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Chemical Characterization of Fine Particle Emissions from Fireplace Combustion of Woods Grown in the Northeastern United States

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A series of source tests was conducted to determine the chemical composition of fine particle emissions from the fireplace combustion of six species of woods grown in the northeastern United States: red maple, northern red oak, paper birch, eastern white pine, eastern hemlock, and balsam fir. Results include fine particle emission rates for total mass, organic and elemental carbon, ionic species, elemental species including potassium, and over 250 specific organic compounds. The data are intended for use in source-apportionment studies that utilize particulate organic compounds as source-specific tracers. The cellulose pyrolysis product levoglucosan was quantified in each of the wood smokes studied and is thus a good candidate as a molecular tracer for wood combustion in general. Differences in emission rates of specific substituted phenols and resin acids can be used to distinguish between the smoke produced when burning hardwoods versus softwoods. Certain organic compounds, such as betulin from paper birch combustion and juvabione and dehydrojuvabione from balsam fir combustion, are unique to those species and can potentially be utilized to trace particulate emissions back to a specific geographical region where those individual tree species are used for firewood.

Introduction

Fine particle emissions from the fireplace combustion of wood make a significant contribution to ambient fine particle levels in the United States. Emissions inventories compiled by the U.S. Environmental Protection Agency show that, in 1995, about 12% of nonfugitive dust fine particle emissions in the United States came from residential wood combustion in fireplaces and wood stoves (*1*). Other studies show that during winter months, 20−30% of the ambient fine particle mass concentration often can been attributed to wood smoke (*2, 3*), with more than half of the fine particle concentration contributed by wood smoke on some occasions (*4*). If compliance with the fine particle ambient air quality standards recently promulgated by the U.S. EPA is to be attained, an accurate account of residential wood combustion must be factored into regional air pollution control strategies.

Methods that estimate the contribution of fireplace wood combustion to ambient fine particle levels based on emissions inventory data and atmospheric transport calculations are difficult to apply to specific pollution events that occur on time scales of hours or days. One reason for this is that residential wood-burning activity is difficult to predict as behavior varies greatly between households and from day to day. In addition, emissions inventories even under average-day conditions are uncertain; emissions rates per kilogram of wood burned vary, as will be shown in this paper, by roughly a factor of 5 between different source tests. Additional uncertainties arise from an incomplete knowledge of the amount of wood burned and the type of wood-burning appliance used. Alternative source-apportionment techniques, however, do exist that utilize chemical mass balance receptor models (*3*−*5*) which compute the best-fit linear combination of the chemical species profiles of the primary particle emissions sources in a particular geographic area that is needed to reproduce the chemical composition of ambient fine particle samples. Nonmineral potassium has been suggested as a tracer for wood smoke in receptor models (*6*). But potassium is also emitted by other major sources such as meat cooking (*7*) and refuse incineration (*8, 9*) and thus cannot be used as a unique wood smoke tracer in mass balance calculations. Carbon isotope ratios that resolve "contemporary" carbon from "fossil" carbon have also been used as markers for wood combustion (*9, 10*). But contemporary carbon has other sources that again include food cooking and refuse incineration as well as the abrasion products from leaf surfaces (*11*), the natural rubber content of tire dust, and the contemporary carbon content of paved road dust.

The wide variety of particle-phase organic compounds emitted from wood combustion provides a rich source of possible chemical tracers for wood smoke that have previously been used in receptor modeling calculations (*3, 4*). Data on the organic speciation of the fine particle emissions from wood combustion have been reported previously (*12*−*15*), and significant differences between hardwood and softwood emissions have been found (*16*−*25*). However, if these source-apportionment methods are to be applied at the national scale, detailed fireplace wood combustion source profiles must be determined for all of the important wood types burned in the United States.

This paper is the first of a series that will present the results from an extensive set of source tests conducted to characterize the particulate organic compound emissions from the fireplace combustion of a wide variety of wood species found in the United States. These results will provide valuable information on the variability in wood smoke tracer emission rates for those organic compounds that are currently used in receptor models and will identify additional tracer compounds that are specific to the smoke from individual wood species. The differences in emissions that occur when different woods are burned can possibly be used to resolve ambient fine particle contributions from combustion of specific wood species and, thus, from the specific geographic regions where those species are burned. The present paper documents the organic compound distribution present in the fine particle emissions from important wood species grown in the northeastern United States.

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TABLE 1. Tree Species Ranked in Order of Nationwide Availability for Residential Wood Burning in the United States[a]

national rank	common name	scientific name	availability index
1	**red maple**	***Acer rubrum***	**6.7**
2	loblolly pine	*Pinus taeda*	5.8
3	Douglas fir	*Pseudotsuga menziesii*	4.9
4	white oak	*Quercus alba*	4.5
5	sugar maple	*Acer saccharum*	4.2
6	**northern red oak**	***Quercus rubra***	**4.2**
7	ponderosa pine	*Pinus ponderosa*	3.2
8	yellow poplar	*Liriodendron tulipifera*	2.9
9	black oak	*Quercus velutina*	2.8
10	**eastern white pine**	***Pinus strobus***	**2.8**
11	white ash	*Fraxinus americana*	2.1
12	sweetgum	*Liquidambar styraciflua*	2.1
(13)	(white fir)	*(Abies concolor)*	(2.0)
14	quaking aspen	*Populus tremuloides*	2.0
(15)	(shortleaf pine)	*(Pinus echinata)*	(1.9)
(16)	(chestnut oak)	*(Quercus prinus)*	(1.9)
17	American beech	*Fagus grandifolia*	1.9
18	**eastern hemlock**	***Tsuga canadensis***	**1.9**
19	black cherry	*Prunus serotina*	1.8
20	hickory	*Carya* sp.	1.7
21	slash pine	*Pinus elliottii*	1.2
36	**paper birch**	***Betula papyrifera***	**0.7**
51	**balsam fir**	***Abies balsamea***	**0.5**
88	white spruce	*Picea glauca*	0.2
139	pinyon pine	*Pinus edulis*	0.1

[a] All woods, except those in parentheses, were obtained for our source testing program. Boldface text indicates woods for which source-testing results are presented in this paper that concerns the northeastern United States. Results for all others will be reported in companion papers.

TABLE 2. Northeastern United States Wood Species Selected for Use in This Study

tree species	scientific name	moisture content of tested wood[a] (%)	U.S. range
red maple	*Acer rubrum*	11	entire eastern U.S.
northern red oak	*Quercus rubra*	14	entire eastern U.S. excluding FL
eastern white pine	*Pinus strobus*	11	New England south through Appalachians, northern Midwest
eastern hemlock	*Tsuga canadensis*	30	entire eastern U.S. excluding FL
paper birch	*Betula papyrifera*	9	New England, New York, northern Midwest
balsam fir	*Abies balsamea*	9	New England, New York, northern Midwest

[a] Dry basis.

Experimental Methods

Wood Selection. Identification of the most common wood species burned in residential fireplaces across the United States was accomplished via a brief review of published data. State-by-state information on residential biomass fuel consumption was taken from U.S. Department of Energy reports (*26*) and converted to mass of wood burned for residential home heating per state. U.S. Forest Service inventories (*27*) provided data on the prevalence of specific tree species in existing wood stands in each state. Previous studies have determined that people tend to burn wood that is available in their immediate vicinity (*28*). By apportioning statewide residential wood fuel consumption in proportion to the tree species distribution within the state and then summing the results over the entire United States, a national ranking of the most commonly available wood species for residential combustion was achieved. Table 1 lists the top 21 wood species ordered by an index equal to 100 times the nationwide firewood availability for a particular species divided by the total of all firewood availability in the United States. Since we are not at this time attempting to compile a national wood smoke mass emission inventory, we do not need to know the precise amount of each wood burned. Thus, our calculations do not take into account such factors as the general preference for hardwood over softwood, which woods are commercially sold as fuel, regulating agency guidelines on tree clearance, or intrastate population/tree distributions. Our resulting national list and rankings were used as a guide for wood species selection that ensured the inclusion of the most available wood species within our test program. Twenty-two wood species were chosen for testing including 18 of the top 21 most commonly available wood species in the United States; four additional species were chosen in order to address particular issues. Three wood species in the top 21 were not available at the time of testing and are shown in parentheses in Table 1. Specimens of the selected woods were then collected from both commercial suppliers and forestry research groups across the United States. In every case, experts at these facilities provided us with positive species identification.

The 22 woods chosen for testing (Table 1) were divided into four groups based on the geographical location in which they grow. Some of the species are found across more than one region. Six wood species found primarily in the northeastern United States are examined in detail in the present paper and are listed in Table 2 along with their scientific names and geographic range over which each is found. Also included is the average moisture content of each wood sample tested, determined by a standard oven-drying method in which 1 in. (2.5 cm) thick cross sections from each of two distinct logs were preweighed and then baked in an oven at 103 ± 2 °C until no further weight loss occurred (*29*). The moisture contents of the northeastern U.S. woods tested here ranged from 9% to 30% calculated on a dry basis. Recom-

mended moisture contents for firewood range from 10% to 20%, but the wider range of moisture contents tested here are intended to examine the effect of this parameter on emission rates. The precombustion mass and moisture content of the logs to be burned were measured within a few hours before each fireplace test with the moisture content taken to be the average determined from the two samples.

Source Tests. Each wood species was burned in a single test in a conventional masonry fireplace located in a residential building. Logs were cut into pieces of 6−12 in. (15−30 cm) in length with diameters between 3 and 5 in. (7−13 cm). Fires were started with 7−9 pieces of crumpled newspaper and small kindling pieces cut from the same log type being burned. Burn times ranged between 82 and 136 min with between 5 and 7 kg of wood burned per test. Tests were stopped after the particle sizing instruments showed few particles being emitted; this typically occurred after 10−20 min of a smoldering fire with no visible flames. Smoke samples were taken from the chimney at a point approximately 4 m above the fire.

An advanced source sampling system has been developed that facilitates the measurement of fine particle mass emission rates, particle-phase organic compounds, and fine particle elemental composition (*7, 30*). In this dilution source sampler, hot exhaust emissions are mixed with a 20−30-fold excess of activated carbon- and HEPA-filtered air which, after sufficient residence time, causes those organic vapors that will form particulate matter upon cooling in the atmosphere downwind of a source to instead condense onto preexisting particles in the source exhaust within the dilution sampler itself. The emissions thus can be sampled at near atmospheric temperature and pressure in order to obtain an accurate representation of the partitioning of organic compounds between the gas and particle phases. A dilution ratio of 20−30 was chosen to ensure that sufficient organic mass was collected for organic speciation analysis. Previous characterizations of this sampling system (*30*) suggest that use of dilution ratios higher than 30 would not cause less organic vapor condensation onto existing particles, and thus our dilution ratio is sufficient to achieve accurate gas/particle partitioning.

The samples are withdrawn from the dilution source sampler through AIHL-design cyclone separators (*31*) that are operated at a nominal flow such that fine particles with aerodynamic diameters smaller than 2.5 μm pass through the cyclones along with all gas-phase species. Fine particles are collected with a series of six sampling trains that operate in parallel, each with its own cyclone separator. In the first sampling train, after passing through the cyclone separator, the flow is divided between three filter assemblies. The first contains two quartz fiber filters (47 mm diameter, Pallflex tissue quartz 2500 QAO) operated in series at a nominal flow rate of 5 L/min. These filters are intended for subsequent analysis for organic carbon (OC) and elemental carbon (EC) (*32*) with the backup filter providing information on the organic vapor adsorption artifact. The second filter assembly, operated at a nominal flow rate of 1 L/min, contains a Teflon filter that is used for gravimetric mass determination as well as ion chromatography (IC) (*33*) or X-ray fluorescence (XRF) analysis (*34*). The third filter assembly, operated at a nominal flow rate of 15 L/min contains an additional Teflon filter also used for gravimetric mass, IC, and XRF analyses as needed.

The second sampling train contains an AIHL-design cyclone separator followed by two identical filter assemblies in parallel each consisting of a single quartz fiber filter operated at a nominal flow rate of 10 L/min. The fine-particle-phase emissions collected by the quartz fiber filter are subjected to detailed organics analysis by gas chromatography/mass spectrometry (GC/MS). The third cyclone separator is followed by two identical filter assemblies each consisting of a quartz fiber filter followed by a backup quartz fiber filter. The backup quartz filters can be analyzed to determine which organic gases are adsorbed onto the filters. The remaining three cyclone separators each are followed by two single quartz fiber filters operated in parallel intended to collect additional organic particulate matter mass that may be needed for GC/MS analysis.

Electronic particle sizing instruments also were connected to the residence time chamber of the dilution source sampler during the fireplace source tests in order to obtain particle size distribution measurements. This instrumentation includes a differential mobility analyzer (TSI model 3071) with a TSI model 3760 condensation nuclei counter and a PMS-ASASP-X 32 channel laser optical particle counter, all operated downstream of a 12-L secondary dilution chamber in which particle concentrations are reduced by mixing with bottled zero air.

Organic Chemical Analyses. Extraction of particle-phase organic compounds collected on quartz fiber filters during the source tests follows the procedures established previously by Mazurek et al. (*35*) and Rogge et al. (*36*). Prior to sampling, the quartz fiber filters are baked at 550 °C for a minimum of 12 h to reduce residual carbon levels associated with new filters. Immediately after being sampled, the filters are stored in a freezer at −21 °C until the samples are extracted. Before the quartz fiber filters are extracted, they are spiked with a mix of deuterated internal recovery standards including four deuterated polycyclic aromatic hydrocarbons (PAH), four deuterated alkanes, and three deuterated alkanoic acids, all spanning a wide range of GC retention times. The samples are extracted twice with hexane (Fischer Optima Grade), followed by three successive benzene/2-propanol (2:1) extractions (benzene, E&M Scientific; 2-propanol, Burdick & Jackson). The benzene is re-distilled prior to use in order to reduce impurity levels. Extracts are filtered, combined, and reduced in volume to approximately 1 mL and are split into two separate fractions. One fraction is then derivatized with diazomethane to convert organic acids to their methyl ester analogues, which are more amenable to GC/MS identification and quantification.

Both the derivatized and the underivatized sample fractions are analyzed by GC/MS in ion scan mode on a Hewlett-Packard GC/MSD (GC model 6890, MSD model 5973) using a 30 m × 0.25 mm diameter HP-5MS capillary column (Hewlett-Packard). 1-Phenyldodecane is used as a co-injection standard for all sample extracts and standard runs. The deuterated PAH and alkanes in the internal standard are used to determine extraction recovery for the compounds quantified in the underivatized samples. The deuterated acids in the internal standard are used to determine the extraction recovery in the derivatized fraction and also to verify that the diazomethane reactions are driven to completion.

Although not all organic compounds emitted from air pollution sources are solvent extractable nor are they all elutable from a GC column, hundreds of compounds can be identified and quantified in source emissions. Hundreds of authentic standards have been prepared for the positive identification and quantification of many of the organic compounds found in the current source test program. When quantitative standards cannot be obtained for a given compound or compound class, significant effort is made to obtain a nonquantitative secondary standard that can be used for unique identification of the organic compounds. When a secondary standard is not available, interpretation of mass spectra and mass spectral libraries is used to aid in identification. The method used to quantify a specific compound is indicated in the notes column of Table 4 and described in the footnotes of that table. All compounds with a footnote b were quantified based on an authentic quantitative standard of that compound. A footnote c indicates

TABLE 3. Fine Particle Mass Emission Rates and Chemical Composition for the Fireplace Combustion of Selected Northeastern U.S. Wood Species[a]

	hardwoods			softwoods		
	red maple	northern red oak	paper birch	eastern white pine	eastern hemlock	balsam fir
Fine Particle Emissions Rate (g kg^{-1} wood burned)						
	3.3 ± 0.3	5.7 ± 0.6	2.7 ± 0.3	11.4 ± 2.0	3.7 ± 0.4	4.8 ± 0.5
Elemental and Organic Carbon (wt % of fine particle mass)						
OC[b]	85.5 ± 5.8	87.5 ± 5.4	86.8 ± 6.0	73.4 ± 6.4	102.3 ± 6.4	106.3 ± 6.5
EC	6.7 ± 1.9	3.8 ± 0.7	22.0 ± 2.9	31.3 ± 2.8	5.4 ± 0.9	7.0 ± 0.8
Ionic Species (wt % of fine particle mass)						
chloride	0.63 ± 0.03	0.40 ± 0.05	0.65 ± 0.03	0.13 ± 0.01	0.39 ± 0.07	0.48 ± 0.07
nitrate	0.60 ± 0.04	0.40 ± 0.07	0.28 ± 0.05	0.17 ± 0.01	0.38 ± 0.10	0.40 ± 0.10
sulfate	0.31 ± 0.03	0.42 ± 0.06	1.68 ± 0.05	0.13 ± 0.01	0.33 ± 0.08	0.30 ± 0.08
ammonium	0.12 ± 0.02	0.06 ± 0.01	0.21 ± 0.02	0.03 ± 0.01	0.04 ± 0.01	0.03 ± 0.01
Elemental Species (wt % of fine particle mass)						
silicon	0.041 ± 0.005	0.009 ± 0.002	0.137 ± 0.007	0.178 ± 0.003	0.029 ± 0.003	0.029 ± 0.003
sulfur	0.127 ± 0.004	0.129 ± 0.002	0.197 ± 0.006	0.080 ± 0.001	0.115 ± 0.003	0.130 ± 0.003
chlorine	0.674 ± 0.014	0.357 ± 0.007	0.784 ± 0.016	0.145 ± 0.003	0.381 ± 0.008	0.488 ± 0.009
potassium	1.235 ± 0.017	1.001 ± 0.008	0.976 ± 0.018	0.439 ± 0.004	1.324 ± 0.012	1.480 ± 0.013
zinc	0.039 ± 0.001	0.012 ± 0.001	0.491 ± 0.008	0.021 ± 0.001	0.012 ± 0.001	0.073 ± 0.001
calcium	<0.020	<0.020	<0.020	0.011 ± 0.002	0.021 ± 0.006	<0.024
bromine	0.004 ± 0.001	0.005 ± 0.001	0.006 ± 0.001	<0.001	<0.002	0.002 ± 0.001
rubidium	0.006 ± 0.001	0.005 ± 0.001	0.006 ± 0.001	0.002 ± 0.001	<0.002	0.008 ± 0.001
lead	<0.005	0.003 ± 0.001	0.014 ± 0.002	<0.002	<0.004	0.004 ± 0.001

[a] The following elements were not quantified due to high blank levels: Al, Fe, Cu, Mn, Ni, and Ag. The following elements were not found at quantities exceeding detection limits: P, Ti, V, Cr, Co, Ga, As, Se, Sr, Y, Zr, Mo, Pd, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, and U. [b] Results will include adsorption of gas-phase organics onto the quartz fiber filter, which may explain weight percents greater than 100.

that quantification was based on analogy to quantitative standard compounds from either the same homologous series or with very similar structures and retention times. The remaining compounds, indicated with a footnote d, were quantified based on the total ion response of authentic standards having similar retention times, functional groups, and degrees of fragmentation. The overwhelming majority of the compounds listed in Table 4 also are present in the NIST mass spectral library, and their mass spectra including key ions can be viewed there.

Results

The emission rates for fine particle mass as well as organic and elemental carbon, ionic species, and key elements from the fireplace combustion of the northeastern U.S. woods studied are listed in Table 3. The fine particle mass emission rates ranged from 2.7 to 11.4 g/kg of wood burned and averaged 5.3 g/kg over all six wood species tested. This is considerably less than the U.S. EPA emission factor for fireplace wood combustion of 17.3 g of $PM_{2.5}$/kg of wood burned (*37*) [making the assumption that the particles emitted are predominantly less than 2.5 μm in diameter (*38*)]. However, our results agree with several previous studies of the fine particle emission rates from fireplaces (*16, 25, 39*−*40*). There was no observed correlation between wood moisture content and fine particle mass emission rate. The highest fine particle mass emission rate resulted from burning eastern white pine. Several logs of the eastern white pine sample burned were visually observed to include much higher amounts of dried sap than the other woods tested. A visible increase in the amount of smoke produced occurred when these logs were added to the fire. Thus, we believe that the increased emissions were a result of sap inclusions in the wood. Excluding the eastern white pine sample, the average $PM_{2.5}$ emission rate from the fireplace combustion of the remainder of the northeastern U.S. woods was 4.0 ± 1.2 g/kg wood burned. Average particle size distributions showed little variation from wood to wood with the peak in the volume distribution occurring between 100 and 200 nm. These results are practically identical to the size distribution results displayed in a previous paper by Kleeman et al. (*41*) where fireplace source tests were conducted using the same sampling equipment and instrumentation

The results in Table 3 also indicate that almost all of the emitted fine particle mass consists of organic compounds. Organic carbon contributes over 80% of the fine particle mass in the emissions from every wood species studied. A true mass balance requires conversion from organic carbon mass to total organic compound mass using a factor that accounts for the hydrogen, oxygen, and sometimes nitrogen and sulfur content of the organic compounds present. This scale factor typically ranges between 1.2 and 1.4 for typical atmospheric samples (*42*) or higher depending primarily on the oxygen content of the compounds. When such a scale factor is applied to the OC data in Table 3, more than 100% of the gravimetric mass of the samples is assigned to measured chemical species. The resulting mass overbalances are most likely caused by organic vapor adsorption onto the quartz fiber filters (*43*). The organic carbon measured on the backup filter was less than 20% of that measured on the front filter for all six wood species. Since it is not completely clear whether this represents a positive or negative artifact, the backup filter data are not used to correct the values measured on the front filter. Instead, the backup filter data help to establish the range of uncertainties involved. We feel that additional research is needed before a simple correction for organic vapor artifacts can be applied. The elemental carbon content of the fine particle emissions generally ranged between 3 and 7% except that combustion of eastern white pine and paper birch produced much higher EC emissions. The high sap content of the eastern white pine may explain the high elemental carbon emissions since the addition of the sap-coated logs to the fire produced a thick visible black smoke. The high elemental carbon emissions from paper birch may be due to the large amount of bark material on the logs, which also produced visible black smoke when burned separately.

Potassium is often used as a marker for wood smoke (*3, 6*), and Table 3 shows fairly consistent results for potassium emissions across all types of woods tested averaging 1.1 ±

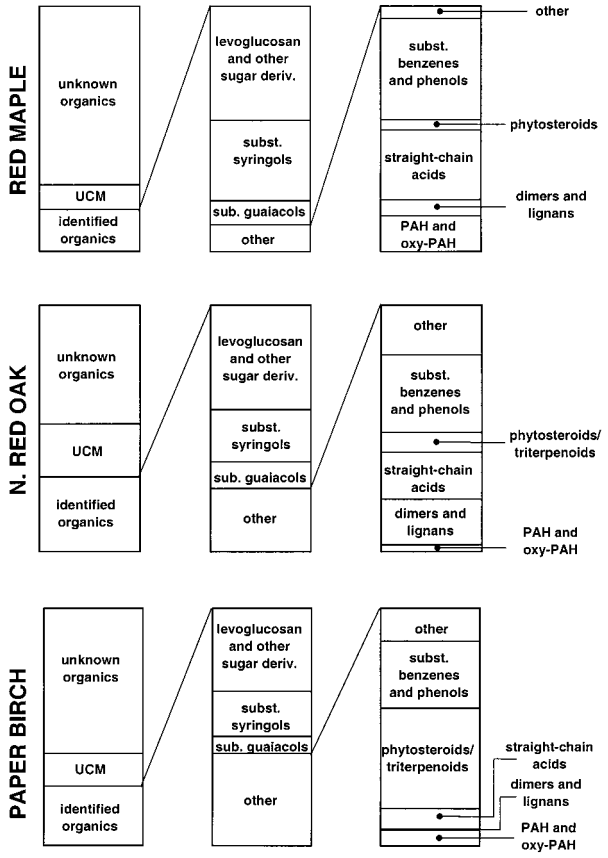

FIGURE 1. Organic compound mass balance for the fine particle emissions from combustion of selected northeastern U.S. hardwood species.

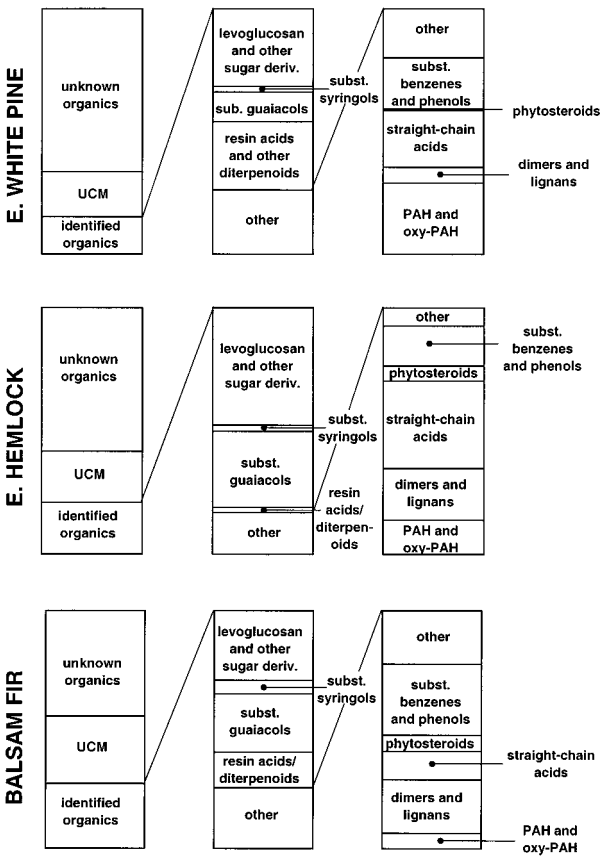

FIGURE 2. Organic compound mass balance for the fine particle emissions from combustion of selected northeastern U.S. softwood species.

0.4 wt % of the fine particle mass and 4.9 ± 1.5 g/kg of wood burned. However, using potassium as a wood smoke marker is confounded by nonwood combustion sources of fine particle potassium such as meat cooking (*7*).

Better candidates for wood combustion markers can be found in the over 250 organic compounds identified and quantified in the fine particle emissions from the woods burned in this study. Emitted compounds are either volatilized components of the original natural molecules in the wood that recondense into the particle phase or pyrolysis products of the combustion reactions. Table 4 lists the detailed organic compound speciation profiles for the six northeastern U.S. wood smokes characterized here, stated in terms of milligrams of each compound per gram of fine particle organic carbon emitted. The data suggest that there are significant differences in the emissions from different wood species. Figures 1 and 2 illustrate some of these differences through construction of a carbon compound mass balance based on major organic compound classes found in the smokes. The total organic compound mass per sample was estimated as 1.4 times the organic carbon mass per sample; standards for the individual compounds were used to compute the quantities of each specific compound, and the individual compounds were summed to arrive at the overall contribution of each compound class.

Between 17% and 32% of the total organic compound mass emitted from each of the six woods was identified and quantified. The remaining mass consists of an unresolved complex mixture (UCM) of branched and cyclic organic compounds that passes through the GC column appearing as a hump underlying the resolved peaks plus an unknown organic fraction that includes compounds that either are not extractable in the organic solvents used here, are not elutable from the GC column, or remain as unidentified peaks in the gas chromatograms. Of the identified compounds, the pyrolysis product of cellulose (levoglucosan) is by far the most abundant. Between 3% and 12% of the fine particle organic compound emissions are accounted for by levoglucosan, yielding an average of 100 ± 40 mg of levoglucosan/g of fine particle organic carbon emitted. The very high emission rates and uniqueness of this compound to biomass combustion make it an important candidate as a marker for biomass combustion in general, as has been proposed previously (*44, 45*).

The use of levoglucosan as a long-range tracer of biomass combustion depends on its atmospheric stability, which has been explored by Fraser et al. (*45*). They show that, with respect to the possible reaction mechanism of acid-catalyzed hydrolysis, levoglucosan is stable up to 10 days under conditions simulating the aqueous chemistry of atmospheric droplets. The atmospheric reactivity of other potential organic wood smoke tracers is largely unknown. Several PAH listed in Table 4 have been shown to degrade in the particle phase when exposed to nitrogen oxides and ozone (*46*). However, since PAH are only a minor component of wood smoke and are also emitted from a variety of other combustion sources, PAH are not ideal candidates as markers for wood smoke. Although their atmospheric stability has not been tested, many of the substituted guaiacols, syringols, and phenols have been measured in ambient particle samples (*3, 4*), suggesting that they at least do not fully degrade in the atmosphere. If the atmospheric reaction products of some of these compounds could be identified in ambient samples, they too might be utilized as wood smoke tracers.

A comparison of Figures 1 and 2 also illustrates the differences in fine particle emissions between hardwoods and softwoods. The hardwood combustion emissions contain greater amounts of substituted syringols than the softwood

TABLE 4. Detailed Speciation of Fine Particle Organic Compounds Emitted from Northeastern U.S. Wood Species[a]

compound	hardwoods: red maple	hardwoods: n. red oak	hardwoods: paper birch	softwoods: e. white pine	softwoods: e. hemlock	softwoods: balsam fir	notes	compound	hardwoods: red maple	hardwoods: n. red oak	hardwoods: paper birch	softwoods: e. white pine	softwoods: e. hemlock	softwoods: balsam fir	notes
_n_-Alkanes															
n-heptadecane	−	−	0.052	0.005	−	−	*c*	*n*-tricosane	+	0.118	+	0.047	0.087	0.082	*c*
n-octadecane	−	−	0.084	0.006	−	−	*b*	*n*-tetracosane	−	0.041	0.018	0.011	0.043	0.035	*b*
n-nonadecane	+	0.024	0.103	0.021	0.036	0.016	*c*	*n*-pentacosane	−	0.038	−	−	0.037	0.018	*c*
n-eicosane	0.084	0.083	0.104	0.026	0.076	0.059	*b*	*n*-hexacosane	−	0.009	−	−	0.012	−	*c*
n-heneicosane	0.134	0.139	0.103	0.027	0.085	0.110	*c*	*n*-heptacosane	−	−	−	−	0.061	−	*c*
n-docosane	+	0.108	+	0.033	0.065	0.141	*b*								
_n_-Alkenes															
1-nonadecene	−	−	0.084	0.042	0.024	−	*c*	1-pentacosene	−	0.229	−	0.023	0.047	0.267	*c*
1-eicosene	0.229	0.259	0.275	0.087	0.120	0.124	*c*	1-hexacosene	−	0.035	−	0.035	0.063	0.000	*c*
1-heneicosene	0.123	0.174	0.185	0.021	0.116	0.359	*c*	1-heptacosene	−	0.162	−	0.023	0.222	0.331	*c*
1-docosene	+	0.225	+	0.073	0.124	0.364	*c*	1-octacosene	−	−	−	−	−	−	*c*
1-tricosene	0.016	0.149	0.057	−	0.045	0.115	*c*	1-triacontene	−	−	−	−	0.048	−	*c*
1-tetracosene	−	0.122	0.017	0.077	0.164	0.174	*c*								
_n_-Alkanols															
n-octadecanol	−	0.059	−	−	−	−	*b*	*n*-eicosanol	−	0.286	−	−	−	0.047	*b*
n-nonadecanol	−	0.093	0.034	−	−	0.034	*b*								
_n_-Alkanals															
n-heneicosanal	−	0.071	0.026	−	−	0.032	*c*	*n*-tetracosanal	−	0.081	−	−	0.048	0.060	*c*
n-docosanal	−	0.121	0.032	−	−	0.076	*c*	*n*-pentacosanal	−	0.034	−	−	−	−	*c*
n-tricosanal	−	0.154	0.037	−	−	0.019	*c*								
Alkanoic Acids															
n-decanoic	+	+	0.245	0.055	+	+	*b,e*	*n*-nonadecanoic	0.024	0.061	0.160	0.035	0.086	0.069	*c,e*
n-undecanoic	0.036	0.018	0.082	0.015	+	+	*c,e*	*n*-eicosanoic	0.107	0.253	0.804	0.316	0.665	0.337	*b,e*
n-dodecanoic	+	0.170	0.359	0.074	+	+	*b,e*	*n*-heneicosanoic	0.074	0.189	0.333	0.034	0.185	0.160	*c,e*
n-tridecanoic	0.057	0.042	−	0.022	0.042	0.040	*c,e*	*n*-docosanoic	0.505	1.236	0.768	0.283	1.540	1.446	*b,e*
n-tetradecanoic	+	0.243	0.498	0.171	+	0.202	*b,e*	20-methyldocosanoic	−	−	−	−	0.013	0.088	*c,e*
n-pentadecanoic	+	0.163	0.286	0.136	0.240	0.217	*c,e*	*n*-tricosanoic	0.139	0.347	0.083	0.028	0.209	0.233	*c,e*
n-hexadecanoic	1.830	1.947	2.802	1.636	1.753	1.389	*b,e*	*n*-tetracosanoic	0.612	4.347	0.166	0.191	4.058	1.526	*c,e*
14-methyl-hexadecanoic	+	+	−	0.182	0.385	0.405	*c,e*	*n*-pentacosanoic	0.063	0.200	0.104	0.005	0.131	0.062	*c,e*
								n-hexacosanoic	0.073	1.837	0.054	0.016	2.039	0.115	*c,e*
n-heptadecanoic	0.072	0.082	0.151	0.072	0.142	0.121	*c,e*	*n*-heptacosanoic	−	0.108	−	−	0.027	−	*c,e*
n-octadecanoic	0.378	0.397	1.434	0.507	0.511	0.402	*b,e*	*n*-octacosanoic	−	0.055	−	−	0.256	−	*c,e*
16-methyloctadecanoic	−	−	−	0.023	0.088	0.060	*b,d*								
Alkenoic Acids															
hexadecenoic	+	0.074	−	0.051	0.129	0.162	*c,e*	heneicosenoic	−	−	−	−	−	−	*c,e*
cis-9-octadecenoic	1.108	1.675	−	4.097	1.068	1.298	*b,e*	docosenoic	0.161	0.241	0.422	−	0.161	0.143	*c,e*
trans-9-octadecenoic	0.159	0.378	0.164	0.474	0.161	0.257	*c,e*	tricosenoic	−	−	−	−	−	−	*c,e*
2-octadecenoic	−	0.055	0.052	−	0.047	0.024	*c,e*	tetracosenoic	−	0.601	−	−	0.122	0.029	*c,e*
9,12-octadecadienoic	1.217	3.893	1.275	3.840	1.564	1.159	*b,e*	pentacosenoic	−	0.196	−	−	−	−	*c,e*
nonadecenoic	−	0.041	−	−	−	−	*c,e*	hexacosenoic	−	0.123	−	−	−	−	*c,e*
eicosenoic[f]	0.153	0.249	0.086	0.137	0.096	0.099	*c,e*								
Alkanedioic Acids															
hexanedioic	0.265	0.132	0.258	0.095	0.132	0.118	*b,e*	octadecanedioic	−	0.067	0.070	−	0.194	0.109	*c,e*
heptanedioic	0.084	0.076	−	0.042	0.058	0.042	*b,e*	eicosanedioic	−	0.065	0.069	0.023	0.137	0.171	*c,e*
octanedioic	0.116	0.122	0.162	0.071	0.085	0.095	*b,e*	docosanedioic	0.100	0.086	0.488	−	0.153	0.182	*c,e*
nonanedioic	+	0.336	0.224	0.114	0.199	0.149	*c,e*	tetracosanedioic	−	0.320	−	−	0.031	−	*c,e*
decanedioic	−	0.065	0.107	0.021	0.026	0.047	*b,e*	pentacosanedioic	−	0.118	−	−	−	−	*c,e*
undecanedioic	−	−	−	−	−	−	*c,e*	hexacosanedioic	−	0.070	−	−	−	−	*c,e*
hexadecanedioic	0.103	0.112	0.101	0.052	0.830	0.645	*c,e*								
Methyl Alkanoates															
methyl hexadecanoate	0.106	0.123	0.082	0.038	0.095	0.076	*b*	methyl heneicosanoate	−	−	0.004	−	−	0.007	*c*
methyl 14-methylhexadecanoate	−	−	−	0.007	−	0.056	*c*	methyl docosanoate	−	0.056	0.005	0.009	0.038	0.094	*c*
								methyl tricosanoate	−	−	0.005	−	−	0.017	*c*
methyl heptadecanoate	−	0.013	0.010	−	−	0.016	*c*	methyl tetracosanoate	−	0.066	0.008	0.010	0.127	0.103	*c*
methyl octadecanoate	0.015	0.016	0.039	0.022	0.028	0.024	*b*	methyl pentacosanoate	−	−	−	−	−	0.015	*c*
methyl eicosanoate	−	0.010	0.019	0.019	0.017	0.017	*c*	methyl hexacosanoate	−	0.016	−	−	0.040	0.014	*c*
Ethyl Alkanoates															
ethyl tetracosanoate	−	−	−	−	0.192	−	*c*	ethyl hexacosanoate	−	−	−	−	0.129	−	*c*
Methyl Alkenoates															
methyl *cis*-9-octadecenoate	−	−	0.048	0.101	0.061	0.066	*b*	methyl docosenoate	−	−	−	−	−	0.014	*c*
								methyl tetracosenoate	−	−	−	−	−	0.011	*c*
methyl 9,12-octadecadienoate	−	0.045	0.105	0.125	0.045	0.368	*c*								
Guaiacol and Substituted Guaiacols															
guaiacol	−	0.190	0.136	0.074	0.184	0.356	*b*	methyl vanillate	+	0.072	0.154	0.165	0.231	0.237	*b*
eugenol	0.066	0.059	0.174	0.075	0.161	0.254	*b*	homovanillic acid	2.474	11.072	1.016	2.889	18.139	24.111	*b*
cis-isoeugenol	0.021	0.041	0.061	0.083	0.124	0.195	*b*	methyl homovanillate	0.071	0.122	0.047	0.064	0.173	0.210	*b*
trans-isoeugenol	0.137	0.268	0.608	0.678	1.299	1.382	*c*	vanillin	+	2.050	7.205	5.164	5.088	5.710	*b*
4-vinylguaiacol	0.252	0.190	0.134	0.123	0.251	0.428	*c*	acetovanillone	1.624	2.357	3.395	2.988	5.425	5.967	*b*
4-ethylguaiacol	0.028	0.050	0.049	0.049	0.090	0.203	*b*	propiovanillone	0.533	1.187	0.584	0.939	2.746	2.960	*c*
4-propylguaiacol	−	0.017	0.026	0.048	0.068	0.121	*b*	guaiacyl acetone	4.352	7.240	4.644	4.436	16.280	17.678	*c*
vanillic acid	0.252	3.787	0.335	0.482	1.629	2.997	*b*	coniferyl aldehyde	13.724	17.271	6.631	7.374	39.003	30.954	*b*

TABLE 4 (Continued)

compound	hardwoods: red maple	hardwoods: n. red oak	hardwoods: paper birch	softwoods: e. white pine	softwoods: e. hemlock	softwoods: balsam fir	notes	compound	hardwoods: red maple	hardwoods: n. red oak	hardwoods: paper birch	softwoods: e. white pine	softwoods: e. hemlock	softwoods: balsam fir	notes
Syringol and Substituted Syringols															
syringol	0.700	2.588	15.354	+	+	0.258	*b*	syringic acid	–	4.930	–	–	–	–	*b*
4-ethylsyringol	2.777	2.821	10.106	0.132	–	0.335	*c*	syringaldehyde	27.022	21.967	13.800	2.355	3.609	7.446	*b*
4-propylsyringol	2.397	1.816	2.034	0.054	–	0.176	*c*	acetosyringone	7.209	9.905	2.979	0.576	1.021	3.122	*b*
methoxyeugenol	5.830	3.035	6.632	0.166	0.100	0.607	*c*	syringyl acetone	19.510	28.593	7.474	1.025	1.773	7.184	*c*
cis-methoxy-isoeugenol	0.786	1.367	0.485	0.125	0.449	0.344	*c*	propionyl syringol	1.582	2.109	0.746	0.167	0.267	0.588	*c*
								sinapyl aldehyde	7.496	8.224	5.987	0.219	–	1.088	*b*
trans-methoxy-isoeugenol	3.121	2.578	0.859	0.024	0.165	0.653	*c*								
Other Substituted Benzenes and Phenols															
1,2-benzenediol (pyrocatechol)	0.799	5.434	1.110	1.512	0.952	7.114	*c*	benzenetriols	–	2.057	–	–	–	0.324	*c*
								hydroxyaceto-phenones	0.205	0.706	0.634	0.501	0.726	1.018	*c*
1,4-benzenediol (hydroquinone)	0.625	5.570	0.919	0.356	1.146	4.793	*b*								
								methyl hydroxy-benzoates	+	0.198	0.262	0.083	0.129	0.176	*c*
1,3-benzenediol (resorcinol)	0.699	2.645	1.326	0.570	0.794	1.134	*b*								
								trimethoxybenzenes	2.056	3.844	23.077	0.169	+	0.395	*c*
methyl benzenediols	0.345	3.543	0.975	2.395	1.092	7.397	*c*	3,4,5-trimethoxy-benzoic acid	5.786	3.062	0.279	–	0.119	1.446	*b*
methoxybenzene-diols	0.281	5.432	1.430	0.088	0.137	1.282	*d*	benzoic acid	+	+	0.464	0.185	+	+	*b,e*
hydroxybenz-aldehydes	+	0.862	3.423	1.782	1.311	1.518	*b*	phenyl acetic acid	+	0.055	0.286	0.130	+	0.077	*c,e*
								phenyl propanoic acid	+	+	0.102	0.237	+	+	*c,e*
cinnamaldehyde	–	0.903	3.942	3.497	1.662	2.323	*c*								
Dimers and Lignans															
diguaiacyl ethanes (divanillyls)	0.715	6.562	0.348	3.303	8.788	14.110	*c*	shonanin (2-de-oxomatairesinol)	0.024	1.069	0.015	0.301	1.377	6.847	*d*
syringyl guaiacyl ethane	0.297	3.853	0.077	–	–	0.077	*c*	methyl-2-deoxo-matairesinol	–	–	–	–	–	0.154	*d*
disyringyl methane	0.072	0.599	0.019	–	–	0.015	*c*	matairesinol	–	0.054	–	–	0.236	0.530	*d*
disyringyl ethane	0.617	8.035	0.213	–	–	0.060	*c*	conidendrin	–	–	–	–	0.027	–	*d*
PAH and Alkyl PAH															
phenanthrene	0.087	0.033	0.269	0.157	0.073	0.073	*b*	benz[*a*]anthracene	0.200	0.088	0.213	0.249	0.168	0.127	*b*
anthracene	0.018	0.010	0.050	0.032	0.021	0.021	*b*	chrysene	0.252	0.107	0.229	0.246	0.176	0.141	*b*
3-methyl-phenanthrene	+	0.008	0.093	0.063	0.020	0.025	*c*	methyl 226 MW PAHs	0.039	0.018	0.044	0.052	0.035	0.024	*c*
2-methyl-phenanthrene	+	0.014	0.117	0.225	0.028	0.037	*c*	methyl 228 MW PAHs	0.026	0.026	0.038	0.055	0.028	0.028	*c*
2-methyl-anthracene	+	0.007	0.061	0.053	0.019	0.023	*b*	benzo[*b*]fluor-anthene	0.131	0.036	0.104	0.157	0.066	0.050	*b*
9-methyl-phenanthrene	+	0.010	0.126	0.096	0.024	0.029	*c*	benzo[*k*]fluor-anthene	0.132	0.048	0.123	0.186	0.084	0.065	*b*
1-methyl-phenanthrene	+	0.013	0.111	0.498	0.022	0.047	*b*	benzo[*j*]fluor-anthene	0.033	0.022	0.042	0.075	0.038	0.030	*c*
phenyl-naphthalenes	+	+	0.266	0.507	0.052	0.107	*c*	benzo[*e*]pyrene	0.079	0.029	0.063	0.078	0.044	0.037	*c*
								benzo[*a*]pyrene	0.124	0.055	0.127	0.177	0.091	0.070	*b*
dimethyl or ethyl 178 MW PAHs	+	+	0.087	1.196	0.103	0.122	*b*	perylene	0.014	0.008	0.013	0.024	0.010	0.009	*b*
								indeno[1,2,3-*cd*]-fluoranthene	0.019	0.010	0.022	0.038	0.017	0.014	*c*
fluoranthene	0.315	0.183	1.083	1.040	0.372	0.286	*b*								
acephenanthrylene	0.117	0.106	0.421	0.500	0.212	0.162	*c*	indeno[1,2,3-*cd*]-pyrene	0.164	0.039	0.108	0.127	0.064	0.053	*b*
pyrene	0.423	0.224	1.080	0.896	0.401	0.310	*b*								
methyl 202 MW PAHs	0.282	0.169	0.299	0.280	0.283	0.235	*c*	benzo[*ghi*]perylene	0.066	0.025	0.056	0.070	0.035	0.031	*b*
								anthanthrene	0.012	0.008	0.014	0.023	0.012	0.011	*c*
retene	+	+	+	5.485	1.666	0.742	*b*	dibenz[*a,h*]-anthracene	0.006	0.003	0.005	0.011	0.004	0.005	*b*
benzo[*ghi*]-fluoranthene	0.157	0.059	0.159	0.198	0.129	0.090	*c*								
								coronene	0.177	0.099	0.156	0.219	0.076	0.099	*b*
cyclopenta[*cd*]-pyrene	0.188	0.084	0.235	0.314	0.187	0.122	*c*								
Oxy-PAH															
1,4-naphthalene-dione	0.010	0.007	0.036	0.051	0.017	0.016	*c*	fluorenone	+	0.046	0.562	0.409	0.127	0.104	*b*
								1*H*-phenalen-1-one	0.197	0.287	0.357	0.428	0.506	0.485	*b*
1-naphthol	0.081	0.060	0.204	0.150	0.089	0.128	*b*								
2-naphthol	+	0.135	0.554	0.348	0.217	0.300	*b*	9,10-anthra-cenedione	0.117	0.066	0.156	0.136	0.162	0.145	*b*
methylnaphthols	0.242	0.597	0.817	0.699	0.809	1.343	*c*								
methoxynaph-thols	0.000	0.074	0.178	0.239	0.212	0.267	*b*	xanthone	+	0.040	0.057	0.028	0.072	0.059	*b*
								benzanthrone	0.086	0.107	0.149	0.250	0.134	0.157	*b*
Sugar Derivatives															
1,4:3,6-dianhy-dro-α-D-gluco-pyranose	+	3.507	11.167	4.037	+	4.720	*d*	mannosan	3.286	4.745	1.313	9.008	25.571	17.398	*b*
								levoglucosan	108.509	168.254	109.539	52.330	95.450	81.445	*b*
								monomethyl-inositol	–	0.226	–	0.496	16.758	4.939	*d*
galactosan	–	3.527	–	1.291	2.472	2.582	*b*								
Coumarins and Flavonoids															
coumarin	0.077	0.049	0.359	0.110	0.080	0.067	*b*	tetramethoxy-isoflavone	0.189	1.099	–	–	–	0.022	*c*
pinostrobin chalcone	–	–	–	1.168	–	–	*c*								

TABLE 4 (Continued)

compound	hardwoods: red maple	hardwoods: n. red oak	hardwoods: paper birch	softwoods: e. white pine	softwoods: e. hemlock	softwoods: balsam fir	notes	compound	hardwoods: red maple	hardwoods: n. red oak	hardwoods: paper birch	softwoods: e. white pine	softwoods: e. hemlock	softwoods: balsam fir	notes
Furans															
5-hydroxymethyl-2-furaldehyde	−	16.131	14.388	7.665	+	16.901	*b*	dibenzofuranols	0.156	0.215	0.174	0.149	0.287	0.330	*b*
5-acetoxymethyl-2-furaldehyde	0.081	0.211	1.328	0.318	0.267	0.231	*b*	benzonaphthofurans	+	0.163	0.252	0.347	0.321	0.280	*d*
Resin Acids															
deisopropylidehydroabietic	−	−	−	0.237	0.021	0.113	*c,e*	levopimaric	−	−	−	1.043	0.063	0.770	*c,e*
16,17-bisnordehydroabietic	−	−	−	0.143	0.003	0.010	*c,e*	abietic	−	−	−	20.481	1.983	19.558	*b,e*
16-nordehydroabietic	−	−	−	0.151	0.016	0.013	*c,e*	7-oxodehydroabietic	−	+	−	0.251	0.051	0.012	*c,e*
secodehydroabietic	−	−	−	0.549	0.107	0.048	*c,e*	abieta-6,8,11,13-tetraen-18-oic	−	−	−	1.988	0.425	0.943	*c,e*
pimaric	−	−	−	0.441	0.107	0.080	*b,e*	abieta-8,11,13,15-tetraen-18-oic	−	−	−	0.520	0.058	0.204	*c,e*
sandaracopimaric	−	−	−	1.340	0.170	0.401	*c,e*	abieta-6,8,11,-13,15-pentaen-18-oic	−	−	−	0.249	0.035	0.198	*c,e*
dehydroabietic	+	+	−	7.811	1.575	2.316	*b,e*	neoabietic	−	−	−	0.415	−	0.132	*c,e*
8,15-pimaradien-18-oic	−	−	−	3.812	0.069	0.116	*c,e*	7-oxoabieta-8,11,13,15-tetraen-18-oic	−	−	−	0.017	0.005	0.025	*c,e*
isopimaric	−	−	−	12.615	0.408	2.000	*b,e*								
Other Diterpenoids															
18-norisopimara-4(19),7,15-triene	−	−	−	0.024	−	−	*c*	methyl 16,17-bisnordehydroabietate	−	−	−	0.073	0.016	0.006	*d*
19-norabieta-8,11,13-triene	−	−	−	0.688	0.010	0.011	*c*	dehydroabietal	−	−	−	0.075	0.045	0.022	*d*
18-norabieta-8,11,13-triene	−	−	−	0.982	0.018	0.011	*b*	methyl 6,8,11,13-abietatetraen-18-oate	−	−	−	0.326	0.115	0.081	*d*
19-norabieta-4,8,11,13-tetraene	−	−	−	1.043	0.053	0.055	*c*	methyl 8,11,13,15-abietatetraen-18-oate	−	−	−	0.118	0.012	0.021	*d*
18-norabieta-4(19),8,11,13-tetraene	−	−	−	0.439	0.027	0.028	*c*	methyl dehydroabietate	−	−	−	1.183	0.342	0.173	*b*
								methyl abietate	−	−	−	0.625	−	−	*b*
dehydroabietane	−	−	−	0.035	0.310	0.012	*d*	methyl-7-oxodehydroabietate	−	−	−	0.104	0.009	0.043	*c*
methyl deisopropyldehydroabietate	−	−	−	0.048	0.005	−	*d*	manoyl oxide	−	−	−	0.229	0.039	0.362	*d*
pimarinal	−	−	−	0.075	0.030	−	*d*	manool	−	−	−	−	+	5.418	*b*
methyl 8,15-pimaradien-18-oate	−	−	−	0.275	0.051	−	*d*	juvabione	−	−	−	−	+	15.434	*b*
								todomatuic acid (norjuvabione)	−	−	−	−	−	0.454	*c*
methyl isopimarate	−	−	−	0.757	0.132	0.056	*b*	dehydrojuvabione	−	−	−	−	−	8.133	*b*
Phytosteroids															
stigmasterol	−	0.429	−	−	−	0.211	*b*	stigmasta-4,6-dien-3-one	−	0.258	−	0.028	0.037	0.120	*c*
β-sitosterol	0.793	6.367	0.645	0.305	2.509	4.980	*b*	stigmastan-3-ol	0.111	0.243	−	−	0.209	0.447	*b*
stigmast-4-en-3-one (sitostenone)	0.090	0.464	0.096	0.022	0.061	0.150	*b*	stigmastan-3-one	0.065	0.124	0.062	0.012	0.058	0.124	*d*
stigmasta-3,5-dien-7-one	−	0.789	0.256	0.055	0.145	0.587	*c*								
Triterpenoids															
allobetul-2-ene	−	−	3.157	−	−	−	*d*	β-amyrone	−	0.006	0.051	−	−	−	*c*
allobetulone	−	−	0.231	−	−	−	*d*	β-amyrin	−	0.019	0.035	−	−	−	*b*
allobetulin	−	−	6.362	−	−	−	*c*	α-amyrone	−	0.014	0.037	−	−	−	*c*
betulin	−	−	46.710	−	−	−	*b*	α-amyrin	−	0.010	0.019	−	−	−	*b*
Other Compounds															
1-indanone	0.035	0.043	0.235	0.128	0.096	0.096	*b*	β-tocopherol	−	0.026	−	−	−	−	*c*
methyl indanones	−	0.074	0.122	0.178	0.208	0.210	*c*	unresolved complex mixt	142	301	194	258	290	399	*c*
squalene	0.076	0.339	0.496	0.114	0.119	0.174	*b*								
α-tocopherol (vitamin E)	−	0.400	−	−	−	−	*b*								

[a] All values expressed as mg g^{-1} organic carbon (OC) emitted. −, not detected. +, detected but not quantified due to comparable levels found in blank samples. [b] Identification and quantification based on authentic quantitative standard. [c] Identification and quantification based on authentic quantitative standards of compounds with similar structures and retention times. [d] 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. [e] Detected and quantified as methyl ester analogue in derivatized fraction. [f] Two isomers.

combustion emissions. Conversely, resin acids such as dehydroabietic acid and other diterpenoids are significant components of softwood emissions but are not found in detectable quantities in the emissions from hardwoods. Furthermore, while phytosteroids were detected in all of the wood smokes, triterpenoids are not present in any of the softwood smokes. The ability to distinguish between hardwood and softwood smoke using organic chemical tracer

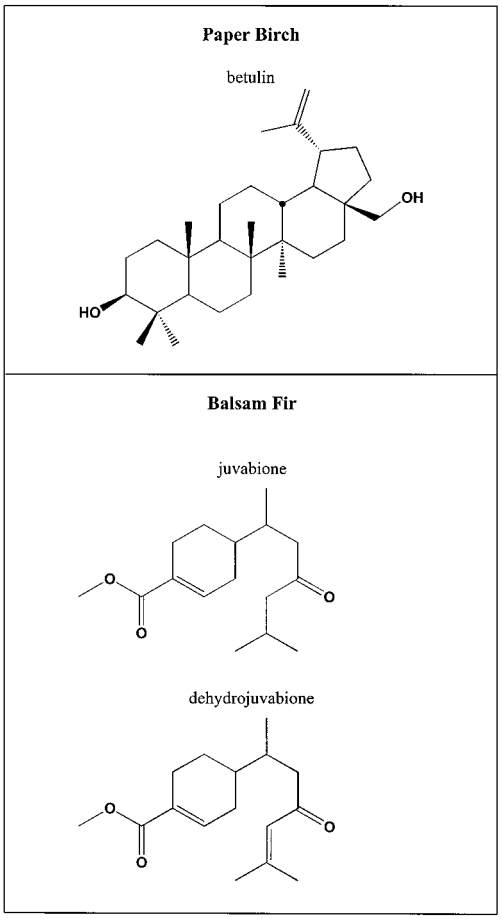

FIGURE 3. Chemical structures of potential species-specific organic tracers for wood smoke.

techniques has already been demonstrated in California's San Joaquin Valley by Schauer et al. (*4*). To extend that method of analysis to other regions of the United States, both hardwood and softwood source profiles are needed for woods characteristic of the geographical areas of interest. Table 4 provides such data for the northeastern United States.

While organic compound markers for biomass combustion in general and for differentiating between hardwoods and softwoods are known conceptually from previous work, our results are the first to suggest possible organic tracers for the combustion of specific wood species (Figure 3). The phytosterol and triterpenoid emissions from burning paper birch illustrated in Figure 1 are dominated by emissions of a single triterpenoid (betulin), which is a known component of birch bark (*47*). About 3% of the total fine particle organic compound mass emitted from paper birch combustion is attributable to betulin. Since betulin was not detected in the emissions from any other wood species, it appears that betulin and/or its atmospheric transformation products may be a good candidate as a species-specific organic tracer.

Two significant components of the balsam fir combustion emissions, making up over 1.7% of the total fine particle organic compound mass emitted, are juvabione and dehydrojuvabione (also shown in Figure 3). These compounds are known components of balsam fir wood (*48*) that protect the tree from potentially damaging insects by acting as hormone disrupters to insect reproduction (*49*). While unique to balsam fir emissions, their use as chemical tracers depends on their atmospheric stability, which has not yet been investigated. The presence of several exposed double bonds indicate that these compounds may be subject to ozone attack in the atmosphere. However, the oxidation products of such atmospheric reactions can also be used as molecular tracers for balsam fir combustion, provided that they prove quantifiable in atmospheric fine particle samples.

Besides these compounds that are unique to specific wood species, a closer look at Table 4 reveals some important differences in the relative amounts of certain compounds emitted that may be used to distinguish between different wood types. Small amounts of alkanes and alkenes are emitted from the combustion of northeastern U.S. wood species with the peak in the compound distributions occurring generally between carbon numbers 20 and 23. Eastern hemlock combustion emitted measurable levels of heptacosane, which was not detected in the other northeastern U.S. woods tested. Small quantities of *n*-alcohols and *n*-alkanals were also measured with northern red oak emissions being enriched in *n*-alkanals in comparison with the other wood species.

Alkanoic acids ranging from carbon number 10 to carbon number 28 were found in the smoke of the woods tested and exhibit the well-known even carbon number preference for acids found in natural material such as plant epicuticular waxes (*50*). While all six wood smokes contained high levels of hexadecanoic acid as found in previous wood smoke analyses (*25*), northern red oak, eastern hemlock, and balsam fir smokes contained tetracosanoic acid as the dominant alkanoic acid. High levels of hexacosanoic acid were also seen in the red oak and eastern hemlock smokes. The dominant alkenoic acids found in all the wood smokes were *cis*-9-octadecenoic acid and 9,12-octadecadienoic acid, although at somewhat different levels. Small amounts of alkanedioic acids as well as methylated or ethylated alkanoic and alkenoic acids were also detected to varying degrees in the emissions from the combustion of the six wood types.

The predominant substituted guaiacols found in the smoke from the six wood species were homovanillic acid, vanillin, acetovanillone, guaiacyl acetone, and coniferyl aldehyde. Coniferyl aldehyde was the dominant compound in this class in all wood smokes except for northern red oak, which produced higher emissions of vanillin. While both hardwoods and softwoods emitted substituted guaiacols at various levels, the substituted syringols were found to a much greater extent in the hardwood smokes. For the fine particle emissions from red maple and northern red oak combustion, syringaldehyde, acetosyringone, syringyl acetone, and sinapyl aldehyde were the most prevalent substituted syringols. Paper birch smoke also contained high levels of syringol and 4-ethylsyringol in the fine particle emissions. Among other substituted benzenes, trimethoxybenzenes were measured to a much greater extent in the paper birch smoke than in any other wood species. In the balsam fir smoke, divanillyls were the dominant lignin-derived dimers, and shonanin (2-deoxomatairesinol) was the dominant lignan. Divanillyls were found in all the other smoke samples, but the dimers with at least one syringyl group were found primarily in the hardwood emissions showing the same distinction between hardwood vs softwood smoke as is the case for the single-ring phenolics. A small amount of conidendrin was found only in the fine particle emissions from eastern hemlock.

PAH are not major contributors to wood smoke mass emissions, but many different PAH compounds can be quantified in wood smoke as shown in Table 4. Retene was the dominant aromatic hydrocarbon found in the softwood smokes with very little detected in the hardwood combustion emissions. Retene is the fully aromatized thermal alteration product of the resin acids present in conifer woods. Eastern white pine smoke contained considerably higher retene levels than the other two softwood smokes examined here. Other than retene, fluoranthene and pyrene were the most prevalent PAH found in both the hardwood and the softwood smoke

samples consistent with previous studies of wood smoke where PAH were measured (*14*, *15*). Several oxy-PAH were detected and quantified at low levels and are also listed in Table 4.

As discussed above, levoglucosan is the most prevalent sugar derivative emitted from wood combustion. Other sugar derivatives found at lower levels include 1,4:3,6-dianhydro-α-D-glucopyranose, monomethylinositol, galactosan, and mannosan. Eastern hemlock and balsam fir smokes contained higher levels of mannosan and monomethyl inositol than the other wood smokes. Coumarin was found at low levels in all the wood smokes, but pinostrobin chalcone was only detected in the eastern white pine. Northern red oak smoke contained higher levels of tetramethoxyisoflavone than the other wood smokes. The dominant furan emitted was 5-hydroxymethyl-2-furaldehyde found in all the wood smokes except in the red maple smoke and at unquantifiable levels in the eastern hemlock.

Resin acids were only emitted in appreciable quantities in the combustion of the softwoods. Abietic acid was the dominant compound in this class, but eastern hemlock smoke contained considerably less abietic acid than the other two softwood smokes. Dehydroabietic acid was the second most abundant resin acid emitted with eastern white pine smoke containing higher levels of dehydroabietic acid than the emissions from the other two softwoods. Other diterpenoids include the methyl esters of the resin acids, diterpenes, and juvabione and dehydrojuvabione, which are found in the balsam fir emissions, as discussed above. Also prevalent in the balsam fir emissions is manool, which was not found at quantifiable levels in any of the other wood smokes discussed here.

β-Sitosterol was the most prevalent phytosterol emitted from the combustion of northeastern U.S. woods and was found at very different levels in the different wood smoke types. For instance, the combustion of northern red oak produced almost 20 times more β-sitosterol than eastern white pine as a fraction of the total fine particle organic carbon emitted. Important differences such as this can potentially be used to distinguish between the smokes from the combustion of different wood species.

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