Chemical Characterization of Fine Particle Emissions from the Wood Stove Combustion of Prevalent United States Tree Species

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ABSTRACT

Residential wood combustion is an important contributor to ambient fine particle levels in the United States. About one-half to two-thirds of the residential wood combustion in the United States occurs in wood stoves as opposed to fireplaces. Thus, any differences between these two sources must be accounted for in chemical mass balance receptor models which attempt to determine the contribution of wood smoke sources to ambient fine particle samples. To fully characterize the fine particle emissions from wood stoves and compare the emissions profiles to those determined from previous fireplace experiments, a series of source tests were conducted on the burning of the most prevalent U.S. tree species in wood stoves. The catalyst-equipped wood stove chosen for these tests was operated under both noncatalytic and catalytic conditions to assess the effects of the catalyst on fine particle emissions. Analysis of the wood smoke includes fine particle mass emission factors, organic and elemental carbon content, ionic and elemental composition, and detailed organic speciation by GC/MS. Between 60 and 90% of the fine particle mass emissions were attributed to measured chemical species. The fine particle emissions from wood stoves show the same general patterns as those from the fireplace combustion of the same tree species; important differences between hardwood and softwood combustion are seen among the substituted phenols and diterpenoids, and levoglucosan is the most abundant individual organic compound emitted. However, fine particle mass emission factors from wood stoves are significantly lower than those from fireplaces. The elemental carbon content of the fine particle mass is generally higher in wood stove smoke than in fire-

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place smoke, and is even higher when the catalyst was employed. Furthermore, a greater fraction of the organic compounds is identifiable by GC/MS methods in the wood stove smoke vs. the fireplace smoke. These results suggest that differences in the source profiles between wood stove and fireplace combustion merit consideration in source apportionment calculations using organic compounds as tracers.

Key words: wood stove; emissions; particle; PM; wood combustion; source profile; organic speciation; GC/MS; wood combustion; levoglucosan

INTRODUCTION

THE U.S. ENVIRONMENTAL PROTECTION AGENCY (U.S. EPA) emission inventories show that in the year 1995 approximately 12% of nonfugitive dust fine particle emissions in the United States were emitted from wood combustion in fireplaces and wood stoves (U.S. EPA, 1998). In certain local pollution events, more than half of the atmospheric fine particle concentration can be attributed to wood smoke (Schauer and Cass, 2000). A brief calculation using U.S. Census figures on appliance ownership and heating practices (U.S. Census, 1993) combined with state-level Department of Energy (U.S. DOE) data on wood consumption (U.S. DOE, 1997) suggest that the amount of wood burned residentially is divided almost equally between wood stoves and fireplaces. Other estimates indicate that as much as 72% of residential wood combustion occurs in wood stoves vs. fireplaces (U.S. EPA, 1990). Therefore, the particulate emissions from wood stoves, and any significant differences between the emissions from wood stoves and fireplaces, should be accounted for in regional control strategies aimed at residential wood combustion.

Source-apportionment techniques that utilize chemical mass balance receptor models can compute the contributions from the primary particle emission sources to a particular ambient fine particle sample (Watson, 1984; Schauer *et al.*, 1996; Schauer and Cass, 2000). These methods require a detailed chemical characterization of the fine particle mass emitted from each pollution source, which can then be compared to the chemical composition of an ambient sample. Nonmineral potassium and "contemporary" carbon have been suggested as a chemical tracers for wood smoke (Currie *et al.*, 1994; Sheffield *et al.*, 1994; Echalar *et al.*, 1995), but since these tracers are also emitted by other major sources such as meat cooking (Schauer *et al.*, 1999) and refuse incineration (Olmez *et al.*, 1988; Sheffield *et al.*, 1994), they cannot be used as unique wood smoke tracers in mass balance calculations. However, the particle-phase organic compounds emitted from wood combustion include numerous unique chemical tracers for wood smoke that have

previously been used in receptor modeling calculations (Schauer *et al.*, 1996; Schauer and Cass, 2000).

Several previous studies of wood stove emissions have measured the emission factors for fine particle mass as well as for certain organic compound classes such as PAH, dioxins, and phenolic compounds (Hall and DeAngelis, 1980; Burnet *et al.*, 1986; Hawthorne *et al.*, 1989; McCrillis and Burnet, 1990; McCrillis *et al.*, 1992; Vikelsoe *et al.*, 1994; Skreiberg *et al.*, 1997; McDonald *et al.*, 2000). The current study focuses on the wood stove combustion of the five most prevalent tree species in the United States. In addition to fine particle mass emissions, ionic and elemental composition, and carbon content, this work provides a detailed organic speciation profile that includes over 250 individual organic compounds. Since the same five wood types burned in the wood stove were also burned in previous studies of fireplace emissions (Fine *et al.*, 2001, 2002, 2004), a direct comparison of the fine particle emission profiles from the two different combustion appliances is possible.

In 1988, the U.S. EPA established New Source Performance Standards (NSPS), which required that all new wood stoves sold are certified to meet certain particulate emission limits by 1992 (Federal Register, 1988). Manufacturers responded by including a catalytic element in their wood stove designs or by designing high-efficiency wood stoves that reduce emissions by careful control of air flow and temperature. Current estimates indicate that about 40% of the new certifiable designs in use are catalytic stoves and 60% are noncatalytic high-efficiency stoves (Houck *et al.*, 1998). However, due to the long lifetime of these appliances, only 11% of the wood stoves in use are EPA certified as of the year 1997 (Houck *et al.*, 1998). For this reason, the goal of this study is to investigate the emissions from a more common conventional technology noncertified wood stove. Since all new stoves must be certified, a catalyst-equipped wood stove was acquired which allowed for operation in a noncatalytic mode, thus simulating a traditional wood stove with no emissions control technology. For two wood types, additional catalytic mode experiments were conducted by operating the same stove in its catalytic configuration.

EXPERIMENTAL METHODS

Source tests

A Vermont Castings Encore Model #2190 (CFM Corp., Mississauga, ON, Canada) catalyst-equipped wood stove was selected for the source tests, and installed according to manufacturer specifications. The medium-sized stove, with an approximately 2.7 ft^3 (0.076 m^3) fire-box, includes a primary air control lever to regulate stove temperature and a damper which directs flow through the catalyst. In accordance with the manufacturer's Owner's Guide, the air control was adjusted during the tests to maintain a stovetop temperature between 500–600°F (260–316°C) as measured by a surface thermometer. For the five noncatalytic mode tests, the flow was never directed through the catalytic element to simulate a traditional wood stove without emissions control technology. Two additional tests were conducted in catalytic-mode according to the Owner's Guide, which directs the user to close the damper and engage the catalyst only after the stovetop temperature reaches 450°F (232°C). The catalytic element is a "honeycomb" ceramic coated with a catalytic material (unspecified by manufacturer, but usually palladium or platinum) designed to lower the combustion temperature of the smoke and thus allow for secondary combustion of smoke material. The primary intent is to increase heating efficiency while reducing volatile organic compound, CO, and particulate emissions. Catalytic elements in wood stoves degrade over time, and typically last between 2 and 6 years. The catalyst used in these test was new, but catalyst degradation may have implications for emissions profiles if the catalytic elements are not replaced appropriately.

The methodology for tree species selection is described in detail in a previous paper (Fine *et al.*, 2001). Briefly, state-level residential wood combustion activity from the U.S. DOE (1997) was combined with state-by-state forestry surveys (U.S. FS, 1998) to compile a list of the most available tree species in the United States. The top five nationally available tree species were chosen for combustion in the wood stove, and are listed in Table 1 along with their scientific names, geographical ranges, and moisture contents. Two tree species, Douglas fir and white oak, were also burned under catalytic conditions. The wood burned came from the same wood samples collected for previous fireplace emissions testing. However, due to a 6-month time lag, the moisture contents of the wood burned in the wood stove were less than those for the same wood type burned in the previous fireplace tests (Fine *et al.*, 2001, 2002, 2004). Methods for determining moisture content have also been described previously (Fine *et al.*, 2001).

The wood was cut into logs of 6–12 inches (15–30 cm) in length, with diameters between 3 and 5 inches (7–13 cm). Fires were ignited with four to six pieces of crumpled newspaper and small kindling pieces cut from the same wood being burned. The stove doors were left open for a few minutes until the fire was well established. Burn times ranged between 112 and 148 min, and between 3 and 4.5 kg of wood was burned per test. Particle sampling began immediately prior to ignition and was ended when particle-sizing instrumentation (Differential Mobility Analyzer and Condensation Particle Counter, TSI, Inc., Shoreview, MN) showed few additional particles being emitted, typically occurring 10 to 20 min after the fire began smoldering with no visible flames. Smoke samples were taken through a port in the stove flue located approximately 3 m above the wood stove.

The same advanced source sampling system used for the previous fireplace emissions studies was utilized for

Table 1. United States tree species selected for wood stove combustion tests.

Tree species	Scientific name	Moisture content of tested wood (dry basis)	U.S. range	National availability ranking
Red Maple	*Acer rubrum*	9%	Entire Eastern U.S.	1
Loblolly Pine	*Pinus taeda*	8%	From New Jersey to Texas including entire Southeastern U.S.	2
Douglas Fir[a]	*Pseudotsuga menziesii*	10%	Western U.S. mountain ranges including Cascades, Sierras, and Rockies	3
White Oak[a]	*Quercus alba*	14%	Entire Eastern U.S. west to S. Minnesota and south to E. Texas	4
Sugar Maple	*Acer saccharum*	13%	Northeastern and Midwestern U.S. south to Missouri north to Minnesota	5

[a]Species tested under both noncatalytic and catalytic conditions.

the wood stove tests. A detailed description of the configuration is provided (see Fine *et al.*, 2001). The dilution source sampler, developed by Hildemann *et al.* (1989), dilutes hot stack emissions with a 25- to 45-fold excess of activated carbon-filtered and HEPA-filtered air. After sufficient residence time and cooling, organic vapors condense onto preexisting particles yielding a more accurate representation of the partitioning of organic compounds between the gas and particle phases under atmospheric temperatures and concentrations. The temperature of the dilution air will affect the partitioning of semivolatile species between the particle and gas phases. During these tests, the temperature of the dilution air averaged about 30°C. This is somewhat warmer than actual ambient conditions in cooler climates and during cooler seasons. Therefore, the results may be more applicable to warmer areas where wood stoves are in use. However, the nonvolatile particle components, which are those used most often in source apportionment calculations, should not be affected by the dilution air conditions.

Smoke samples are withdrawn from the dilution source sampler through an array of AIHL-design cyclone separators (John and Reischel, 1980) operated at the nominal flow required to achieve a 2.5-μm size cut. A pair of Teflon filters collects fine particle samples which are analyzed for gravimetric mass, ionic content by ion chromatography (IC) (Mueller *et al.*, 1978), and elemental composition by X-ray fluorescence (XRF) (Dzubay, 1977). Several quartz fiber filters (47 mm diameter, Pallflex tissue quartz 2500 QAO) collect samples which are analyzed for elemental and organic carbon (EC/OC) by thermal evolution/optical transmission methods (Birch and Cary, 1996) as well as individual organic compound speciation by gas chromatography/mass spectrometry (GC/MS).

Organic chemical analyses

Organic compound speciation of the wood stove samples was accomplished with the procedures developed by Mazurek *et al.* (1987) and Rogge *et al.* (1991). The methods are the same as those used for the previous fireplace emissions testing, and are described in a paper concerning those tests (Fine *et al.*, 2001). In short, quartz fiber filters containing fine particle samples were spiked with a suite of deuterated internal recovery standards. Solvent extractions were performed by mild sonication twice in hexane (Fischer Optima Grade) and then three times in a benzene/isopropanol mixture (2:1) (benzene: E&M Scientific, Gibbstown, NJ; isopropanol: Burdick & Jackson, Muskegon, MI). Extracts were filtered, combined, and reduced to a nominal volume of 1 mL. The concentrated extracts were then split into two separate volumes, one

of which was then derivatized with diazomethane to convert organic acids to their methyl ester analogs. After further volume reduction, the derivatized and underivatized sample fractions were analyzed by GC/MS on a Hewlett-Packard GC/MSD (GC model 6890, MSD model 5972) using a 30 m × 0.25-mm diameter HP-5MS capillary column (Hewlett-Packard, Greely, CO). The GC is operated from 65 to 300°C, with a heating rate of 5°C min^{-1}, and the MSD uses 70 eV ionization energy and HP Chemstation data acquisition. A coinjection standard 1-phenyldodecane is used to normalize overall instrument response across all sample and standard runs. Hundreds of authentic standards have been prepared for the positive identification and quantification of many of the organic compounds found in the smoke from wood combustion. When quantitative standards cannot be obtained for a given compound, nonquantitative secondary standards (compounds which are not be commercially available in pure form but have been identified in other standards or samples) are sometimes used for identification and the responses of other compounds with similar polarities, retention times, and degrees of fragmentation are used for quantification. Interpretation of mass spectra and mass spectral libraries are also used to aid in identification.

RESULTS AND DISCUSSION

Emission factors for fine particle mass from all seven wood stove source tests, including two catalytic tests, are listed in Table 2. Emission factors ranged between 0.88 and 3.4 g fine particulate per kg of wood burned with a noncatalytic wood stove average of 1.8 g kg^{-1} wood burned. While the use of the catalytic element reduced the fine particle emission factor of white oak from 3.4 to 2.2 g kg^{-1} wood burned, it did not change the fine particle emission factor from Douglas fir. It has been reported that the large majority of fine particle mass emitted from wood stoves occurs in the start-up phase (Hueglin *et al.*, 1997), a result supported by preliminary data from our particle sizing instrumentation. In the catalytic-mode tests, the catalyst was not engaged until after the stove had reached the prescribed operating temperature, which occurred between 30 and 45 min after ignition. It is not surprising that the catalyst does not have a larger effect on fine particle mass emissions, since most of the fine particle mass was most likely emitted prior to catalytic operation. Fine particle mass emission factors from wood stoves depend on many factors including burn rate, firebox size, stove type, fuel type, and fuel moisture content (Hall and DeAngelis, 1980; Burnet *et al.*, 1986; McDonald *et al.*, 2000). While some estimates of fine particle emission factors are comparable to our results,

Table 2. Fine particle mass emission factors and chemical composition from wood stove combustion.

	Hardwoods				Softwoods		
	Red Maple	White Oak	White Oak	Sugar Maple	Loblolly Pine	Douglas Fir	Douglas Fir
Catalytic red engaged	no	no	yes	no	no	no	yes
Fine particle mass (g kg^{-1} wood burned)	0.88 ± 0.16	3.4 ± 0.5	2.2 ± 0.4	1.4 ± 0.2	2.0 ± 0.3	1.1 ± 0.2	1.2 ± 0.2
Elemental and organic carbon (Wt % of fine particle mass)							
Organic carbon (OC)	59.4 ± 7.1	55.4 ± 3.2	55.1 ± 3.6	51.2 ± 3.1	43.6 ± 4.6	77.8 ± 7.8	64.7 ± 6.0
Elemental carbon (EC)	22.8 ± 2.8	3.3 ± 0.3	10.4 ± 0.8	5.8 ± 0.5	13.4 ± 1.5	7.6 ± 0.1	21.9 ± 2.1
Ionic species (Wt % of fine particle mass)							
Chloride	1.32 ± 0.14	0.39 ± 0.02	0.48 ± 0.03	0.34 ± 0.02	0.35 ± 0.04	0.32 ± 0.05	0.26 ± 0.04
Nitrate	0.73 ± 0.10	0.38 ± 0.02	0.52 ± 0.03	0.43 ± 0.03	0.19 ± 0.05	0.42 ± 0.07	0.24 ± 0.05
Sulfate	0.55 ± 0.07	0.97 ± 0.03	1.37 ± 0.06	0.33 ± 0.03	0.18 ± 0.04	0.37 ± 0.06	0.27 ± 0.04
Ammonium	0.24 ± 0.03	0.05 ± 0.01	0.06 ± 0.01	0.14 ± 0.01	0.27 ± 0.03	<0.030	0.16 ± 0.02
Elemental species (Wt % of fine particle mass)							
Silicon	0.130 ± 0.014	0.0071 ± 0.0012	0.068 ± 0.004	0.034 ± 0.003	0.192 ± 0.018	0.200 ± 0.017	0.146 ± 0.012
Sulfur	0.169 ± 0.018	0.236 ± 0.006	0.508 ± 0.020	0.149 ± 0.005	0.099 ± 0.010	0.141 ± 0.013	0.121 ± 0.010
Phosphorus	<0.007	<0.003	<0.007	<0.005	<0.005	0.021 ± 0.003	0.013 ± 0.002
Chlorine	0.839 ± 0.089	0.278 ± 0.009	0.488 ± 0.022	0.366 ± 0.013	0.184 ± 0.017	0.190 ± 0.018	0.199 ± 0.016
Potassium	1.680 ± 0.180	1.514 ± 0.038	2.740 ± 0.100	1.014 ± 0.031	0.458 ± 0.041	1.171 ± 0.099	0.621 ± 0.047
Copper	<0.001	<0.001	0.0018 ± 0.0003	<0.001	<0.001	0.0016 ± 0.0004	<0.001
Zinc	0.047 ± 0.005	0.0055 ± 0.0005	0.014 ± 0.001	0.053 ± 0.002	0.048 ± 0.001	0.016 ± 0.002	0.0094 ± 0.0016
Manganese	<0.002	<0.001	<0.002	<0.002	<0.001	0.0026 ± 0.0007	<0.002
Bromine	0.0050 ± 0.0010	0.0014 ± 0.0003	0.0032 ± 0.0005	0.0042 ± 0.0004	0.0020 ± 0.0009	0.0036 ± 0.0012	0.0021 ± 0.0009
Rubidium	0.0074 ± 0.0009	0.0009 ± 0.0001	0.0014 ± 0.0003	<0.001	0.0011 ± 0.0003	0.0017 ± 0.0004	<0.001
Strontium	<0.001	<0.001	<0.001	<0.001	<0.001	0.0048 ± 0.0006	0.0021 ± 0.0003
Lead	<0.003	0.0013 ± 0.0004	0.0052 ± 0.0008	0.010 ± 0.001	<0.002	<0.003	<0.003

The following elements were not quantified due to high blank levels: Al, Fe; the following elements were not found at quantities exceeding detection limits: Ag, Ni, Cr, Ti, V, Co, Ga, As, Se, Y, Zr, Mo, Pd, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, U.

ranging from about 1 to 7 g kg^{-1} wood burned (Hall and DeAngelis, 1980; Skreiberg *et al*., 1997; McDonald *et al*., 2000), others are much higher, surpassing 20 g kg^{-1} wood burned (Burnet *et al*., 1986). The lower emission factors observed in this and other studies may be due to the dilution techniques employed, or other differences in testing or sampling procedures. Different wood stove types, configurations, and sizes could also result in differences in emissions patterns. Particle mass emissions factors in the current study may also be lower due to the warmer conditions in Los Angeles leading to less condensation of semivolatile species into the particle phase. The wide uncertainty in fine particle emission factors from wood stoves suggests that chemical mass balance receptor techniques, which do not rely on overall emission factors (i.e., particulate mass emitted per unit of wood burned or unit of time) but instead on relative source profiles (i.e., normalized to mass or organic carbon emitted), may be preferable in determining the impact of wood stoves on ambient fine particle levels. Figure 1 compares fine particle mass emission factors from the combustion of the same tree species in both fireplaces (Fine *et al*., 2001, 2002, 2004) and wood stoves. In general, wood stoves emit considerably less fine particulate matter than fireplaces.

Table 2 also shows that, as was the case with fireplace emissions (Fine *et al*., 2001, 2002, 2004), the fine particle mass emitted is composed primarily of organic compounds with the second largest component being elemental carbon (3–23% of $PM_{2.5}$ mass, 12% on average).

A previous study found an average of 9% of the particle mass emitted from hardwood combustion in wood stoves consisted of EC (McDonald *et al*., 2000). The elemental carbon content of the wood stove emissions is, with the exception of burning loblolly pine, generally higher than the corresponding fireplace combustion test. Furthermore, the use of the catalyst tended to increase elemental carbon emissions. The further pyrolysis of organic compounds during catalytic secondary combustion may produce more elemental carbon. The remaining emission factors in Table 2 are comparable to those determined from the fireplace tests of these wood types. Potassium, often used as a wood smoke marker, was the most abundant element measured by XRF, but still exhibits a significant degree of variability among different wood types as was found in the fireplace tests (Fine *et al*., 2001, 2002, 2004).

The over 250 organic compounds listed in Table 3 provide a rich source of potential wood smoke markers. These compounds can be volatilized molecules of the original naturally occurring compounds in the wood that recondense into the particle phase or alternatively, chemical products of pyrolysis during combustion. Figures 2 and 3 depict an organic compound mass balance of the wood stove emissions. The total organic compound mass was estimated by multiplying the organic carbon content by a factor of 1.4 to account for the additional mass of primarily hydrogen and oxygen present in the molecules (Gray *et al*., 1986). Each compound class is the sum of quantified organic compounds as determined by GC/MS.
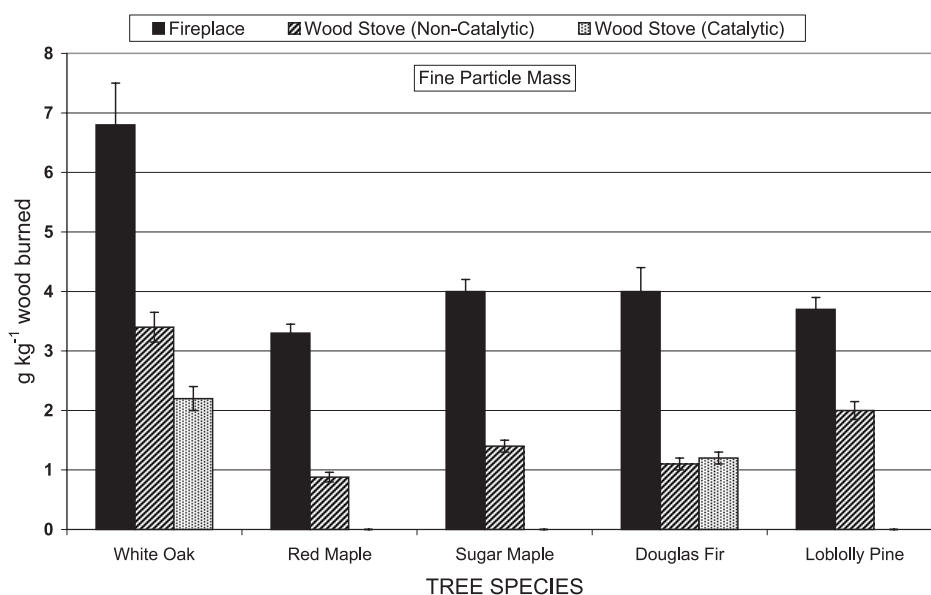

Figure 1.   Comparison of fine particle mass emission factors from the combustion of U.S. tree species in a fireplaces, a non-catalytic wood stove, and a catalytic wood stove.

Table 3. Detailed speciation of fine particle organic compounds emitted from wood stoves.

	Hardwoods				Softwoods			
Compound (mg g⁻¹ OC)	White Oak	White Oak (catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (catalyst)	Loblolly Pine	Notes

$Compound\ (mg\ g^{-1}\ OC)$

	White Oak	White Oak (catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (catalyst)	Loblolly Pine	Notes
n-Alkanes								
n-Heptadecane	—	—	—	—	0.021	0.013	—	b
n-Octadecane	—	—	—	—	0.017	—	—	a
n-Nonadecane	0.020	0.044	0.032	0.056	0.087	0.109	—	b
n-Eicosane	0.073	0.092	0.076	0.122	0.064	0.042	0.038	a
n-Heneicosane	0.108	0.126	0.114	0.275	0.210	0.207	0.071	b
n-Docosane	0.173	0.164	0.110	0.160	0.141	0.225	0.107	a
n-Tricosane	0.184	0.180	0.090	0.216	0.136	0.309	0.132	b
n-Tetracosane	0.139	0.203	0.054	0.160	0.067	0.132	0.063	a
n-Pentacosane	0.169	0.221	0.085	0.108	0.052	0.140	0.059	b
n-Hexacosane	0.059	0.130	0.035	0.192	0.028	0.048	0.036	b
n-Heptacosane	e	e	e	e	e	e	e	b
n-Octacosane	0.023	0.052	0.034	0.025	e	e	0.019	a
n-Nonacosane	0.024	0.067	0.028	—	0.008	0.009	0.021	b
n-Alkenes								
1-Eicosene	0.165	0.373	0.259	0.263	0.245	0.115	—	b
1-Heneicosene	0.116	0.145	0.144	0.283	0.201	0.234	0.047	b
1-Docosene	0.590	0.455	0.240	0.297	0.410	0.977	0.323	b
1-Tricosene	0.317	0.209	0.065	0.195	0.063	0.132	0.059	b
1-Tetracosene	0.541	0.375	0.086	0.590	0.193	0.686	0.185	b
1-Pentacosene	1.314	0.862	0.094	0.106	0.040	0.169	—	b
1-Hexacosene	0.115	0.083	—	0.662	0.054	0.132	—	b
1-Heptacosene	0.697	0.488	—	0.966	e	0.190	0.099	b
n-Alcohols								
n-Octadecanol	—	0.173	—	—	—	—	—	a
n-Nonadecanol	—	0.072	—	—	—	—	—	a
n-Eicosanol	0.851	0.730	0.131	0.045	—	—	—	a
n-Alkanals								
n-Heneicosanal	0.131	0.101	—	—	—	—	—	b
n-Docosanal	0.286	0.247	0.068	0.098	—	0.042	—	b
n-Tricosanal	0.276	0.159	0.102	e	—	0.047	—	b
n-Tetracosanal	0.117	0.101	—	0.188	—	0.035	—	b
n-Pentacosanal	0.047	—	—	—	—	—	—	b
n-Alkanoic acids								
n-Octanoic acid	0.104	0.106	0.122	0.124	0.162	0.131	0.197	a,d
n-Nonanoic acid	0.045	0.054	+	+	0.079	0.067	0.109	b,d
n-Decanoic acid	0.057	0.087	0.074	0.075	0.078	0.080	0.142	a,d
n-Undecanoic acid	0.022	0.050	—	0.017	0.009	0.013	0.012	b,d
n-Dodecanoic acid	0.248	0.307	0.287	0.211	0.414	0.299	0.342	a,d
n-Tridecanoic acid	0.062	0.071	0.069	0.080	0.078	0.221	0.078	b,d
n-Tetradecanoic acid	0.231	0.259	0.325	0.241	0.246	0.440	0.474	a,d
n-Pentadecanoic acid	0.224	0.204	0.201	0.200	0.248	0.788	0.582	b,d
n-Hexadecanoic acid	2.347	1.926	2.456	2.675	1.032	1.966	5.522	a,d
14-Methylhexadecanoic acid	—	—	0.022	0.021	0.382	0.649	0.740	b,d
n-Heptadecanoic acid	0.213	0.224	0.232	0.188	0.127	0.361	0.311	b,d
n-Octadecanoic acid	0.548	0.606	0.965	0.396	0.315	0.531	2.567	a,d

(*continued*)

Table 3.   Detailed speciation of fine particle organic compounds emitted from wood stoves (Cont'd).

	Hardwoods				Softwoods			
Compound (mg g^{-1} OC)	White Oak	White Oak (catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (catalyst)	Loblolly Pine	Notes
16-Methyloctadecanoic acid	—	—	—	—	0.043	0.065	0.049	b,d
n-Nonadecanoic acid	0.087	0.072	0.099	0.080	0.061	0.164	0.108	b,d
n-Eicosanoic acid	0.283	0.223	0.375	0.478	0.293	0.600	0.402	a,d
n-Heneicosanoic acid	0.299	0.235	0.266	0.192	0.056	0.192	0.059	b,d
n-Docasanoic acid	0.899	0.740	1.215	2.252	0.997	3.101	0.341	a,d
n-Tricosanoic acid	0.500	0.445	0.361	0.303	0.066	0.216	0.068	b,d
n-Tetracosanoic acid	2.720	2.171	1.185	1.817	1.505	6.342	0.417	b,d
n-Pentacosanoic acid	0.297	0.223	0.193	0.172	0.024	0.084	0.023	b,d
n-Hexacosanoic acid	2.246	1.187	0.360	0.469	0.210	1.299	0.080	b,d
n-Heptacosanoic acid	0.102	0.067	0.069	0.031	—	—	—	b,d
n-Octacosanoic acid	0.146	0.057	0.088	0.051	—	0.024	—	b,d
				n-Alkenoic acids				
Hexadecenoic acid	0.263	0.163	0.288	0.191	0.274	0.973	0.325	b,d
cis-9-Octadecenoic acid	2.088	2.031	2.488	0.861	0.930	1.302	24.123	a,d
trans-9-Octadecenoic acid	0.358	0.270	0.386	0.145	0.211	0.336	1.971	b,d
2-Octadecenoic acid	0.105	0.067	0.038	0.084	0.088	0.227	—	b,d
9,12-Octadecadienoic acid	2.045	1.946	2.156	1.120	0.774	0.964	2.682	a,d
Nonadecenoic acid	0.096	0.078	0.067	0.096	0.022	0.102	—	b,d
Eicosenoic acids—2 isomers	0.185	0.094	0.188	0.166	0.118	0.377	0.309	b,d
Heneicosenoic acid	0.110	0.073	0.044	0.051	—	0.055	—	b,d
Docosenoic acid	0.318	0.181	0.561	0.453	0.086	0.415	0.022	b,d
Tricosenoic acid	0.077	0.047	—	—	—	—	—	b,d
Tetracosenoic acid	2.123	0.604	0.262	0.315	—	0.132	—	b,d
Pentacosenoic acid	0.294	0.214	0.290	0.232	—	—	—	b,d
Hexacosenoic acid	1.517	0.543	—	0.042	—	—	—	b,d
				Alkanedioic acids				
Hexanedioic acid	0.269	0.230	0.204	0.302	0.147	0.223	0.317	a,d
Heptanedioic acid	0.062	0.088	0.178	0.134	0.062	0.070	0.155	a,d
Octanedioic acid	0.119	0.130	0.211	0.329	0.143	0.220	0.350	a,d
Nonanedioic acid	0.305	0.263	0.314	0.637	0.302	0.625	0.749	b,d
Decanedioic acid	0.097	0.102	0.053	0.106	0.044	0.095	0.113	a,d
Hexadecanedioic acid	0.277	0.212	0.298	0.317	0.913	3.559	0.303	b,d
Octadecanedioic acid	0.170	0.132	0.110	0.059	0.209	0.751	—	b,d
Eicosanedioic acid	0.124	0.113	0.081	0.058	0.094	0.254	0.040	b,d
Docosanedioic acid	0.081	0.109	0.343	0.046	0.022	0.133	—	b,d
Tetracosanedioic acid	0.218	0.235	0.057	0.019	—	—	—	b,d
Pentacosanedioic acid	0.119	0.123	—	—	—	—	—	b,d
Hexacosanedioic acid	0.298	0.192	—	—	—	—	—	b,d
Heptacosanedioic acid	0.104	0.067	—	—	—	—	—	b,d
				Methyl alkanoates				
Methyl hexadecanoate	0.103	0.132	0.085	0.200	0.120	0.079	0.180	a
Methyl 14-methylhexadecanoate	—	—	—	—	—	0.021	—	b
Methyl heptadecanoate	0.014	0.014	0.013	0.019	0.021	0.020	—	b
Methyl octadecanoate	0.030	0.029	0.015	0.033	0.025	0.013	0.047	a
Methyl nonadecanoate	0.016	0.012	—	0.010	0.006	0.005		b
Methyl eicosanoate	0.027	0.025	0.008	0.109	0.014	0.012	0.023	b
Methyl heneicosanoate	0.027	0.035	0.009	0.028	—	—	0.015	b

Table 3. Detailed speciation of fine particle organic compounds emitted from wood stoves (Cont'd).

	Hardwoods				Softwoods			
Compound (mg g⁻¹ OC)	White Oak	White Oak (catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (catalyst)	Loblolly Pine	Notes
Methyl docosanoate	0.079	0.091	0.026	0.948	0.029	0.087	0.024	b
Methyl tricosanoate	0.071	0.071	0.016	0.045	—	—	0.016	b
Methyl tetracosanoate	0.365	0.341	0.077	0.754	0.028	0.132	0.022	b
Methyl pentacosanoate	0.035	0.033	—	0.018	—	—	—	b
Methyl hexacosanoate	0.192	0.166	0.008	0.107	0.005	0.016	0.006	b
Methyl heptacosanoate	0.019	0.017	—	—	—	—	—	b
				Ethyl alkanoates				
Ethyl docosanoate	—	—	—	—	0.024	0.141	—	b
Ethyl tetracosanoate	—	—	—	—	0.018	0.179	—	b
				Methyl alkenoates				
Methyl *cis*-9-octadecenoate	0.093	0.062	0.038	0.078	0.032	0.030	0.434	a
Methyl 9, 12-octadecadienoate	0.055	0.009	0.037	—	0.033	0.041	—	b
Methyl eicosenoate	—	—	—	0.048	—	—	—	b
Methyl docosenoate	0.055	0.064	—	0.230	—	—	—	b
Methyl tetracosenoate	0.321	0.306	0.042	0.107	—	—	—	b
Methyl hexacosenoate	0.234	0.168	—	—	—	—	—	b
				Guaiacol and substituted guaiacols				
Guaiacol	0.520	0.675	0.699	0.448	0.401	0.231	0.994	a
Eugenol	0.175	0.300	0.333	0.350	0.690	0.278	0.523	a
cis-Iso-eugenol	0.139	0.120	0.102	0.123	0.197	0.052	0.231	a
trans-Iso-eugenol	0.929	0.824	0.476	0.708	0.763	0.397	1.106	b
4-Vinylguaiacol	0.681	0.696	0.593	0.545	0.608	0.263	1.055	b
4-Ethylguaiacol	0.151	0.133	0.134	0.150	0.841	0.216	0.463	a
4-Propylguaiacol	0.051	0.049	0.052	0.058	0.336	0.101	0.146	a
Vanillic acid	7.259	8.032	3.688	7.798	8.368	5.463	15.748	a
Methyl vanillate	0.271	0.313	0.084	0.134	0.092	0.073	0.283	a
Homovanillic acid	33.658	24.437	13.658	18.583	14.108	17.220	90.582	a
Methyl homovanillate	0.275	0.185	0.079	0.151	0.091	0.034	0.316	a
Vanillin	7.183	6.008	4.934	5.621	7.577	4.802	9.019	a
Acetovanillone	6.414	4.376	1.884	3.773	3.919	2.000	7.423	a
Propiovanillone	2.514	1.791	0.816	1.537	2.203	0.889	4.596	b
Guaiacyl acetone	11.888	7.719	3.654	6.804	15.223	9.835	15.075	b
Coniferyl aldehyde	31.410	31.229	33.795	40.325	18.469	27.850	44.690	a
				Syringol and substituted syringols				
Syringol	2.657	2.746	2.305	1.829	0.252	0.040	0.086	a
4-Ethylsyringol	7.972	5.148	2.318	2.228	0.964	0.183	0.091	b
4-Propylsyringol	4.746	2.764	0.951	2.083	0.720	0.072	0.075	b
Methoxyeugenol	11.854	5.952	3.260	5.781	0.731	0.076	0.144	b
cis-Methoxy-iso-eugenol	7.473	2.306	0.086	1.791	0.350	0.178	0.716	b
trans-Methoxy-iso-eugenol	23.704	6.175	2.442	4.866	0.057	0.032	0.216	b
Syringic acid	6.061	4.708	4.055	5.762	—	—	—	a
Syringaldehyde	47.108	41.371	49.557	57.058	10.736	5.375	6.508	a
Acetosyringone	16.408	12.146	13.687	15.513	2.905	1.655	1.920	a
Syringyl acetone	49.293	31.728	28.232	34.752	3.699	1.627	3.311	b

(*continued*)

Table 3. Detailed speciation of fine particle organic compounds emitted from wood stoves (Cont'd).

Compound (mg g⁻¹ OC)	Hardwoods				Softwoods			
	White Oak	White Oak (catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (catalyst)	Loblolly Pine	Notes
Propionyl syringol	3.310	2.507	3.061	3.228	0.828	0.376	0.368	b
Sinapyl aldehyde	12.411	11.828	16.065	14.369	0.234	0.655	0.806	a
				Other substituted benzenes and phenols				
1,2-Benzenediol (pyrocatechol)	29.460	12.018	3.619	5.501	5.810	2.172	5.946	b
1,4-Benzenediol (hydroquinone)	1.434	3.641	1.207	3.180	0.691	0.522	1.067	a
1,3-Benzenediol (resorcinol)	22.141	7.721	3.822	6.814	3.134	0.987	4.866	a
Methyl benzenediols	18.990	9.366	2.600	4.705	3.921	1.579	5.808	b
Methoxybenzenediols	15.815	9.469	3.488	3.046	0.362	0.161	0.665	c
Hydroxybenzaldehydes	3.937	3.929	1.660	2.957	1.255	0.708	4.025	a
Methyl hydroxybenzoates	0.498	0.362	0.096	0.187	0.088	0.022	0.138	b
Trimethoxybenzenes	6.147	4.578	3.030	2.809	0.553	0.043	0.100	b
3,4,5-Trimethoxybenzoic acid	9.835	8.125	5.876	3.738	8.312	5.875	—	a
Benzoic acid	0.122	0.223	0.230	0.209	0.304	0.220	0.312	a,d
Phenyl acetic acid	0.193	0.185	0.142	0.137	0.080	0.138	0.129	b,d
Phenyl propanoic acid	0.094	0.057	0.020	0.037	0.027	0.038	0.041	b,d
				Dimers and lignans				
Diguaiacyl ethanes (divanillyls)	1.706	0.790	0.409	0.780	1.814	1.715	3.278	b
Syringyl guaiacyl ethane	0.628	2.245	0.142	0.250	—	—	—	b
Disyringyl methane	0.097	0.025	0.021	0.024	—	—	—	b
Disyringyl ethane	0.767	0.242	0.255	0.283	—	—	—	b
Shonanin (2-deoxomatairesinol)	0.289	0.111	0.016	0.025	0.166	0.076	0.328	c
Matairesinol	0.006	—	—	—	—	—	—	c
				PAH and alkyl PAH				
Naphthalene	+	+	+	+	0.066	+	0.063	a
Phenanthrene	0.194	0.272	0.561	0.398	0.963	0.598	0.586	a
Anthracene	0.032	0.045	0.084	0.054	0.140	0.096	0.029	a
3-Methylphenanthrene	0.091	0.062	0.046	0.043	0.058	0.063	0.092	b
2-Methylphenanthrene	0.103	0.073	0.055	0.056	0.083	0.112	0.177	b
Cinnamaldehyde	0.484	0.722	0.937	0.845	1.615	0.466	1.454	b
Benzenetriols	0.181	0.076	0.108	0.130	0.298	0.095	0.359	b
Hydroxyacetophenones	1.040	1.304	0.666	1.090	1.489	1.048	1.745	b
2-Methylanthracene	0.054	0.036	0.025	0.024	0.029	0.033	0.054	a
9-Methylphenanthrene	0.089	0.065	0.047	0.050	0.066	0.072	0.094	b
1-Methylphenanthrene	0.072	0.054	0.036	0.033	0.079	0.154	0.244	a
Phenylnaphthalenes	0.200	0.211	0.144	0.163	0.253	0.719	0.440	b
Dimethyl or ethyl 178 MW PAHs	0.215	0.166	0.098	0.103	0.257	0.579	0.652	a
Fluoranthene	0.562	0.783	0.746	0.706	1.112	2.200	1.260	a
Acephenanthrylene	0.216	0.265	0.261	0.239	0.310	1.035	0.438	b
Pyrene	0.552	0.812	0.823	0.719	1.100	2.559	1.339	a
Methyl 202 MW PAHs	0.325	0.397	0.433	0.381	0.545	1.337	0.883	b
Retene	0.018	0.011	0.008	0.016	1.987	2.594	3.893	a
Benzo[ghi]fluoranthene	0.118	0.248	0.296	0.234	0.385	0.763	0.642	b
Cyclopenta[cd]pyrene	0.100	0.159	0.150	0.086	0.096	0.602	0.212	b
Benz[a]anthracene	0.147	0.272	0.277	0.235	0.351	0.962	0.628	a
Chrysene	0.179	0.322	0.340	0.269	0.393	1.084	0.679	a
Methyl 226 MW PAHs	0.032	0.063	0.067	0.046	0.065	0.192	0.083	b

Table 3. Detailed speciation of fine particle organic compounds emitted from wood stoves (Cont'd).

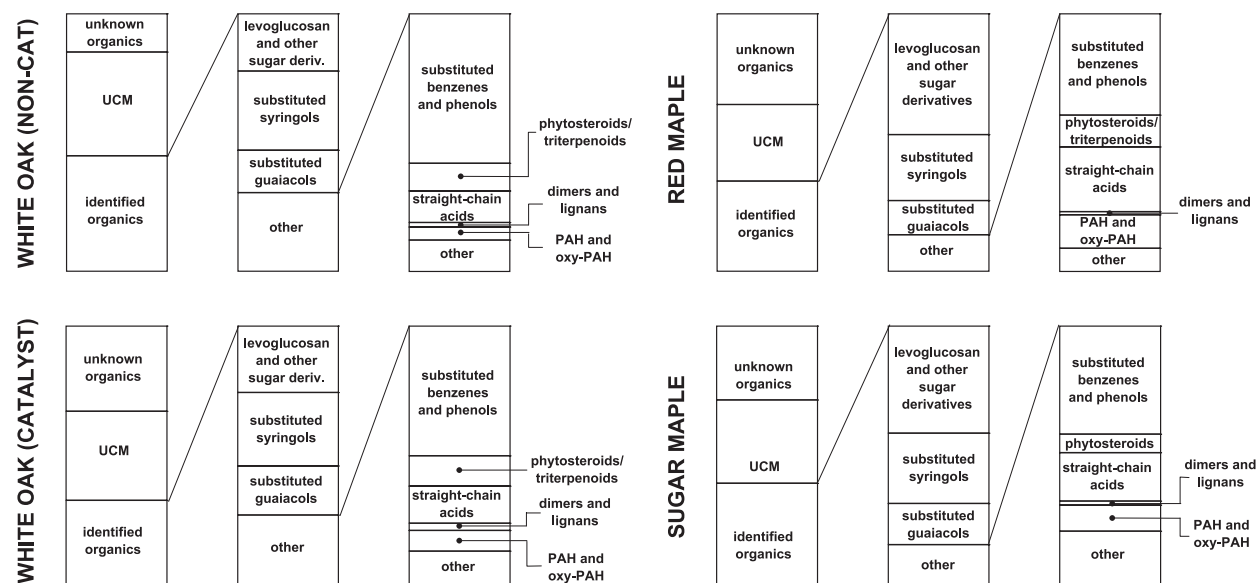|	Hardwoods				Softwoods			
Compound (mg g⁻¹ OC)	White Oak	White Oak (catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (catalyst)	Loblolly Pine	Notes
Benzo[b]fluoranthene	0.087	0.211	0.183	0.184	0.192	0.457	0.437	a
Benzo[k]fluoranthene	0.098	0.227	0.285	0.206	0.276	0.729	0.445	a
Benzo[j]fluoranthene	0.043	0.069	0.074	0.058	0.055	0.220	0.103	b
Benzo[e]pyrene	0.065	0.132	0.162	0.118	0.146	0.351	0.267	b
Benzo[a]pyrene	0.112	0.217	0.253	0.188	0.230	0.673	0.381	a
Perylene	0.017	0.030	0.037	0.027	0.029	0.078	0.057	a
Indeno[1,2,3-cd]fluoranthene	0.023	0.050	0.051	0.051	0.055	0.133	0.109	b
Indeno[1,2,3-cd]pyrene	0.077	0.164	0.191	0.139	0.198	0.450	0.325	a
Benzo[ghi]perylene	0.058	0.119	0.138	0.102	0.122	0.271	0.230	a
Anthanthrene	0.017	0.021	0.020	0.018	0.014	0.037	0.024	b
Dibenz[a,h]anthracene	0.009	0.017	0.016	0.014	0.015	0.044	0.028	a
Coronene	0.153	0.240	0.284	0.198	0.183	0.307	0.519	a
				Oxy-PAH				
1,4-Naphthalenedione	0.032	0.023	0.026	0.019	0.030	0.028	0.024	b
1-Naphthol	0.605	0.294	0.082	0.192	0.152	0.158	0.149	a
2-Naphthol	0.997	0.647	0.239	0.480	0.570	0.574	0.491	a
Methylnaphthols	2.064	1.334	0.553	1.095	1.108	1.192	1.397	b
Methoxynaphthols	0.435	0.265	0.098	0.169	0.469	0.355	0.355	a
Fluorenone	0.639	0.324	0.377	0.274	0.217	0.378	0.324	a
1-H-Phenalen-1-one	0.397	0.427	0.674	0.522	0.523	1.872	0.822	a
9,10-Anthracenedione	0.148	0.184	0.229	0.169	0.255	0.512	0.314	a
Xanthone	0.107	0.148	0.111	0.095	0.108	0.124	0.151	a
Benzanthrone	0.175	0.328	0.439	0.297	0.304	1.180	0.490	a
				Sugar derivatives				
1,4:3,6-Dianhydro-α-D-glucopyranose	2.916	2.329	1.940	1.705	2.486	1.222	2.116	c
Galactosan	6.548	3.535	3.973	2.552	24.170	11.424	11.450	a
Mannosan	5.513	4.131	11.062	12.879	117.654	68.198	46.328	a
Levoglucosan	125.144	107.599	213.162	210.067	408.799	396.778	253.106	a
				Coumarins and flavonoids				
Coumarin	0.187	0.229	0.260	0.198	0.228	0.156	0.259	a
Methoxyhydroxycoumarin	2.418	0.837	—	0.065	—	—	0.097	b
Tetramethoxyisoflavone	1.254	0.428	0.218	0.341	—	—	—	b
				Furans				
5-Hydroxymethyl-2-furaldehyde	9.117	5.409	2.269	7.781	6.549	3.593	8.464	a
5-Acetoxymethyl-2-furaldehyde	0.088	0.086	0.164	0.185	0.204	0.069	0.166	a
Dibenzofuranols	0.447	0.573	0.373	0.472	1.003	1.417	0.981	a
Benzonaphthofurans	0.397	0.565	0.506	0.462	0.621	1.002	0.848	c
				Resin Acids				
Deisopropyldehydroabietic acid	—	—	—	—	0.121	0.122	0.092	b,d
16,17-Bisnordehydroabietic acid	—	—	—	—	0.053	0.062	0.052	b,d
16-Nordehydroabietic acid	—	—	—	—	0.029	0.030	0.056	b,d
Seco-dehydroabietic acids	—	—	—	—	0.113	0.090	0.159	b,d

(*continued*)

Table 3. Detailed speciation of fine particle organic compounds emitted from wood stoves (Cont'd).

| | Hardwoods | | | | Softwoods | | | |
Compound (mg g⁻¹ OC)	White Oak	White Oak (catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (catalyst)	Loblolly Pine	Notes
Pimaric acid	—	—	—	—	0.028	0.057	2.217	a,d
Sandaracopimaric acid	—	—	—	—	0.514	0.775	0.477	b,d
Dehydroabietic acid	+	+	+	+	5.587	4.424	10.807	a,d
8,15-Pimaradien-18-oic acid	—	+	+	—	0.440	0.263	0.194	b,d
Iso-pimaric acid	+	+	+	+	3.012	2.321	0.677	a,d
Levo-pimaric acid	+	+	+	+	0.244	0.304	0.233	b,d
Abietic acid	—	—	—	—	1.670	3.685	2.810	a,d
7-Oxodehydroabietic acid	—	—	—	—	0.321	0.233	0.672	b,d
Abieta-6,8,11,13-tetraen-18-oic acid	+	+	+	+	1.659	1.141	2.537	b,d
Abieta-8,11,13,15-tetraen-18-oic acid	+	+	+	+	0.266	0.251	0.546	b,d
Abieta-6,8,11,13,15-pentaen-18-oic acid	—	—	—	—	0.146	0.138	0.310	b,d
7-Oxo-abieta-8,11,13,15-tetraen-18-oic acid	—	—	—	—	0.022	0.018	0.057	b,d
Other Diterpenoids								
19-Norabieta-8,11,13-triene	—	—	—	—	0.032	0.021	0.037	b
18-Norabieta-8,11,13-triene	—	—	—	—	0.049	0.030	0.050	a
19-Norabieta-4,8,11,13-tetraene	—	—	—	—	0.486	0.262	0.290	b
18-Norabieta-4(19),8,11,13-tetraene	—	—	—	—	0.173	0.104	0.131	b
Dehydroabietane	—	—	—	—	0.022	0.008	—	c
Methyl deisopropyldehydroabietate	—	—	—	—	0.006	—	0.018	c
Pimarinal	—	—	—	—	—	—	0.047	c
Methyl 8,15-pimaradien-18-oate	—	—	—	—	0.018	0.018	—	c
Methyl iso-pimarate	—	—	—	—	0.016	0.034	—	a
Methyl 16,17-bisnordehydroabietate	—	—	—	—	0.010	0.011	0.022	c
Dehydroabietal	—	—	—	—	0.037	0.033	0.018	c
Methyl 6,8,11,13-abietatetraen-18-oate	—	—	—	—	0.158	0.181	0.930	c
Methyl 8,11,13,15-abietatetraen-18-oate	—	—	—	—	0.010	0.010	0.118	c
Methyl dehydroabietate	—	—	—	—	0.164	0.158	0.852	a
Methyl-7-oxodehydroabietate	—	—	—	—	0.054	0.028	0.285	b
Juvabione	—	—	—	—	1.040	0.817	0.497	a
Todomatuic acid (norjuvabione)	—	—	—	—	3.293	0.518	—	b
Phytosteroids								
Stigmasterol	1.101	1.158	1.389	1.470	—	—	0.257	a
β-Sitosterol	5.963	3.513	5.864	3.383	1.276	1.155	1.090	a
Stigmast-4-en-3-one (sitostenone)	1.721	0.678	0.317	0.072	0.085	0.123	0.091	a
Stigmasta-3,5-dien-7-one	0.755	0.452	0.342	0.745	0.238	0.220	0.644	b
Stigmasta-4,6-dien-3-one	0.661	0.432	0.174	0.090	0.049	0.125	0.111	b
Stigmastan-3-ol	0.379	0.267	0.253	0.241	0.131	—	0.096	a
Stigmastan-3-one	1.108	0.649	0.204	0.091	0.034	0.028	0.044	c
Triterpenoids								
Friedelin	8.621	6.942	—	—	—	—	—	a
β-Amyrone	0.068	0.058	0.005	—	—	—	—	b
β-Amyrin	0.144	0.113	0.007	—	—	—	—	a
α-Amyrone	0.059	0.041	0.009	—	—	—	—	b
α-Amyrin	0.104	0.061	0.013	—	—	—	—	a

Table 3. Detailed speciation of fine particle organic compounds emitted from wood stoves (Cont'd).

	Hardwoods				Softwoods			
Compound (mg g^{-1} OC)	White Oak	White Oak (catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (catalyst)	Loblolly Pine	Notes
				Other compounds				
1-Indanone	0.066	0.105	0.141	0.120	0.249	0.070	0.179	a
Methyl indanones	0.028	0.025	0.010	0.030	0.072	0.022	0.113	b
Squalene	0.107	0.106	0.108	0.090	0.136	0.056	0.547	a
α-Tocopherol (vitamin E)	0.772	0.146	—	—	—	—	—	a
β-Tocopherol	0.131	0.025	—	—	—	—	—	b
Unresolved complex mixture (UCM)	563	481	416	452	397	393	664	b

[a]Identification and quantification based on authentic quantitative standard; [b]identification and quantification based on authentic quantitative standards of compounds with similar structures and retention times; [c]identification based on relative retention times, mass spectra interpretation, and/or mass spectra libraries, quantification based on TIC response of authentic quantitative standards for other compounds that have similar retention times, functional groups and degree of fragmentation; [d]Detected and quantified as methyl ester analog in derivatized fraction; [e]detected but not quantified due to coelution of other compounds; —not detected; + detected but not quantified due to comparable levels found in blank samples.

Compared to the previous results for fireplace emissions (Fine *et al*., 2001; 2002; 2004), more of the total organic compound mass was identifiable as either individual organic species or an unresolved complex mixture (UCM) in the wood stove combustion emissions. While the unidentified fraction of organics typically ranged between 30 and 70% for the fireplace tests, only 5 to 35% of the woodstove organic PM emissions were unidentified. UCM appears as an unresolved hump in the GC/MS trace made up of long-chain, highly branched hydrocarbons. It is quantified assuming the same response factors as those determined for alkanes. Wood stove combustion

Figure 2. Organic compound mass balance for the fine particle emissions from the wood stove combustion of U.S. hardwood species.
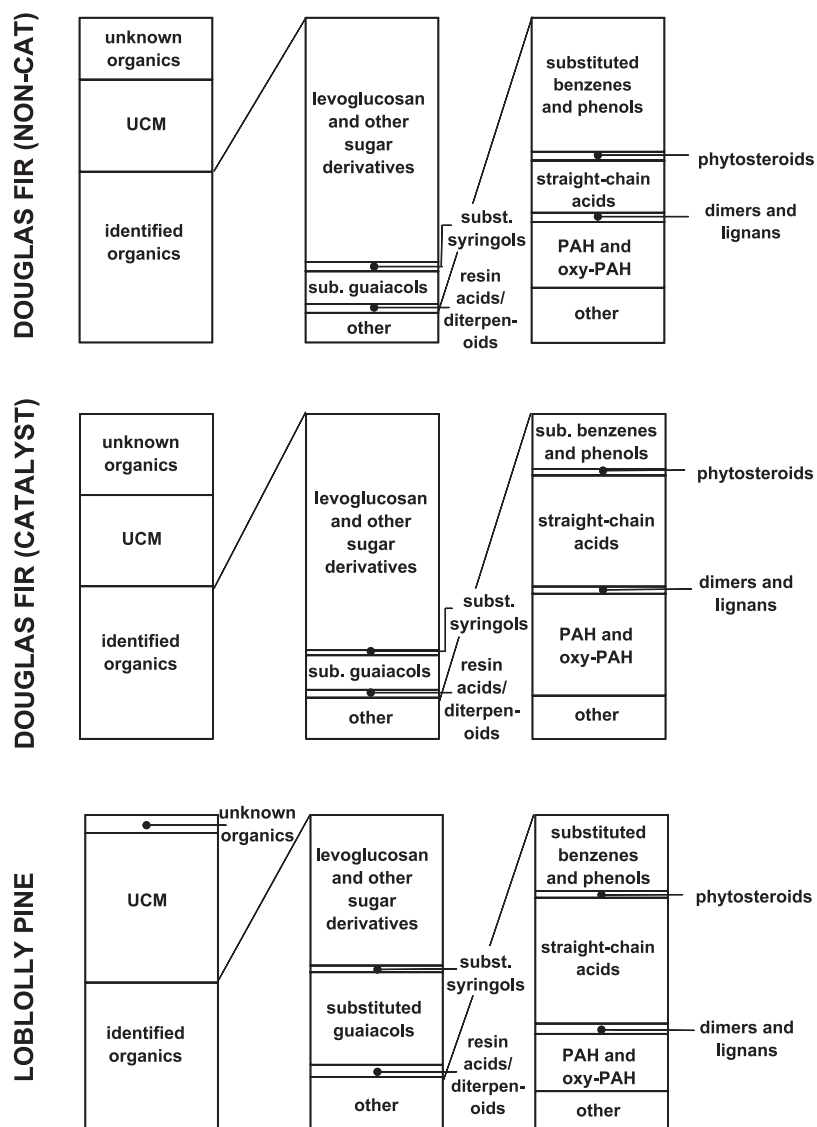
Figure 3. Organic compound mass balance for the fine particle emissions from the wood stove combustion of U.S. softwood species.

involves controlled air intake, which acts to create a richer combustion process with less air, and thus oxygen, available. It is therefore possible that lower quantities of polar organic compounds with a high oxygen content are produced by wood stoves vs. fireplaces. Since some of the highly polar compounds are not identifiable with our methods, it may explain the higher unidentified organic compound fraction in the fireplace tests. Figures 2 and 3 also demonstrate some of the previously reported differences between hardwood and softwood combustion that were also found in the fireplace emissions (Standley and Simoneit, 1990; Fine *et al.*, 2001, 2002, 2004); the hard-

wood smoke contains more substituted syringols than the softwood smoke, and the resin acids and diterpenoids are only present in softwood smoke.

The general qualitative pattern of individual organic compound emissions shown in Table 3 corresponds closely to the results discussed in previous works concerning the same woods burned in a fireplace (Fine *et al.*, 2001, 2002, 2004). The individual organic compounds that were most abundant in the fireplace smoke are also abundant in wood stove smoke. But when normalized to total organic carbon, organic compounds from wood stove combustion are generally emitted at higher relative
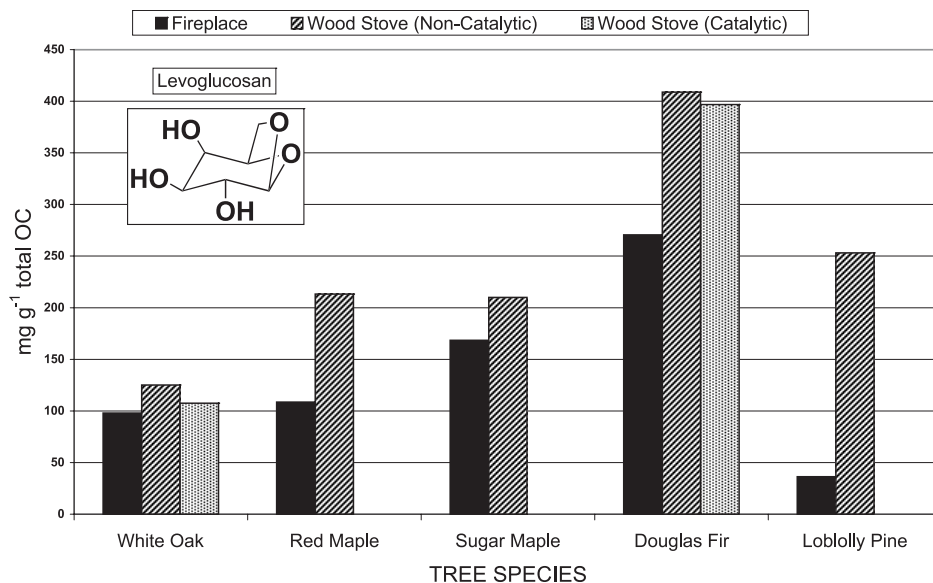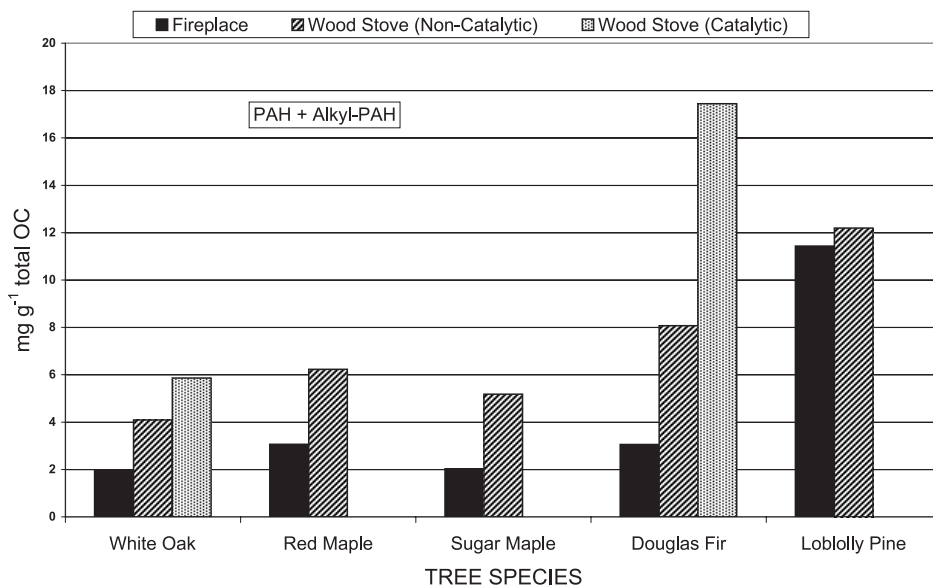
Figure 4. Comparison of fine particle levoglucosan emissions from the combustion of U.S. tree species in a fireplaces, a non-catalytic wood stove, and a catalytic wood stove.

levels than the corresponding fireplace test of the same wood type. The increase is, at least in part, due to the higher unidentified portion of organics in fireplace smoke. Thus, the normalized emission factors are higher from wood stoves whose emissions contain a lower fraction of unidentified compounds. However, since the over-all fine particle mass emission factors per kilogram wood burned are significantly lower for wood stoves, emissions of these compounds on a per kg wood burned basis are still generally lower than the emissions from fireplaces.

Like the fireplace source tests (Fine *et al*., 2004), the triterpenone friedelin was only detected in the smoke

Figure 5. Comparison of fine particle PAH and alkyl-PAH emissions from the combustion of U.S. tree species in a fireplaces, a noncatalytic wood stove, and a catalytic wood stove.

from the combustion of white oak in the catalytic and noncatalytic wood stove emissions. The fraction of total organic carbon quantified as friedelin was higher in the two wood stove tests (8.6 and 6.9 mg g^{-1} organic carbon) than in the corresponding fireplace test (4.4 mg g^{-1} organic carbon). Due to the uniqueness of this compound to white oak combustion, friedelin is a promising candidate as a species-specific wood smoke tracer. Another molecular tracer for wood combustion, levoglucosan (Simoneit *et al*., 1999), was the most abundant individual organic compound emitted in all fireplace and wood stove tests. Figure 4 compares the levoglucosan content of the organic emissions from fireplaces and wood stoves. In general, the levoglucosan content of wood stove emissions is higher than that for fireplace combustion of the same tree species. Across all 22 tree species burned in the fireplace study (Fine *et al*., 2001, 2002, 2004), the average levoglucosan emission factor was 129 $\pm$ 78 mg g^{-1} organic carbon compared to the seven wood stove tests, producing an average of 245 $\pm$ 114 mg g^{-1} organic carbon. If levoglucosan is used as a wood smoke tracer in chemical mass balance receptor models, differences in its emissions between wood stove and fireplace combustion need to be taken into account.

Another important difference between the fireplace, noncatalytic wood stove and catalytic wood stove emissions is seen in the particle-phase emissions of the PAH and alkyl PAH. Figure 5 shows that as a fraction of total organic carbon, more PAH compounds are emitted from wood stoves vs. fireplaces when the same wood type is burned. In addition, the catalytic tests resulted in even higher PAH emissions, most likely for the same reasons that the elemental carbon emissions were higher for the catalytic tests. As discussed above, the additional pyrolysis that occurs in the catalytic bed can further aromatize the natural wood components into PAH.

The differences between the fine particle organic compound emissions from fireplaces and wood stoves should be accounted for in chemical mass balance models that use organic compounds as tracers. It is possible that the contribution to an ambient sample from these two sources cannot be separated by the model calculations due to the similarity of the compounds being emitted. However, one can calculate a weighted composite residential wood combustion source profile based on the wood stove and fireplace usage patterns in a particular region and then use the composite profile for the mass balance calculations.

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REFERENCES

BIRCH, M.E., and CARY, R.A. (1996). Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci. Technol*. **25,** 221.

BURNET, P.G., EDMISTEN, N.G., TIEGS, P.E., HOUCK, J.E., and YODER, R.A. (1986). Particulate, carbon monoxide, and acid emission factors for residential wood burning stoves. *JAPCA* **36,** 1012.

CURRIE, L.A., KLOUDA, G.A., KLINEDINST, D.B., SHEFFIELD, A.E., JULL, A.J.T., DONAHUE, D.J., and CONNOLLY, M.V. (1994). Fossil-mass and bio-mass combustion—C-14 for source identification, chemical tracer development, and model validation. *Nucleic Instrum. Methods Phys. Res B* **92,** 404.

DZUBAY, T.G. (1977). *X-ray Analysis of Environmental Samples*. Ann Arbor, MI: Ann Arbor Science.

ECHALAR, F., GAUDICHET, A., CACHIER, H., and ARTAXO, P. (1995). Aerosol emissions by tropical forest and savanna biomass burning—Characteristic trace-elements and fluxes. *Geophys. Res. Lett*. **22,** 3039.

FEDERAL REGISTER. (1988). *Standards of Performance for New Residential Wood Heaters*, v. 53, p. 5873.

FINE, P.M., CASS, G.R., and SIMONEIT, B.R.T. (2001). Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States. *Environ. Sci. Technol*. **35,** 2665.

FINE, P.M., CASS, G.R., and SIMONEIT, B.R.T. (2002). Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the southern United States. *Environ. Sci. Technol*. **36,** 1442.

FINE, P.M., CASS, G.R., and SIMONEIT, B.R.T. (2004). Chemical characterization of the fine particle emissions from the fireplace combustion of wood types grown in the midwestern and western United States. *Environ. Eng. Sci*. **21**(3), 387.

GRAY, H.A., CASS, G.R., HUNTZICKER, J.J., HEYERDAHL, E.K., and RAU, J.A. (1986). Characteristics of atmospheric organic and elemental carbon particle concentrations in Los-Angeles. *Environ. Sci. Technol*. **20,** 580.

HALL, R.E., and DEANGELIS, D.G. (1980). EPA's research program for controlling residential wood combustion emissions. *JAPCA* **30,** 862.

HAWTHORNE, S.B., KRIEGER, M.S., MILLER, D.J., and MATHIASON, M.B. (1989). Collection and quantitation of methoxylated phenol tracers for atmospheric pollution from residential wood stoves. *Environ. Sci. Technol*. **23,** 470.

HILDEMANN, L.M., CASS, G.R., and MARKOWSKI, G.R. (1989). A dilution stack sampler for collection of organic aerosol emissions: Design, characterization, and field tests. *Aerosol Sci. Technol*. **10,** 193.

HOUCK, J.E., TIEGS, P.E., MCCRILLIS, R.C., KEITHLEY, C., and CROUCH, J. (1998). Air emissions from residential heating: The wood heating option put into environmental perspective. *Proceedings of a U.S. Environmental Protection Agency and Air and Waste Management Association Conference, Emission Inventory: Living in a Global Environment*, pp. 373–384.

HUEGLIN, C., GAEGAUF, C., KUNZEL, S., and BURTSCHER, H. (1997) Characterization of wood combustion particles: Morphology, mobility, and photoelectric activity. *Environ. Sci. Technol*. **31,** 3439.

JOHN, W., and REISCHL, G.J. (1980). A cyclone for size-selective sampling of ambient air. *Air Pollut. Control Assoc*. **30,** 872.

MAZUREK, M.A., SIMONEIT, B.R.T., CASS, G.R., and GRAY, H.A. (1987). Quantitative high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry analyses of carbonaceous fine aerosol particles. *Int. J. Environ. Anal. Chem*. **29,** 119.

MCCRILLIS, R.C., and BURNET, P.G. (1990). Effects of burnrate, wood species, altitude, and stove type on woodstove emissions. *Toxicol. Industr. Health* **6,** 95.

MCCRILLIS, R.C., WATTS, R.R., and WARREN, S.H. (1992). Effects of operating variables on PAH emissions and mutagenicity of emissions from woodstoves. *J. Air Waste Manage. Assoc*. **42,** 691.

MCDONALD, J.D., ZIELINSKA, B., FUJITA, E.M., SAGE-BIEL, J.C., CHOW, J.C., and WATSON, J.G. (2000). Fine particle and gaseous emission rates from residential wood combustion. *Environ. Sci. Technol*. **34,** 2080.

MUELLER, P.K., MENDOZA, B.V., COLLINS, J.C., and WILGUS, E.S. (1978). Application of ion chromatography to the analysis of anions extracted from airborne particulate matter. In E. Sawicki, J.D. Mulik, and E. Wittgenstein, Eds. *Ion Chromatographic Analysis of Environmental Pollutants*. Ann Arbor, MI: Ann Arbor Science, pp. 77–86.

OLMEZ, I., SHEFFIELD, A.E., GORDON, G.E., HOUCK, J.E., PRITCHETT, L.C., COOPER, J.A., DZUBAY, T.G., and BENNETT, R.L. (1988). Compositions of particles from selected sources in Philadelphia for receptor modeling applications. *Air Pollut. Control Assoc*. **38,** 1392.

ROGGE, W.F., HILDEMANN, L.M., MAZUREK, M.A., CASS, G.R., and SIMONEIT, B.R.T. (1991). Sources of fine organic aerosol: 1. Charbroilers and meat cooking operations. *Environ. Sci. Technol*. **25,** 1112.

SCHAUER, J.J., and CASS, G.R. (2000). Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environ. Sci. Technol*. **34,** 1821.

SCHAUER, J.J., KLEEMAN, M.J., CASS, G.R., and SIMONEIT, B.R.T. (1999) Measurement of emissions from air pollution sources. 1. C-1 through C-29 organic compounds from meat charbroiling. *Environ. Sci. Technol*. **33,** 1566.

SCHAUER, J.J., ROGGE, W.F., HILDEMANN, L.M., MAZUREK, M.A., CASS, G.R., and SIMONEIT, B.R.T. (1996). Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos. Environ*. **30,** 3837.

SHEFFIELD, A.E., GORDON, G.E., CURRIE, L.A., and RIEDERER, G.E. (1994). Organic, elemental, and isotopic tracers of air-pollution sources in Albuquerque, NM. *Atmos. Environ*. **28,** 1371.

SIMONEIT, B.R.T., SCHAUER, J.J., NOLTE, C.G., OROS, D.R., ELIAS, V.O., FRASER, M.P., ROGGE, W.F., and CASS, G.R. (1999). Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmos. Environ*. **33,** 173.

SKREIBERG, O., KARLSVIK, E., HUSTAD, J.E., and SONJU, O.K. (1997). Round robin test of a wood stove: The influence of standards, test procedures and calculation procedures on the emission level. *Biomass Bioenergy* **12,** 439.

STANDLEY, L.J., and SIMONEIT B.R.T. (1990). Preliminary correlation of organic molecular tracers in residential wood smoke with the source of fuel. *Atmos. Env*. B-URB **24**(1), 67–73.

U.S. CENSUS. (1993). *American Housing Survey, 1993 AHSN Data*, U.S. Census Bureau. www.census.gov/hhes/www/ahs.html

U.S. DOE. (1997). *State Energy Data Report 1995*. Washington, DC: Energy Information Administration, U.S. Department of Energy.

U.S. EPA. (1998). *National Air Pollutant Emissions Trends Update, 1970–1997*, Research Triangle Park, NC: Office of Air Quality Planning and Standards.

U.S. EPA (1990). *Emissions Inventory of Forty Potential Section 112(k) Pollutants, Appendix A*. Research Triangle Park, NC: U.S. Environmental Protection Agency. (May 21, 1999, A-260).

U.S. FS. (1998). *Forest Inventory and Analysis Database*. U.S. Forest Service, U.S. Department of Agriculture. http://fia.fs.fed.us

VIKELSOE, J., MADSEN, H., and HANSEN, K. (1994). Emissions of dioxins from Danish wood-stoves. *Chemosphere* **29,** 2019–2027.

WATSON, J.G. (1984). Overview of receptor model principles. *JAPCA* **34,** 619.