	10.96	0.9
levoglucosan	146.94	22.6	143.66	28.9	43.32	17.0	31.10	35.5

^a 14 "heavy" PAHs.

(background-corrected) to that of the background HxCBz concentration was 1.3/1.

The 1996 (U.S.) National Toxics Inventory (35) reports a total of 59 kg of HxCBz emissions from minor source categories and 907 kg total for all sources. If the HxCBz emission factors derived here for RWC applied to forest fires, then annual HxCBz emissions would range from 0.5 kg (WS-oak) to 12.1 kg (FP-oak and FP-pine), based on an average annual forest fire consumption of 1.7 million ha (36) at 23 000 kg/ha (37). This suggests that HxCBz emissions from wood combustion may be a minor source, although more tests with different wood and facility types would improve confidence in this estimate.

Particulate Measurements. The particulate matter (PM) emission factors range from 2 to 13 g/kg (Table 7), showing apparent fuel-type and appliance-specific values, as seen by others (20). FP-Logs have the highest emission factor on a fuel mass basis, but are similar to temporal emission rates from FP-oak. PM emission factors are fairly consistent: precision values are <22% for mass-specific measurements. PM emitted from the woodstove/oak tests are found to be primarily in the submicrometer size [$>99.5\%$ of the particulate matter is classified as having an aerodynamic diameter of $<2.5 \mu\text{m}$ (PM_{2.5})]. Fine particle mass emissions from the woodstove were measured to be 9.58 g/kg, which is in agreement with others' work (9, 38). PM emissions from burning oak in the fireplace (FP-oak, 5.56 g/kg) are less than those for the woodstove, but still within the range of PM reported for hardwood species [3.5–6.8 g/kg average (39); 6.6 g/kg (38)]. PM emission factors for the fireplace burning pine wood fuel were 2.8 g/kg, lower than the reported PM₁₀ emission factors of 17.3 g/kg for fireplaces burning cordwood published in ref 9. The emission factor for artificial logs was measured to be 16.6 g/kg, higher than a reported (40) average

of 4.1 g/kg but consistent with PM emissions from burning artificial logs in fireplaces, 25.9 g/kg (9); this difference is likely primarily due to manufacturer-specific variations in log composition. The PM emission factor (mg/kg) correlates poorly ($R < 0.35$) with PCDD/F Total and PCDD/F TEQ, suggesting that PCDD/F emissions cannot be inferred from PM measurements.

PAHs and Related Compounds. Fuel- and appliance-specific organic emission factors, expressed as mg/kg, are shown in Table 8 for 14 heavy PAHs, oxy-PAHs, retene, and levoglucosan. An extended table including 32 PAH compounds is included in Part 2 of our Supplemental Information. These values are compared among themselves and with literature values to understand their levels and variance on a fuel- and appliance-specific basis. In all, 32 PAH compounds, ranging in concentration from 0.06 to 7 mg/kg, amounted to 0.25, 0.38, 0.31, and 0.12% of the PM mass for WS-oak, FP-oak, FP-pine, and FP-log experiments, respectively.

Quantified emission factors in the literature for particle-phase PAHs from oak-fired woodstoves are scarce. PAH concentrations from this work, normalized to the PM mass collected, are compared to results of ref 38. Twelve PAHs were selected for emission comparison based on the compound overlap between data sets and our confidence to ensure complete compound sampling without volatile loss or gain (see ref 41). The latter criterion was met by selecting compounds for comparison that exist primarily in the particle phase [202–300 amu mol wt; benzo[b+k+j]-fluoranthene are summed] under these sampling conditions. McDonald et al. (38) used results from multiple, in-series substrates of a sampling array to operationally define gas- and solid-phase PAH partitioning by the chromatographic elution order. Mean analytical precisions for PAH concen-

trations for work in ref 38 and the work reported here are virtually identical (~70%), and observed PAH concentrations are inversely proportional to mol wt. Weight % (defined as species mass \times 100/total PM mass) concentrations of PAHs (mol wt \geq 202 amu) between this work and ref 38 agree to within 37% on average (8–63%). Considering that ref 38 implements different chemical analysis methods and composites eight tests that, by design, vary fuel load, hardwood species, and burn rate, agreement between these studies is remarkable.

Of studies that have inventoried PAH emissions from fireplace combustion (38, 39, 42–44), only two (38, 42) quantify emissions from artificial logs. Of the PAHs studied in the work reported here, 15 PAHs (178 \leq mol wt \leq 302) overlapped with ref 38 (using Durafume7 artificial logs) and 18 PAHs (178 \leq mol wt \leq 302) overlapped with ref 42 (using Pine Mountain7 artificial logs). Rogge et al. (42) used chemical speciation methods identical to those of our own, but did not detect anthanthrene or acepyrene. This work saw acepyrene, but at abnormally high levels due to a matrix interference, so it was not considered further. PAH emissions (202 \leq mol wt \leq 300, wt % basis) from artificial log burning were an average of 1.7 and 2.5 higher than those reported in refs 38 and 42, respectively. These differences could be due to differences in the chemical analysis methods (38) or in artificial log brands and, hence, composition. Data from our sampling also show up to an order of magnitude higher retene concentration than refs 38 and 42. Retene is commonly observed in artificial log aerosols and is a proposed molecular marker of conifer fire (45). This suggests that artificial logs commonly contain a pine resin constituent of varying concentration. By a factor of about 3, we show higher PAH concentrations in the lower mol wt range (\leq 202) than ref 42, whose definition of particle phase is similar.

PAH emission concentration profiles from fireplace combustion of oak wood are documented (38, 39, 42–44) although each cited study covers a different species. The PAH emissions should remain comparable across these angiosperm species because their main lignin pyrolysis products, monomers of sinapyl alcohol (C₁₁H₄O₄), may be linked to PAH formation (46). Particle-phase PAH concentrations for these taxa decrease as mol wt increases, as shown previously with oak burns. PAH concentrations are at least twice those of past investigations (39, 42–43) in which identical chemical analysis methods are used (data are normalized to a common moisture basis). The data of ref 43 contrast with ours and others (39, 42) by not detecting several high mol wt PAHs (indeno[1,2,3-c,d]pyrene, benzo[*g,h,i*]perylene, anthanthrene, dibenz[*a,h*]anthracene, and coronene). In similar contrast, ref 42 did not report detection of coronene.

Wood of *Pinus* sp. is readily available and among the most widely burned. Previously cited investigations (38, 39, 42–44) offer PAH signatures for pine wood combustion emissions. In these studies, loblolly pine (*Pinus taeda*), western pine (*Pinus lambertiana*), ponderosa pine (*Pinus ponderosa*), and pinion pine (*Pinus pinea*) are examined, among other pine genera. The fireplace combustion of pine resulted in greater interstudy variation (by a factor of ~2) of PAH concentrations than for oak. This variation may be due to the large concentration range of flammable resin in the different pine woods tested (and not present in *Quercus* sp.). For example, retene, which is a thermal decomposition product of pinewood resins, is detected in variable quantities over the five cited studies (0.005–0.09 wt %). Emission factors for the select 32 PAHs of this effort are consistently higher than those of others.

Use of PAHs as indicators of PCDD/F TEQ and Total. The ability to identify biomass-specific markers and relate their concentrations to PCDD/F (and other related pollutants) concentrations would aid source apportionment, pollutant

transport, and population exposure studies. Several of these compounds are considered unique markers for wood combustion, distinguishable from other fuel sources as having biomass origins. Levoglucosan (18) and retene (45) have been suggested as markers; the former is a marker of cellulose combustion, and the latter is associated with conifer combustion. Analyses of intercorrelations among non-Log PAHs showed that levoglucosan had a relatively poor correlation with “the heavy 14 PAHs”, averaging $R = 0.32$. Coronene had an average intercorrelation of 0.87, but is not a unique biomass indicator. Retene was observed for the pine and log runs only, but loss of one pine PAH data set and the limited number of runs preclude meaningful analyses.

Comparison of PAH, levoglucosan, and retene compounds with Total PCDD/F concentrations among the non-Log runs showed poor correlations, R : the best is an inverse correlation with levoglucosan (-0.31). HxCbz improves on this estimate, with $R = 0.41$. For PCDD/F TEQ, $R = 0.70$ for pentaphene, 0.64 for benzo[*b*]chrysene, 0.62 for benzo[*ghi*]perylene, and 0.59 for coronene. Levoglucosan retains an inverse correlation, $R = -0.47$.

To explore the effect of two indicators to model the non-Log dataset, multiple linear regression analyses were conducted on the 14 heavy PAHs, levoglucosan, and retene gleaned from the Table 8 compounds to identify the best two-parameter candidate models for predicting PCDD/F TEQ emissions factors (ng TEQ/kg). Models with $R^2 = 0.82$ were found using benzo[*a*]anthracene + benzo[*k*]fluoranthene and benzo[*b*]chrysene + levoglucosan. In all cases, the predictors are significant ($p < 0.05$) and the semipartial correlations (R^2_{sp} , the amount of TEQ variance accounted for solely by variation of the predictor) are > 0.45 . The second model is particularly interesting because the biomass marker levoglucosan, in combination with a PAH, reasonably predicts PCDD/F TEQ for both the pine and oak logs, across both facility types. Similarly, models for total PCDD/F resulted in $R^2 = 0.77$ using benzo[*ghi*]perylene + anthanthrene ($p < 0.005$, $R^2_{sp} > 0.74$) and $R^2 = 0.72$ using levoglucosan + retene. Although the latter model is interesting because both compounds have been implicated as biomass combustion indicators, the levoglucosan term was not statistically significant.

These analyses suggest that biomass combustion indicators, in combination with other nonvolatile PAHs, may provide a means of apportioning observed PCDD/F, both total and TEQ, among biomass and fossil fuel combustion sources. Additional data, including more wood species and different burn conditions, would help confirm this possibility.

Principal Component Analysis. PCDD, PCDF, PAH, and PM emissions were compared to examine similarities and associations between experiments using principal component analysis (PCA). The analysis of homologue fraction (concentration of homologue divided by PCDD or PCDF), the PM-mass-normalized PAH concentration (mg/g), the PCDD and PCDF total and TEQ values, and the PM mass showed, in each run-type case but one (FP-oak), closely paired experiments with one distinctive value (not shown). These distinctive “outliers” confirm the variability in the emission patterns caused by random (e.g., flame condition) [uncontrolled] variables (i.e., not appliance type, fuel type, or procedures). All three FP-oak values were collocated.

The loading plots confirm the regression analyses: strong correlations of PCDD/F total and TEQ with single PAH compounds are not observed. In fact, the first principal component (57% of variation) suggests that PAHs are not associated with PCDD/F measures. This is consistent with the need for oxychlorination reactions to form PCDD/F and oxygen-limited conditions for PAH formation. Only in the second principal component are associations noted.

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Supporting Information Available

The PCDD/F isomer and homologue distributions and PCB, PAH, and other related compound emissions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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