



A method for smoke marker measurements and its potential application for determining the contribution of biomass burning from wildfires and prescribed fires to ambient PM_{2.5} organic carbon

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Received 2 April 2008; revised 28 August 2008; accepted 5 September 2008; published 20 November 2008.

[1] Biomass burning is an important source of particulate organic carbon (OC) in the atmosphere. Quantifying this contribution in time and space requires a means of routinely apportioning contributions of smoke from biomass burning to OC. Smoke marker (for example, levoglucosan) measurements provide the most common approach for making this determination. A lack of source profiles for wildfires and prescribed fires and the expense and complexity of traditional smoke marker measurement methods have thus far limited routine estimates of these contributions to ambient aerosol concentrations and regional haze. We report here on the collection of source profiles for combustion of numerous wildland fuels and on the development of an inexpensive and robust technique for routine smoke marker measurements. Hi-Volume filter source samples were collected during two studies at the Fire Science Laboratory in Missoula, MT in 2006 and 2007. Levoglucosan (and other carbohydrates) were measured in these samples using high-performance anion-exchange chromatography with pulsed amperometric detection. Results of this analysis along with water-soluble potassium, OC, and elemental carbon are presented. The results show that emissions of levoglucosan are fairly correlated with OC with an average ratio of 0.031 $\mu\text{g C}/\mu\text{g C}$. Further, there was a definite pattern that emerged based on fuel component burned with the typical levoglucosan/OC ratio of branches > straw > needles > leaves. Additionally, this carbohydrate measurement method appears to provide fingerprint information about the type of fuel burned that could help constrain profiles chosen for aerosol source apportionment and lead to a better determination of source contributions from biomass burning.

Citation: Sullivan, A. P., A. S. Holden, L. A. Patterson, G. R. McMeeking, S. M. Kreidenweis, W. C. Malm, W. M. Hao, C. E. Wold, and J. L. Collett Jr. (2008), A method for smoke marker measurements and its potential application for determining the contribution of biomass burning from wildfires and prescribed fires to ambient PM_{2.5} organic carbon, *J. Geophys. Res.*, 113, D22302, doi:10.1029/2008JD010216.

1. Introduction

[2] One of the major sources of organic carbon aerosol is biomass burning. Biomass burning smoke from wildfires and prescribed fires can have a significant impact on PM_{2.5} concentrations, affecting air quality from local to regional and global scales. This smoke can also be a significant contributor in causing visibility impairment and affecting the Earth's radiation balance. In addition, there is evidence

in the Western U.S. for increased wildfires since the 1970s because of increased temperatures during the spring and summer [Westerling *et al.*, 2006]. The use of prescribed fire has also grown in recent decades in order to reduce large accumulations of wildland fuel resulting from many decades of an active fire suppression policy. In more populated areas, residential wood combustion, another form of biomass burning, can also be an important source of PM_{2.5}. This all suggests that it is important to be able to routinely apportion the contribution of biomass burning to the total organic carbon aerosol concentrations.

[3] One common approach to quantify the contribution of biomass burning to the total organic carbon aerosol is through the use of smoke marker measurements. In this approach, a compound produced as part of the smoke emitted is monitored as the plume is transported downwind and diluted. If the mass ratio of the marker to the

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total organic carbon is known at the source and the marker is conserved during transport, then a measurement of the marker's concentration at a downwind location can be used to determine the contribution of primary biomass smoke to the total organic carbon.

[4] This marker approach has been used by many investigators to apportion contributions of residential wood combustion [e.g., *Rogge et al.*, 1998] to urban particle concentrations [e.g., *Schauer et al.*, 1996; *Schauer and Cass*, 2000; *Fraser et al.*, 2003; *Rinehart et al.*, 2006]. However, few studies [e.g., *Hays et al.*, 2002; *Engling et al.*, 2006; *Mazzoleni et al.*, 2007] have attempted to characterize emissions by fuel types involved in wildfires or prescribed fires. Because of the lack of information available on emissions from wildfires and prescribed fires and the focus of most studies on urban settings, the results determined for the contribution of biomass burning are generally more skewed toward residential wood burning.

[5] One of the most commonly used smoke markers is levoglucosan, a sugar anhydride produced during the combustion of cellulose [*Simoneit et al.*, 1999]. Water-soluble potassium has also been used as a less specific indicator of biomass burning contributions to ambient aerosols [*Andreae*, 1983]. While water-soluble potassium is often routinely measured in aqueous extracts of filter-based aerosol samples using cation-exchange chromatography, analysis of levoglucosan can be much more challenging.

[6] Traditionally, levoglucosan in aerosol samples is extracted and analyzed using a multi-step, labor-intensive procedure [*Nolte et al.*, 2001; *Hays et al.*, 2002; *Zdrahal et al.*, 2002; *Simpson et al.*, 2004]. In the first steps, the filters are typically extracted in one or two organic solvents and then the extracts are concentrated. The concentrated extract is next chemically derivatized by use of a silylating reagent to create silylestere for levoglucosan and other compounds related to biomass burning (for example, mannosan and galactosan). In the final step, the derivatized sample is analyzed by Gas Chromatography/Mass Spectrometry (GC/MS). Overall, this analysis is quite labor intensive and expensive because of the solvents, reagents, and instrumentation needed. Therefore these analyses are generally conducted only for selected filter samples from special studies or on composited filter samples.

[7] All this information suggests there is a need for two things in order to be able to obtain a better determination for the contribution of wildfires and prescribed fires to the total organic carbon aerosol. One is an inexpensive and robust way to measure smoke marker compounds. Basically, there is a need for a method to measure smoke markers that could be applied on a routine basis. The second is source profile information about smoke markers from relevant fire types (i.e., emission information from fuels known to be involved in prescribed fires and wildfires).

[8] In order to address the first need, an inexpensive and robust technique that could be used for routine sampling has been developed for measuring concentrations of levoglucosan and other carbohydrates in collected aerosol samples. This technique couples high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD). This approach offers numerous advantages, including extraction of the filter directly in water, the ability to directly analyze the filter extract for levoglucosan, and

the use of ion chromatography (IC), an analytical platform already in widespread use by aerosol monitoring networks for analysis of the major inorganic aerosol species. Unlike GC/MS this method does not detect other classes of biomass burning tracers such as resin acids or methoxyphenols or provide mass spectra that can identify other known source markers. This technique has previously been applied to studies of biomass combustion contributions to fine particles in urban and rural settings as well as to source samples [*Gao et al.*, 2003; *Gorin et al.*, 2006; *Engling*, 2006; *Engling et al.*, 2006; *Puxbaum et al.*, 2007].

[9] The second need was addressed in the Fire Lab at Missoula Experiment (FLAME). This was a multi-investigator study designed to collect chemical, physical, and optical property information about smoke by conducting a series of burn experiments at the United States Forest Service Fire Science Laboratory (FSL) in Missoula, MT. The goal was to generate smoke source profiles that can be used to assess the contribution of wildfires and prescribed fires to the total organic carbon aerosol concentrations. With this in mind, fuels from key fire-prone areas, such as the Western and Southeastern U.S., were tested during FLAME I (May–June 2006) and FLAME II (May–June 2007).

[10] In this paper, the application of an alternative method to measure levoglucosan, along with measurements of water-soluble potassium, organic carbon (OC), and elemental carbon (EC), to the source samples collected during FLAME I and II will be shown (i.e., the emission information). Additional analysis of this data will be discussed to show how these measurements can inform a better determination of the impact of biomass burning.

2. Methods

2.1. Particulate Collection

[11] To collect ambient particles onto quartz filters for off-line analysis a Thermo Anderson Hi-Volume Air Sampler was used. A Hi-Volume Sampler was used so that the filter samples collected could be shared among multiple investigators. All samples were collected during the FLAME I and II experiments conducted at the FSL in Missoula, MT. The FSL has a 12.5-m width \times 12.5-m length \times 22-m height combustion chamber where test burns of fuels relevant to prescribed fires and wildfires can be performed. More details about the facility itself can be found in *Christian et al.* [2004].

[12] Two different types of burns were conducted during both FLAME campaigns: stack and chamber burns. In stack burns, the Hi-Volume Sampler was located on a measurement platform approximately 16 m above the ground, where the Hi-Volume Sampler was connected directly to the stack via a sampling port designed by FSL. The fuel was burned directly under the 1.5-m diameter stack, and the emissions were forced up the stack because of the positive air pressure inside the chamber that was vented through the stack. Stack burns were generally short in duration and lasted anywhere from a few to 30 minutes. Therefore stack burns were generally conducted in duplicate or triplicate for a particular fuel and one Hi-Volume filter sample was collected across the whole series of replicates.

[13] For chamber burns, the fuel bed was placed about 5 m from the stack and the smoke was allowed to completely fill

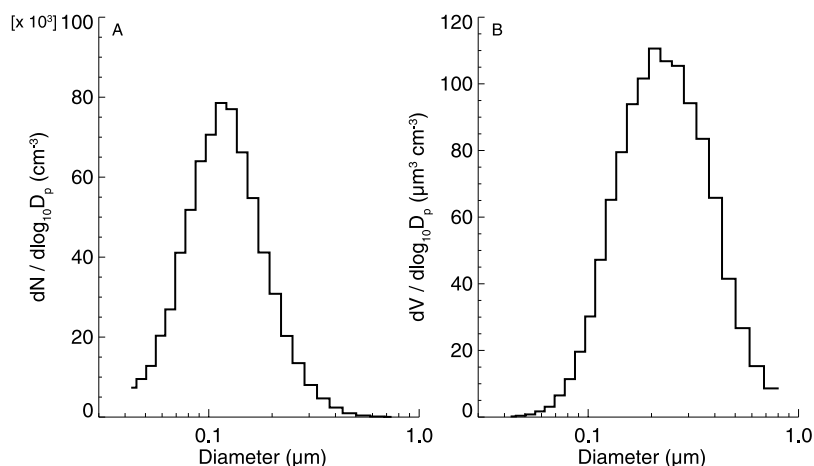


Figure 1. Example of a typical (A) number and (B) volume distribution for one of the burns conducted during the FLAME studies. The data shown is a 10-minute scan collected using a TSI 3080 Long Differential Mobility Analyzer and TSI 3785 Water-Condensation Particle Counter. Particles were not dried, but relative humidity was below 30 to 40%.

the entire burn chamber (i.e., there was no stack flow during these burns). The Hi-Volume Sampler was placed on the floor of the chamber and collected a sample directly from the smoke that filled the entire burn chamber. Chamber burns were generally longer in duration than the stack burns, lasting anywhere from 1.5 to 2 hours. One Hi-Volume filter sample was collected across each chamber burn.

[14] For both types of burns the fuel bed continuously sat on top of a balance, allowing for determination of the total amount of fuel consumed. During FLAME I the burns were ignited by either a butane lighter or propane torch. To try and allow for more even heating during FLAME II, this was switched to having the fuel itself sit on top of heating tapes wetted with ethanol. At the beginning of a burn a variac, which controlled the heating of the tapes, was turned on until the fuel was ignited. No noticeable differences were observed in parameters reported here as a result of making this switch and therefore data collected from both ignition methods will be presented.

[15] The Hi-Volume Sampler used for both the stack and chamber burns draws ambient air at nominally $1.13 \text{ m}^3/\text{min}$ through a two-filter assembly to isolate the ambient aerosol into two size groups, particles with aerodynamic diameters greater than or less than $2.5 \text{ }\mu\text{m}$. An impactor in combination with a slotted filter collects the particles with aerodynamic diameters greater than $2.5 \text{ }\mu\text{m}$, followed by a $20.3 \text{ cm} \times 25.4 \text{ cm}$ filter to collect the $\text{PM}_{2.5}$. Previous filter-based work [Gorin *et al.*, 2006; Herckes *et al.*, 2006] has demonstrated that most of the ambient smoke is found in submicron particles. As can be seen in Figure 1, size distribution measurements made during FLAME I and II also show this. Therefore only the $\text{PM}_{2.5}$ filters were analyzed. The quartz filters were wrapped in aluminum foil and pre-baked in an oven over a 36-hour period. In the first 12-hours the temperature of the oven was ramped up to 550°C and for the remaining 24-hours the oven cooled naturally to prevent the filters from absorbing water vapor. After baking, the aluminum foil wrapped filters were stored in plastic bags in a sealed box until loaded into the filter holder. The filter holder was cleaned with isopropanol before filter loading. After sampling the filters were stored

in a freezer. Typically, two 25 mm diameter punches of the $\text{PM}_{2.5}$ filter were extracted in 5 ml of deionized water (DI Water) in a Nalgene Amber HDPE bottle, sonicated with heat [Baumann *et al.*, 2003] for 1.25 hours, and then filtered using a $0.2 \text{ }\mu\text{m}$ PTFE syringe filter to remove any quartz filter fibers. The liquid extracts were analyzed for the carbohydrates the same day the filters were extracted. They were stored at room temperature in the amber bottles and were not refrigerated until all analyses being performed on the liquid extracts were complete.

[16] Additionally, six-day integrated ambient Hi-Volume quartz filter samples were collected in Phoenix, AZ, Tonto National Monument, AZ, Grand Canyon, AZ, and Rocky Mountain National Park, CO as part of the IMPROVE Radiocarbon Study from June to August 2005 [Schichtel *et al.*, 2008]. These samples were collected with the same Hi-Volume Samplers used in the FLAME studies. The filters were extracted in the same manner as the FLAME samples with the exception that ten 25-mm diameter punches of the $\text{PM}_{2.5}$ filter were extracted in 20 ml of DI Water.

[17] Because of the high flowrate of a Hi-Volume Sampler, the samples collected from them were not denuded. This makes them susceptible to positive artifacts from organic vapor adsorption to the collected aerosol particles and quartz filter fibers. In order to assess this, a comparison between the Hi-Volume samples and denuded on-line measurements can be made. Figure 2 compares the OC from the Hi-Volume filter samples to co-located on-line measurements of OC (both measured using a Sunset Labs EC/OC analyzer as described below in section 2.2) made during the chamber burns from both FLAME I and II. Observed differences between these methods could potentially be due to positive artifacts, negative artifacts, sample flowrates, $\text{PM}_{2.5}$ cut sizes, and particle losses in sampling trains. On the basis of the linear regression slope shown in Figure 2 there is very good agreement between the two measurements, suggesting the influence from at least positive artifacts may be quite small. Semi-volatile organic compounds associated with aerosol particles may be partly lost from the Hi-Volume filter samples. Possible interfer-

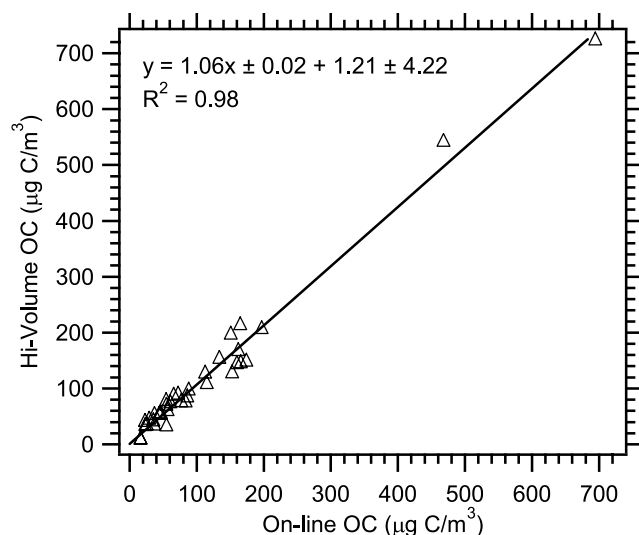


Figure 2. Comparison of the non-denuded Hi-Volume filter OC and the denuded on-line OC. Both measurements were made using a Sunset EC/OC analyzer. Uncertainties with the least square regression are one standard deviation.

ences from the filter's background were found to be negligible on pre-baked Hi-Volume quartz filters set aside as blanks during both types of burns.

2.2. Measurement Approach

[18] Each of the Hi-Volume filters collected was analyzed individually for $PM_{2.5}$ levoglucosan, water-soluble potassium (K^+), OC, and EC. These analyses are described below. The levoglucosan method is described in detail since a modified version of the original method discussed in *Engling et al.* [2006] is being used here. The modifications made to the levoglucosan method were done to help in shortening the run time and had no effect on the response for levoglucosan.

[19] After each filter was extracted the aqueous sample was analyzed for levoglucosan (and various other carbohydrates) using high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) and for K^+ using IC.

[20] The levoglucosan measurement was made using a Dionex DX-500 series ion chromatograph with a Dionex GP-50 gradient pump and Dionex ED-50 electrochemical detector operating in integrating amperometric mode using waveform A. The electrochemical detector is connected to a Dionex ED-50/ED-50A electrochemical cell, which contains a "standard" gold working electrode and pH-Ag/AgCl (silver/silver chloride) reference electrode.

[21] In HPAEC-PAD once the analytes are eluted from the column they enter an electrochemical cell where they are electroanalytically oxidized on the surface of a gold working electrode by applying a positive potential. However, if this continued to happen, the electrode surface would be poisoned by the oxidation products. To prevent this from happening, an entirely different potential is applied to clean the surface of the electrode. PAD is essentially the repeated application of this whole series of potentials, referred to as a waveform.

[22] The eluents are DI Water and 200 mM sodium hydroxide (NaOH). In order to minimize carbonate ions in the eluents, which can be a potential interference, the eluents are continuously degassed with ultra high purity helium. In addition, the 200 mM NaOH is made from 50% w/w NaOH and allowed to equilibrate overnight before using for analysis.

[23] Separation was completed on Dionex CarboPac PA-10 guard (4×50 mm) and analytical (4×250 mm) columns. Each run has an eluent flowrate of 0.5 ml/min and takes approximately 54 minutes. For the first 10 minutes isocratic elution with 18 mM NaOH is performed to detect anhydrosugars such as levoglucosan and mannosan. Next, a linear gradient from 18 to 60 mM NaOH is run for 14 minutes to detect sugars such as galactose, mannose, and glucose. Since carbonate ions can bind to the active sites of the resin and affect the chromatography, the column is cleaned for 14 minutes with 180 mM NaOH. Finally, a 16-minute re-equilibration step is performed to return to the starting conditions. Generally a sample volume of 50 μ L is injected onto the column.

[24] The method is capable of readily separating a mix of common carbohydrates, including sugars glucose and mannose along with the anhydrosugars that are recognized as important chemical constituents of wood smoke. We would point out that this method is not capable of separating the sugar alcohols (for example, arabitol and mannitol) from the anhydrosugars. This means that arabitol can potentially overlap with levoglucosan and mannitol with mannosan. However, for these source samples this was found not to be an issue as we have additionally run them on a Dionex CarboPac PA-1 column which can completely resolve mannitol and mannosan and partially resolve arabitol and levoglucosan [*Caseiro et al.*, 2007]. Sugar alcohols could be a factor in ambient samples as both have been detected as indicators of fungal spores for samples collected in Vienna, Austria [*Bauer et al.*, 2008a, 2008b].

[25] A sample calibration chromatogram using the CarboPac PA-10 column method described is shown in Figure 3. The anhydrosugars are detected in the first ten minutes and the sugars at around 25 minutes. Calibrations are linear over a wide concentration range and the method is extremely sensitive. Measurements of levoglucosan by this approach have been compared with measurements by both GC/MS and LC/MS (liquid chromatography/mass spectroscopy) with good results [*Engling et al.*, 2006]. The limit of detection (LOD) for the various carbohydrates is less than approximately 0.10 μ g/ m^3 (or 2.26 μ g). It should be noted that all the LODs listed in this section are for only this particular data set and were calculated assuming a flowrate of 1.13 m^3 /min and sampling time of 20 min, the average sampling time during stack burns. Lower LODs have easily been achieved for all the measurements with an increased integration time more typical of ambient filter samples.

[26] Water-soluble potassium was measured in the liquid extract using a Dionex DX-500 series ion chromatograph with a Dionex CD-20 conductivity detector, Dionex IP-20 isocratic pump, and self-regenerating cation SRS-ULTRA suppressor. A Dionex IonPac CS12A analytical (3×150 mm) column, with a sample volume injection of 25 μ L, was used to achieve separation of the common inorganic

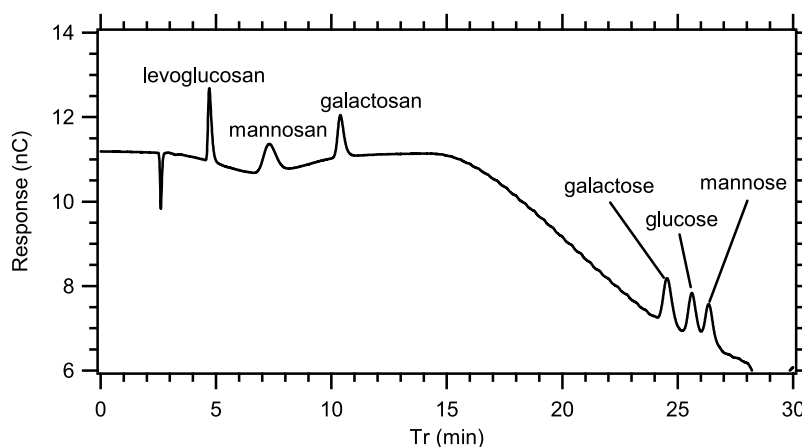


Figure 3. Calibration chromatogram for the injection of a mixed carbohydrate standard using the HPAEC-PAD method, where Tr is retention time.

cations in 15 minutes. A 20-mM methanesulfonic acid eluent at a flowrate of 0.5 ml/min was used. The LOD for water-soluble potassium is about $0.36 \mu\text{g}/\text{m}^3$.

[27] Organic and elemental carbon were determined using a Sunset Labs EC/OC semi-continuous analyzer (Forest Grove, Oregon). It quantifies OC and EC carbon mass by thermal/optical transmission (TOT) [Birch and Cary, 1996]. The instrument was operated following the NIOSH Method 5040 [Eller and Cassinelli, 1996]. Each filter was analyzed by running the analyzer in off-line mode. The average concentration determined from two 1.4 cm^2 filter punches was used. The LODs for OC and EC in a 20 minute Hi-Volume sample are approximately $6.0 \mu\text{g C}/\text{m}^3$ and $1.0 \mu\text{g C}/\text{m}^3$, respectively. For the on-line measurements, the instrument was run continuously with a 20-minute collection time. The LODs for the on-line measurements are $0.2 \mu\text{g C}/\text{m}^3$ and $0.5 \mu\text{g C}/\text{m}^3$ for OC and EC, respectively.

3. Results and Discussion

[28] During FLAME I and II approximately 252 burns involving 30 different fuels were tested. These experiments included either burning a single component of a fuel (for example, branches only), a mixture of components of a fuel (for example, leaves and branches together), or a mixture of more than one type of fuel. The data analysis presented in sections 3.1 and 3.2 focuses mainly on the experiments involving the burning of a single fuel component.

[29] Table 1 lists the various burn experiments performed along with the observed carbohydrate, water-soluble potassium, OC, and EC concentrations. Levoglucosan was measured in all the fuels tested. The anhydrosugars appear in higher concentrations than the sugars, with levoglucosan being the dominant carbohydrate observed. Water-soluble potassium was observed in most of the burns. At times water-soluble potassium could be found in higher concentrations than levoglucosan. OC was observed in all the fuels tested; however, EC was not. Although generally OC concentrations were much higher than EC concentrations, there were some fuels that emitted considerable amounts of EC (for example, Chamise). Although the absolute concentrations are being shown, it should be noted that the focus

should be on the relative amounts of the different species since the absolute concentration can depend on the amount of fuel burned, the burn rate, and for stack burns potentially the flowrate of air up the stack. Therefore Table 1 also contains data for the total mass of fuel burned, the stack and Hi-Volume Sampler flowrates, and sampling time for each of the burns so the ratios of any of the measured species to the fuel burned could be examined. The work presented here in the next section will, however, focus on the ratios of levoglucosan to OC and water-soluble potassium.

3.1. Correlation of Levoglucosan to OC and Water-Soluble Potassium

[30] Figure 4a shows levoglucosan vs. OC on a carbon mass basis for the individual fuel component burns presented in Table 1. Table 2 lists the levoglucosan to OC ratios for this subset of data. This subset of data includes 73 burns, 7 of which are for grasses, 10 for branches, 7 for duffs, 10 for needles, 7 for straw, and 32 for leaves.

[31] There is an overall correlation between levoglucosan and OC ($R^2 = 0.68$) as can be seen in Figure 4a. Although these two measurements are correlated, the fraction of OC made up of levoglucosan is actually small, as indicated by a slope forced through zero of $0.023 \mu\text{g C}/\mu\text{g C}$ ($0.052 \mu\text{g levoglucosan}/\mu\text{g OC}$).

[32] The data are segregated by fuel component burned in Figure 4b. A pattern in the levoglucosan to OC ratio emerges. The levoglucosan and OC are highly correlated for branches, straw, needles, and leaves, with branches generally having the highest average ratio. However, for duffs and grasses the levoglucosan is poorly correlated with the OC.

[33] The observed pattern in levoglucosan to OC ratios for fuel components is similar to the cellulose to hemicellulose ratio presented in a review paper by Hoch [2007] (see Figure 1 of this reference). While hemicellulose contents of these biomass components are similar, cellulose contents vary. Components with higher cellulose content (for example, branches) are found to yield higher levoglucosan to OC ratios. This is not surprising since levoglucosan is a product of thermal degradation of cellulose.

[34] Although there is a pattern in the levoglucosan to OC ratio based on fuel component, as can be seen in Figure 5

Table 1. Carbohydrate Concentrations, Water-Soluble Potassium Concentration, OC Concentration, Stack Flowrate, Hi-Volume Sampler Flowrate, Sampling Time, and Mass of Fuel Burned for the Various Burn Experiments, Where ND = Concentration not Detected or Stack Flowrate Could not be Determined, I = Measured During FLAME I, II = Measured During FLAME II, s = Stack Burn, c = Chamber Burn, G = Grass, B = branches, D = Duff, N = Needles, S = Straw, L = Leaves, and NL = Needle Litter^a

Fuel	Levoglucosan ($\mu\text{g}/\text{m}^3$)	Mannosan ($\mu\text{g}/\text{m}^3$)	Galactosan ($\mu\text{g}/\text{m}^3$)	Galactose ($\mu\text{g}/\text{m}^3$)	Galactose ($\mu\text{g}/\text{m}^3$)	Glucose ($\mu\text{g}/\text{m}^3$)	Mannose ($\mu\text{g}/\text{m}^3$)	Water-Soluble Potassium ($\mu\text{g}/\text{m}^3$)	OC ($\mu\text{g C}/\text{m}^3$)	EC ($\mu\text{g C}/\text{m}^3$)	Stack Flowrate (m^3/min)	Hi-Volume Flowrate (m^3/min)	Sampling Time (min)	Mass Burned (g)	Comment ^b
Alaskan Duff	12.59	11.60	7.07	ND	ND	ND	ND	2.20	126.42	ND	ND	1.13	118.00	58.0	II, c, D
	14.67	6.32	2.11	ND	ND	ND	ND	ND	95.89	ND	ND	1.10	88.00	19.4	II, c, D
Black Needle Rush (FL)	23.71	17.79	10.46	ND	ND	ND	ND	1.09	182.14	ND	414.6	1.08	38.88	181.7	II, s, D
	14.46	14.64	8.04	ND	ND	ND	ND	1.12	166.45	ND	ND	1.22	120.00	96.1	I, c, D
Black Spruce (AK)	6.66	0.51	0.50	ND	ND	ND	ND	12.21	83.57	3.27	ND	1.10	88.00	45.5	II, c, G
Black Spruce, dried (AK)	5.64	1.35	0.42	ND	ND	ND	ND	1.05	77.29	24.11	ND	1.08	118.00	62.5	II, c, N
Black Spruce, fresh (AK)	25.53	8.32	2.89	ND	ND	0.12	ND	4.66	309.40	26.87	336.0	1.15	28.00	438.8	II, s, N
Ceanothus (CA)	28.32	6.72	2.80	ND	ND	0.19	ND	4.37	359.43	3.67	339.0	1.15	18.00	469.7	II, s, N
Chamise (CA)	9.95	0.68	0.75	ND	ND	0.20	ND	75.65	184.15	29.06	436.8	1.18	14.00	442.3	II, s, L
	7.64	0.34	0.65	ND	ND	ND	ND	20.10	147.69	5.75	ND	1.25	119.00	181.4	I, c, L
Chamise, dried (CA)	1.60	0.22	0.17	ND	ND	0.17	ND	19.86	43.60	43.98	ND	1.10	88.00	95.4	II, c, L
	8.16	0.79	0.84	ND	ND	0.17	ND	56.77	189.76	49.16	397.8	1.16	15.00	328.0	II, s, L
Chamise, fresh (CA)	20.32	0.81	2.89	ND	ND	0.19	ND	46.36	320.15	5.18	ND	1.03	30.35	684.0	I, c, L
	1.97	0.34	0.19	ND	ND	ND	ND	26.92	44.66	61.98	ND	1.22	125.00	186.2	I, c, L
Chamise, dried (CA)	6.81	0.97	0.61	ND	ND	ND	ND	1.67	64.90	ND	375.6	1.03	60.97	506.9	I, s, B
Chamise, fresh (CA)	21.98	0.93	3.48	0.06	ND	ND	ND	35.37	380.53	ND	395.4	1.03	36.04	630.1	I, s, L
Chamise, fresh (CA)	6.19	1.00	0.60	ND	ND	ND	ND	2.36	60.22	ND	387.0	1.03	59.19	571.1	I, s, B
Fir, dried (MT)	4.76	1.64	1.24	ND	ND	ND	ND	0.70	180.22	ND	ND	1.19	36.00	99.2	II, s, N
Fir, dried (MT)	12.51	2.96	3.34	ND	ND	0.12	ND	1.78	172.83	ND	437.4	1.16	16.00	196.0	II, s, B
Fir, fresh (MT)	30.84	8.94	7.44	ND	ND	0.69	0.10	2.95	631.78	ND	337.2	1.16	46.00	325.0	II, s, N
Gallberry (MS)	1.53	ND	0.13	ND	ND	ND	ND	8.69	52.43	51.89	337.8	1.10	88.00	44.7	II, c, L
Grass, dried (MT)	13.52	0.62	1.13	ND	ND	0.17	ND	57.08	370.70	425.20	ND	1.02	12.50	401.2	II, s, L
	8.73	0.62	0.74	ND	ND	ND	ND	29.34	219.77	10.89	417.6	0.98	16.42	126.2	I, s, G
Grass, fresh (MT)	4.77	0.52	0.51	ND	ND	0.11	ND	58.51	225.44	ND	404.4	0.98	32.70	243.6	I, s, G
Hickory (NC)	10.83	1.14	2.21	ND	ND	0.18	ND	27.22	290.35	12.38	336.0	1.13	11.00	193.9	II, s, L
Juniper (UT)	0.78	0.23	0.16	ND	ND	ND	ND	14.56	52.70	182.06	ND	1.13	112.00	197.3	I, c, L
Kudzo (GA)	18.04	7.57	1.72	ND	ND	0.23	ND	16.04	711.31	ND	331.2	1.10	11.00	173.4	II, s, L
Lodgepole Pine Needle Duff (MT)	9.87	5.86	2.25	ND	ND	ND	ND	ND	73.55	ND	404.4	1.01	88.61	455.9	I, s, D
Lodgepole Pine, dead/small (MT)	9.74	2.68	1.34	ND	ND	0.26	ND	0.70	52.39	54.60	433.8	1.01	42.75	675.2	I, s, B
Lodgepole Pine, fresh (MT)	12.70	8.97	4.88	ND	ND	0.26	ND	5.53	240.20	1.14	430.2	1.01	94.47	504.3	I, s, N
Longleaf Pine (MS)	25.01	14.25	5.19	ND	ND	0.13	ND	7.19	345.94	14.67	353.4	1.12	43.00	401.9	II, s, N
Manzanita (CA)	27.54	1.13	2.27	ND	ND	0.20	ND	26.02	315.27	21.06	436.2	1.16	16.00	471.2	II, s, L
Manzanita, dried (CA)	4.74	0.38	0.38	ND	ND	ND	ND	15.46	59.14	47.70	ND	1.26	110.00	192.8	I, c, L
	15.08	0.28	5.16	ND	ND	0.17	ND	6.90	476.74	2.16	377.4	1.01	87.45	685.5	I, s, L
Manzanita, fresh (CA)	14.49	0.30	3.15	ND	ND	0.13	ND	7.28	294.83	ND	ND	1.03	73.67	547.2	I, s, L
Manzanita, fresh (CA)	24.03	3.72	4.25	ND	ND	0.16	ND	6.21	213.46	ND	398.4	1.03	30.13	673.1	I, s, B
Oak (NC)	24.57	1.98	4.53	ND	ND	0.17	ND	24.80	394.18	14.99	353.4	1.13	11.50	218.2	II, s, L
Palmetto (FL)	3.35	0.34	0.39	ND	ND	ND	ND	126.30	86.69	27.72	393.6	1.03	26.57	693.5	I, s, L
Palmetto (FL coastal)	5.03	0.48	0.27	ND	ND	ND	ND	14.02	75.17	16.75	ND	1.22	125.00	187.0	I, c, L
	24.00	1.39	1.03	ND	ND	0.18	ND	37.89	323.26	38.27	338.4	1.10	14.50	469.6	II, s, L
Palmetto (FL inland)	0.62	0.12	ND	ND	ND	ND	ND	6.85	25.78	34.53	ND	1.13	118.00	91.0	II, c, L
Palmetto (MS)	19.31	1.37	1.50	ND	ND	0.14	ND	22.66	417.91	63.66	ND	1.08	15.50	451.4	II, s, L
Phragmites (LA)	28.83	1.73	1.80	ND	ND	0.17	ND	18.81	361.24	23.02	345.6	1.13	120.00	458.5	II, s, L
	2.35	0.18	0.11	ND	ND	ND	ND	4.86	40.55	13.49	ND	1.09	14.00	87.5	II, c, L
	16.85	0.92	1.59	ND	ND	0.33	0.14	4.44	224.08	4.29	355.2	1.13	10.50	101.8	II, s, G

Table 1. (continued)

Fuel	Water-Soluble										Stack Flowrate (m ³ /min)	Hi-Volume Flowrate (m ³ /min)	Sampling Time (min)	Mass Burned (g)	Comment ^b
	Levoglucoosan (μg/m ³)	Mannosan (μg/m ³)	Galactosan (μg/m ³)	Galactose (μg/m ³)	Glucose (μg/m ³)	Mannose (μg/m ³)	Potassium (μg/m ³)	OC (μg C/m ³)	EC (μg C/m ³)	Stack Flowrate (m ³ /min)					
Ponderosa Pine Duff	8.41	4.37	2.27	ND	ND	ND	0.37	110.24	1.40	404.4	1.01	82.53	456.0	I, s, D	
Ponderosa Pine, dead/large (MT)	11.94	11.97	4.49	ND	ND	ND	0.70	195.98	1.12	359.4	1.30	119.00	107.2	I, c, D	
Ponderosa Pine, dead/small (MT)	6.35	1.80	1.41	ND	ND	ND	0.57	49.86	38.05	359.4	1.01	64.19	706.3	I, s, B	
Ponderosa Pine, fresh (MT)	5.41	1.26	1.09	ND	ND	ND	0.61	69.92	57.11	385.2	1.01	50.38	385.5	I, s, B	
Ponderosa Pine, fresh/large (MT)	8.73	2.10	1.44	ND	ND	ND	1.66	100.60	ND	362.4	1.01	124.03	612.1	I, s, N	
Ponderosa Pine, fresh/small (MT)	7.80	1.84	1.06	ND	ND	ND	0.78	87.58	ND	345.6	1.00	44.67	212.2	I, s, B	
Puerto Rican Fern	11.80	11.12	5.04	ND	ND	ND	2.04	334.00	ND	356.4	1.00	57.00	497.3	I, s, B	
Puerto Rican Mixed Woods	10.13	9.17	1.46	ND	ND	ND	7.46	144.63	8.34	ND	1.27	127.00	173.9	I, c, L	
Rhododendron (NC)	7.30	0.62	0.26	ND	ND	ND	1.47	56.79	5.88	ND	1.25	130.00	83.8	I, c, B	
Rice Straw (Taiwan)	6.89	0.57	0.55	ND	ND	ND	3.94	68.38	6.88	ND	1.10	118.00	94.8	II, c, L	
	1.97	0.16	0.15	ND	0.02	ND	6.84	33.34	ND	429.6	1.13	118.50	79.6	II, c, S	
	28.76	1.53	2.30	0.12	0.25	0.11	39.49	550.67	ND	400.2	1.10	13.73	438.0	II, s, S	
	33.02	0.60	3.43	ND	0.16	ND	36.29	363.69	ND	435.0	1.01	23.79	514.3	I, s, S	
	12.02	0.85	1.00	ND	0.13	0.11	25.26	182.01	10.04	ND	1.03	13.00	202.0	I, s, S	
	25.69	0.76	1.77	ND	0.17	0.13	21.09	290.97	ND	ND	1.03	11.58	164.3	I, s, S	
	25.05	0.81	1.84	ND	0.16	0.14	38.58	321.74	ND	413.4	1.03	10.50	215.8	I, s, S	
	7.44	0.15	0.40	ND	ND	ND	25.66	74.59	1.63	ND	1.32	116.00	172.9	I, c, S	
Sage (MT)	28.33	6.51	4.59	0.11	0.28	0.11	96.33	690.01	19.73	398.4	1.08	19.03	452.7	II, s, L	
Sage (UT)	4.57	1.23	0.77	ND	ND	ND	26.20	308.32	5.27	471.6	1.16	9.00	122.0	II, s, L	
Saw Grass (LA)	18.88	1.64	1.81	ND	0.17	ND	301.98	462.45	57.45	407.4	1.12	11.25	273.2	II, s, G	
Southern Pine, dried	10.53	6.42	1.34	ND	ND	ND	1.07	107.42	7.29	ND	1.27	117.00	72.8	I, c, N	
Titi (FL)	6.40	0.62	0.55	ND	0.13	ND	26.84	126.61	43.37	ND	1.15	16.00	255.8	II, s, L	
Turkey Oak (NC)	52.87	3.60	12.48	ND	0.18	ND	60.72	1124.38	50.07	427.2	1.08	20.00	485.6	II, s, L	
Wax Myrtle (FL)	7.07	1.59	1.23	ND	ND	ND	24.93	126.79	16.60	351.6	1.30	125.00	152.9	I, c, L	
Wax Myrtle (MS)	18.92	1.34	2.16	ND	0.16	ND	41.27	320.92	12.29	ND	1.13	18.50	336.1	II, s, L	
White Spruce (AK)	7.31	1.35	0.43	ND	ND	ND	3.14	55.07	ND	ND	1.13	88.00	36.9	II, c, N	
Wiregrass (FL)	7.98	0.36	0.21	ND	ND	ND	0.84	39.75	2.62	328.2	1.10	88.00	44.7	II, c, G	
Wiregrass (MS)	20.36	0.52	0.41	ND	0.12	ND	2.25	118.48	11.59	ND	1.10	19.00	207.6	II, s, G	
Chamise (CA)	2.66	0.24	0.42	ND	ND	ND	29.85	73.42	35.16	403.8	1.01	32.47	690.5	I, s, L, B	
Fir, dried (MT)	1.61	0.12	0.15	ND	ND	ND	20.82	31.60	64.11	ND	1.30	114.83	282.4	I, c, L, B	
	3.68	1.00	0.83	ND	ND	ND	0.46	98.58	ND	436.2	1.13	103.00	82.6	II, c, N, B	
	2.23	0.61	0.36	ND	ND	ND	1.96	86.66	ND	ND	1.13	88.00	23.5	II, c, N, B	
	6.34	1.90	1.87	ND	ND	ND	0.79	131.44	ND	388.2	1.13	56.00	201.0	II, s, N, B	
Fir, fresh (MT)	2.53	0.51	0.30	ND	ND	ND	6.84	57.03	27.46	ND	1.08	126.00	95.7	II, c, N, B	
	45.64	9.32	7.85	ND	0.84	0.12	9.50	675.45	2.95	ND	1.16	24.00	433.6	II, s, N, B	
Lodgepole Pine (MT)	13.40	12.32	6.03	ND	ND	ND	0.45	160.83	9.75	ND	1.03	105.96	610.9	I, s, NL	
Lodgepole Pine, dried (MT)	15.72	11.28	4.53	ND	ND	ND	0.58	212.63	14.33	ND	1.25	93.00	147.5	I, c, N, B	
Ponderosa Pine (MT)	21.05	14.15	6.17	ND	0.12	ND	1.20	312.11	6.11	405.0	1.00	52.77	682.8	I, s, NL	
	41.52	40.15	14.98	ND	0.17	ND	1.91	678.81	ND	420.6	1.01	30.34	634.9	I, s, NL	
	23.48	17.62	6.23	ND	0.11	ND	1.35	285.23	6.39	415.2	1.01	44.44	655.3	I, s, NL	
	25.15	18.22	8.13	ND	0.10	ND	1.12	335.40	1.55	ND	1.01	52.02	636.2	I, s, NL	
	25.74	18.13	8.11	ND	ND	ND	0.93	364.61	2.69	412.8	1.01	50.45	668.0	I, s, NL	
Ponderosa Pine, dried (MT)	10.48	5.58	1.54	ND	ND	ND	0.61	143.42	8.39	ND	1.33	117.25	103.9	I, c, N, B	
	19.41	23.20	9.66	ND	0.18	ND	0.71	541.06	45.38	ND	1.30	94.67	184.6	I, c, N, B	

Component Mixtures

Table 1. (continued)

Fuel	Levoglucosan ($\mu\text{g}/\text{m}^3$)	Mannosan ($\mu\text{g}/\text{m}^3$)	Galactosan ($\mu\text{g}/\text{m}^3$)	Galactose ($\mu\text{g}/\text{m}^3$)	Glucose ($\mu\text{g}/\text{m}^3$)	Mannose ($\mu\text{g}/\text{m}^3$)	Potassium ($\mu\text{g}/\text{m}^3$)	Water-Soluble OC ($\mu\text{g}/\text{m}^3$)	EC ($\mu\text{g}/\text{m}^3$)	Stack Flowrate (m^3/min)	Hi-Volume Flowrate (m^3/min)	Sampling Time (min)	Mass Burned (g)	Comment ^b
Black Needle Rush and Salt Marsh Grass (NC)	57.59	3.07	7.49	ND	0.36	ND	151.08	684.55	11.08	424.8	1.10	16.02	458.9	II, s, G, G
Hickory and Oak (NC)	4.96	0.51	0.84	ND	ND	ND	15.21	115.03	10.52	ND	1.16	125.00	93.2	II, c, L, L
Longleaf Pine and Wiregrass	17.17	1.23	3.06	0.20	0.22	ND	15.43	334.19	ND	ND	1.15	13.00	236.7	II, s, L, L
Longleaf Pine and Wiregrass (MS)	12.50	10.10	2.75	ND	ND	ND	8.39	189.75	8.84	317.4	1.13	133.00	114.0	II, c, N, G
Palmetto and Gallberry (MS)	18.45	4.19	1.79	ND	0.11	ND	2.54	137.62	ND	336.6	1.14	58.50	399.6	II, s, N, G
Rabbitbrush and Sage (UT)	36.17	2.87	3.61	0.21	0.28	ND	17.48	500.02	ND	ND	1.13	28.50	443.4	II, s, L, L
	2.10	0.40	0.21	ND	ND	ND	58.52	53.01	111.70	ND	1.23	60.00	182.8	I, c, L, L

^aThe table is separated into three sections: individual component burns, burns involving a mixture of components, and burns involving a mixture of different types of fuels. If available, in parenthesis by the fuel name is the location from where the fuel was obtained.
^bFor the individual component burns there are a total of 7 for grasses, 10 for branches, 7 for duffs, 10 for needles, 7 for straw, and 32 for leaves. For the burns involving a mixture of components there are a total of 2 for leaf and branch mixtures, 8 for needle and branch mixtures, and 6 for needle litter. For the burns involving a mixture of different fuels there are a total of 1 with two types of grasses, 4 with two types of leaves, and 2 with needles mixed with grasses.

and Table 2, the majority of the ratios for all fuels fall between 0.005 and 0.060 $\mu\text{g C}/\mu\text{g C}$ (0.011 and 0.135 μg levoglucosan/ μg OC), with an average ratio and standard deviation of $0.031 \pm 0.017 \mu\text{g C}/\mu\text{g C}$ ($0.070 \pm 0.038 \mu\text{g}$ levoglucosan/ μg OC). When comparing this range of ratios to literature values, it appears that a larger range in ratios is generally observed for residential wood burning. For example, Schauer *et al.* [2001], which focused on residential wood burning, found a range of ratios for the three fuels tested of 0.060 to 0.230 $\mu\text{g C}/\mu\text{g C}$ (0.135 μg levoglucosan/ μg OC). Fine *et al.* [2004], which also focused on residential wood burning, found ratios that ranged from 0.004 to 0.148 $\mu\text{g C}/\mu\text{g C}$ (0.010 to 0.334 μg levoglucosan/ μg OC) when testing 10 fuels. However, for a study more similar to

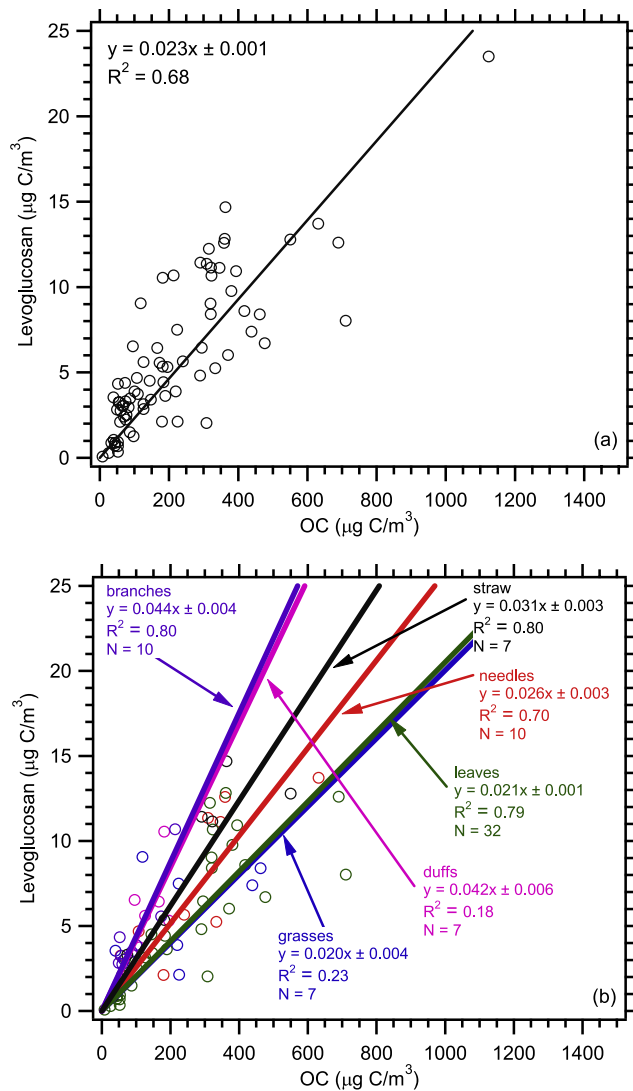


Figure 4. Correlation between levoglucosan and OC on a carbon mass basis forced through zero for (a) all the data and (b) with the data segregated by fuel component for all the experiments involving the burning of a single component of fuel. Branches are in purple, straw in black, duffs in pink, needles in red, leaves in green, and grasses in blue. Uncertainties with the least square regression are one standard deviation. N indicates the number of samples analyzed for each of the six different fuel components burned.

Table 2. Levoglucosan to OC Ratios for all the Experiments Involving the Burning of an Individual Component of a Fuel^a

Fuel	Stack Levoglucosan/OC ($\mu\text{g levoglucosan}/\mu\text{g OC}$)	Chamber Levoglucosan/OC ($\mu\text{g levoglucosan}/\mu\text{g OC}$)	Stack Levoglucosan/OC ($\mu\text{g C}/\mu\text{g C}$)	Chamber Levoglucosan/OC ($\mu\text{g C}/\mu\text{g C}$)	Comment
Alaskan Duff	0.131	0.099, 0.153, 0.0878	0.058	0.044, 0.068, 0.039	D
Black Needle Rush (FL)		0.079		0.035	G
Black Spruce (AK)		0.072		0.032	N
Black Spruce, dried (AK)	0.083		0.037		N
Black Spruce, fresh (AK)	0.079		0.035		N
Ceanothus (CA)	0.054	0.052	0.024	0.023	L
Chamise (CA)	0.043	0.036, 0.045	0.019	0.016, 0.020	L
Chamise, dried (CA)	0.063		0.028		L
Chamise, dried (CA)	0.106		0.047		B
Chamise, fresh (CA)	0.059		0.026		L
Chamise, fresh (CA)	0.104		0.046		B
Fir, dried (MT)	0.027		0.012		N
Fir, dried (MT)	0.072		0.032		B
Fir, fresh (MT)	0.050		0.022		N
Gallberry (MS)	0.036	0.029	0.016	0.013	L
Grass, dried (MT)	0.041		0.018		G
Grass, fresh (MT)	0.020		0.009		G
Hickory (NC)	0.038		0.017		L
Juniper (UT)		0.016		0.007	L
Kudzo (GA)	0.025		0.011		L
Lodgepole Pine Needle Duff (MT)	0.135		0.060		D
Lodgepole Pine, dead/small (MT)	0.187		0.083		B
Lodgepole Pine, fresh (MT)	0.054		0.024		N
Longleaf Pine (MS)	0.072		0.032		N
Manzanita (CA)	0.088	0.081	0.039	0.036	L
Manzanita, dried (CA)	0.032		0.014		L
Manzanita, fresh (CA)	0.050		0.022		L
Manzanita, fresh (CA)	0.113		0.050		B
Oak (NC)	0.063		0.028		L
Palmetto (FL)	0.038	0.068	0.017	0.030	L
Palmetto (FL coastal)	0.074	0.025	0.033	0.011	L
Palmetto (FL inland)	0.047		0.021		L
Palmetto (MS)	0.079	0.059	0.035	0.026	L
Phragmites (LA)	0.074		0.033		G
Ponderosa Pine Duff	0.077	0.061	0.034	0.027	D
Ponderosa Pine, dead/large (MT)	0.128		0.057		B
Ponderosa Pine, dead/small (MT)	0.076		0.034		B
Ponderosa Pine, fresh (MT)	0.036		0.016		N
Ponderosa Pine, fresh/large (MT)	0.090		0.040		B
Ponderosa Pine, fresh/small (MT)	0.088		0.039		B
Puerto Rican Fern		0.070		0.031	L
Puerto Rican Mixed Woods		0.128		0.057	B
Rhododendron (NC)		0.101		0.045	L
Rice Straw (Taiwan)	0.052, 0.090, 0.065, 0.088, 0.079	0.059, 0.099	0.023, 0.040, 0.029, 0.039, 0.035	0.026, 0.044	S
Sage (MT)	0.041		0.018		L
Sage (UT)	0.016		0.007		L
Saw Grass (LA)	0.041		0.018		G
Southern Pine, dried		0.099		0.044	N
Titi (FL)	0.050		0.022		L
Turkey Oak (NC)	0.047		0.021		L
Wax Myrtle (FL)		0.056		0.025	L
Wax Myrtle (MS)	0.059		0.026		L
White Spruce (AK)		0.133		0.059	N
Wiregrass (FL)		0.200		0.089	G
Wiregrass (MS)	0.171		0.076		G

^aThe ratios are presented in units of $\mu\text{g levoglucosan}/\mu\text{g OC}$ and $\mu\text{g C}/\mu\text{g C}$. The latter is presenting the ratio on a carbon mass basis (i.e., the levoglucosan concentrations in the top part of Table 1 have been multiplied by both the ratio of the molecular weight of carbon to levoglucosan and the number of carbons in a molecule of levoglucosan). The ratios have been separated into stack and chamber burns. Comments indicating fuel component burned are the same as listed in Table 1. If available, in parenthesis by the fuel name is the location from where the fuel was obtained.

FLAME, conducted by *Hays et al.* [2002] using a burn enclosure, a range of ratios from 0.016 to 0.025 $\mu\text{g C}/\mu\text{g C}$ (0.036 to 0.056 $\mu\text{g levoglucosan}/\mu\text{g OC}$) was found when testing six different fuels.

[35] The levoglucosan to OC ratios obtained for Ponderosa Pine from FLAME can also be compared to literature values. *Schauer et al.* [2001], who did not specify the type

of pine burned, and *Fine et al.* [2004] found ratios of 0.115 $\mu\text{g C}/\mu\text{g C}$ (0.259 $\mu\text{g levoglucosan}/\mu\text{g OC}$) and 0.032 $\mu\text{g C}/\mu\text{g C}$ (0.072 $\mu\text{g levoglucosan}/\mu\text{g OC}$) respectively. The study of *Hays et al.* [2002] using a burn enclosure, found a ratio of 0.019 $\mu\text{g C}/\mu\text{g C}$ (0.043 $\mu\text{g levoglucosan}/\mu\text{g OC}$). *Mazzoleni et al.* [2007], who also burned fuels at FSL, found an average ratio of 0.020 \pm

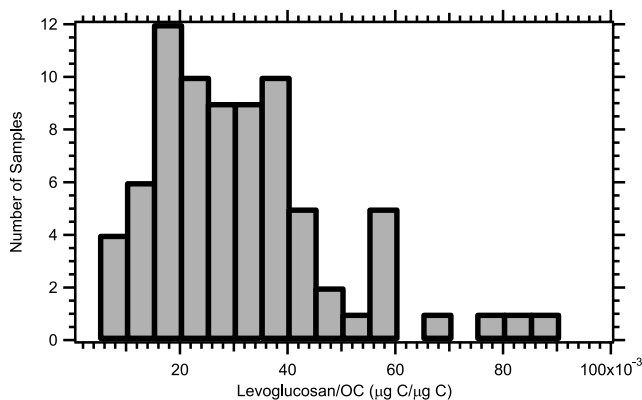


Figure 5. Frequency distribution for the levoglucosan to OC ratios on a carbon mass basis for the experiments involving the burning of a single component of a fuel. The bins are $0.005 \mu\text{g C}/\mu\text{g C}$ wide.

$0.004 \mu\text{g C}/\mu\text{g C}$ ($0.045 \pm 0.069 \mu\text{g levoglucosan}/\mu\text{g OC}$) for sticks and $0.019 \pm 0.015 \mu\text{g C}/\mu\text{g C}$ ($0.043 \pm 0.034 \mu\text{g levoglucosan}/\mu\text{g OC}$) for needles. The ratios measured during FLAME (see Table 2) are fairly similar to those of *Hays et al.* [2002] and *Mazzoleni et al.* [2007]. Although for this particular fuel the results of *Fine et al.* [2004] agree pretty well with the FLAME results, a much larger range of ratios was often observed in their work.

[36] Interestingly, as can be seen in Table 2, a similar ratio was generally observed regardless of whether the fuel component was burned in the stack or chamber burn approach. In addition, fairly good reproducibility was observed as indicated by a pooled standard deviation, based on the four burns with replicates in Table 2, of $0.010 \mu\text{g C}/\mu\text{g C}$ ($0.023 \mu\text{g levoglucosan}/\mu\text{g OC}$).

[37] There also appears to be a less prominent pattern in the levoglucosan to OC ratio based on the type of fuel burned. The highest levoglucosan to OC ratios seem to generally occur for fuels such as Manzanita and Ceanothus. Fuels with the lowest levoglucosan to OC ratios, like Gallberry and Chamise, generally had the highest EC concentrations (see Table 1).

[38] The effect of combustion efficiency on the levoglucosan to OC ratio can also be examined by calculating the

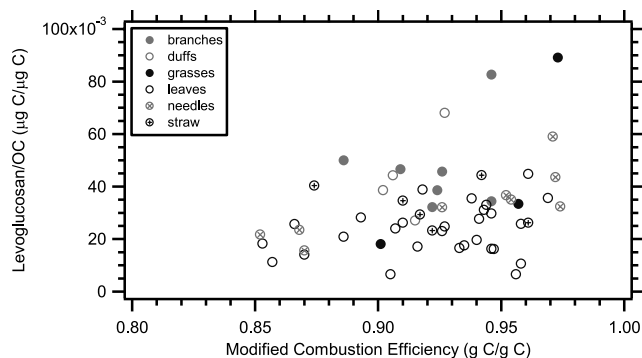


Figure 6. Levoglucosan to OC ratio on a carbon mass basis vs. the calculated modified combustion efficiency (MCE) with the data segregated by fuel component for all the experiments involving the burning of a single component of fuel.

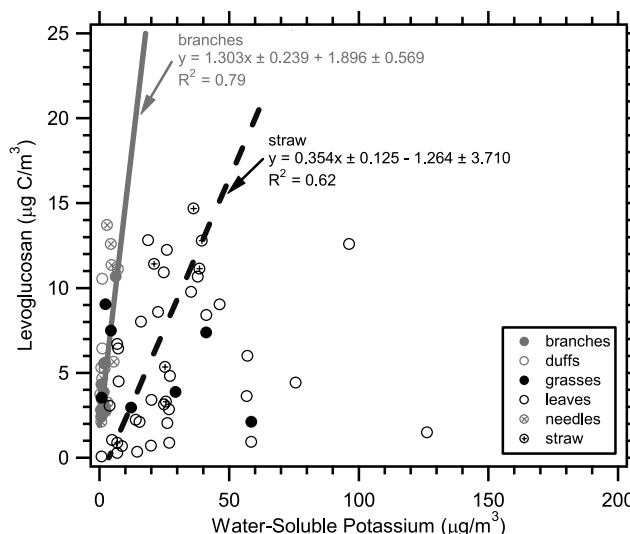


Figure 7. Correlation between levoglucosan on a carbon mass basis and water-soluble potassium with the data segregated by fuel component for all the experiments involving the burning of a single component of fuel. Uncertainties with the least square regression are one standard deviation.

modified combustion efficiency (MCE) for each burn. MCE is determined from the ratio (on a carbon mass basis) of the change in carbon dioxide to the sum of the changes in carbon monoxide and carbon dioxide ($\Delta\text{CO}_2/(\Delta\text{CO} + \Delta\text{CO}_2)$) [*Ward and Radke, 1993*]. CO was measured during FLAME I and II using a variable range gas filter correlation analyzer (Model 48C, Thermo Environmental, Franklin, MA). Carbon dioxide was measured using a non-dispersive infrared gas analyzer (Model 6262, Li-Cor, Lincoln, NE). Both measurements were provided by FSL at approximately a 2 s time resolution. Prior to each burn both analyzers were calibrated with a low and high concentration of CO or CO₂ standard.

[39] A higher MCE value indicates the burn likely undergoes a more intense or extended flaming phase. Consistent with this pattern, EC concentrations tend to be higher in burns with higher MCE values. Many gas phase species measured in the burns (not reported here) changed strongly with MCE as well. As can be seen in Figure 6 especially for the burns involving leaves, generally the levoglucosan to OC ratios, however, show no clear dependence on MCE. This result suggests again that the levoglucosan to OC ratio really is more dependent on the fuel component (for example, branches or leaves) being burned rather than the type of fuel or combustion efficiency.

[40] The correlation of levoglucosan with water-soluble potassium, an inorganic biomass burning tracer, is examined in Figure 7. In contrast to the situation for OC, there is no overall correlation between levoglucosan and water-soluble potassium. If the data are again segregated by fuel component, levoglucosan shows a correlation with water-soluble potassium for straw and branches (Figure 7). It can also be seen that duff and needle burns emit very little water-soluble potassium, but varying amounts of levoglucosan. Interestingly, these results are very similar to those of water-soluble

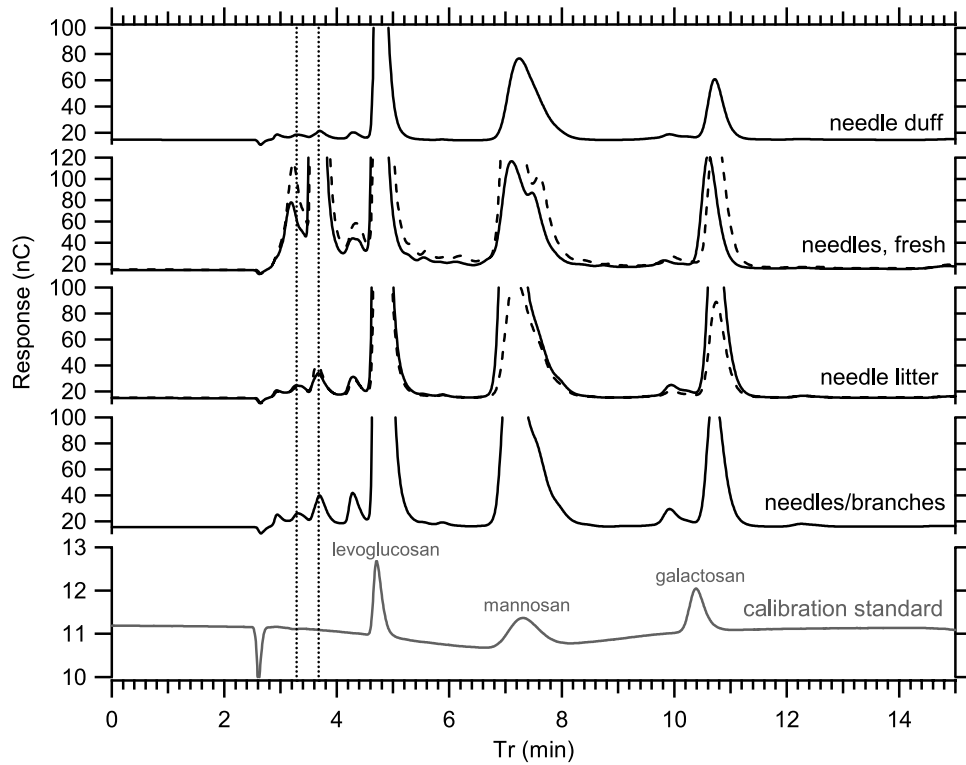


Figure 8. Comparison of chromatograms for only the anhydrosugars for a calibration standard and various burns of Lodgepole Pine (solid black lines) and Ponderosa Pine (dashed black lines), where Tr is retention time. The two vertical dashed lines correspond to the two retention times described in section 3.2, whose correlation is presented in Figure 9.

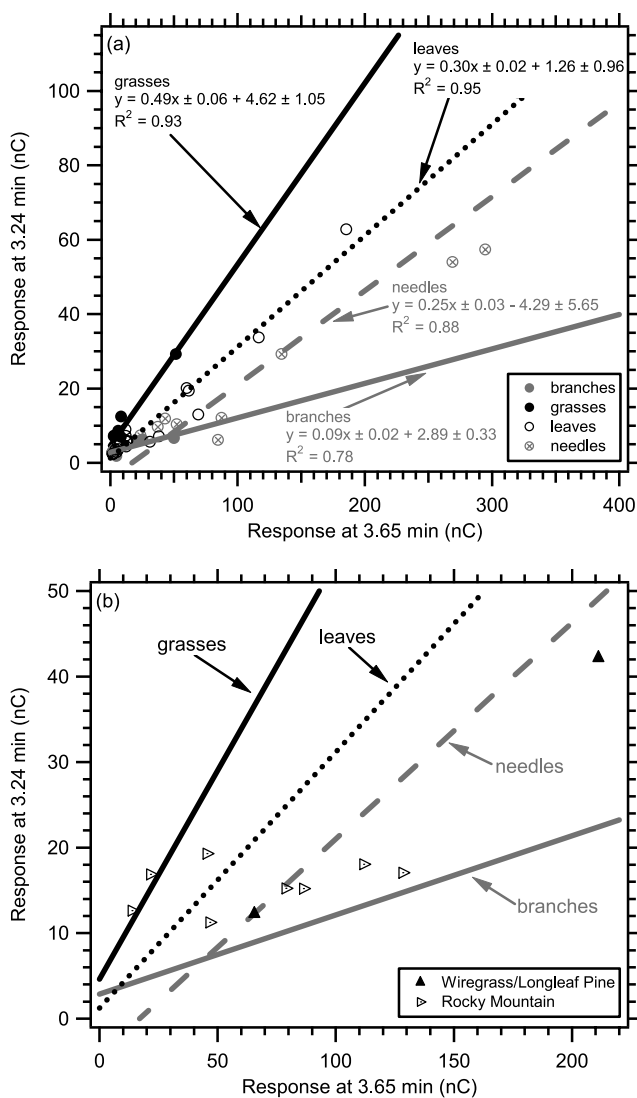


Figure 9. (a) Correlation between the peak response at 3.24 minutes and 3.65 minutes with the data segregated by fuel component for all the experiments involving the burning of a single component of fuel. The uncertainties associated with the regressions are one standard deviation. (b) Correlation between the peak response at 3.24 minutes and 3.65 minutes for the least square regression fits in a along with the data for burning two different mixtures of Wiregrass and Longleaf Pine needles and ambient data collected during the IMPROVE Radiocarbon Study at the Rocky Mountain National Park site. All data plotted have been corrected for the response from the background (~ 12 nC) because the baseline for the chromatogram was not automatically zeroed.

potassium versus OC (not shown), which are correlated for branches, straw, and grasses.

3.2. Potential Fingerprint Information

[41] It appears that information contained in the HPAEC-PAD chromatogram may provide insight about the type of fuel component burned. Figure 8 shows a comparison of typical chromatograms from a calibration standard and

burns of different fuel components for two different types of fuel, Lodgepole and Ponderosa Pine. First, it can be seen that there are noticeable extra peaks that occur for the burn samples that are not seen in the calibration standard. Second, there are unique patterns that occur for the various component burns. For example, when fresh needles are burned, instead of observing the typical four small peaks before the levoglucosan peak, only three peaks are seen with the first two dominating. Also when fresh needles are burned a more prominent side bump appears on the mannosan peak. Even more interestingly, these unique patterns in the component burns are observed in two different types of pine. Overall, this suggests the chromatograms may contain fingerprint information about the fuel beyond the typically analyzed anhydrosugars.

[42] To examine this further for the experiments involving the burning of an individual fuel component, the relation between the peak response at 3.24 min and 3.65 min is shown in Figure 9a. These two retention times have been examined as it has been observed that changes often occur in the first four peaks that elute before levoglucosan (see Figure 8). The peak response for these two retention times is highly correlated within individual fuel components. (Note for simplicity duffs and straw have not been included, but the same pattern is observed with these two fuel components.) The ratio of these two peaks changes between fuel components (typically grasses > leaves > needles > branches).

[43] It appears that the peak ratio from the individual component burns create bounds that could potentially be used to determine the dominant fuel component involved in the burn. One example of this is from the data for the burning of both a 1:1.4 and 1:2 mixture of Wiregrass to Longleaf Pine needles. The levoglucosan to OC ratios for these two mixtures were 0.060 and $0.029 \mu\text{g C}/\mu\text{g C}$ (0.135 and $0.065 \mu\text{g levoglucosan}/\mu\text{g OC}$), respectively. When comparing these ratios to those for their individual components, it appears the ratio for the mixtures is not a linear combination of its individual components (see Table 2). However, when the data for these two mixture burns is added into Figure 9b, the data follows the line for needles, the dominant component in the mixture.

[44] In addition, data from ambient samples which have been impacted by biomass burning appear to also follow the lines created from the burning of the individual fuel components. The Hi-Volume filter samples collected as part of the IMPROVE Radiocarbon Study were analyzed for the same suite of measurements as the FLAME I and II filter samples since satellite data, back trajectory analysis, and observational data suggest that the sampling sites were impacted by smoke. Although the data from all four of the sites fall along the bounds created by the burning of the individual fuel components, only the data from Rocky Mountain National Park are shown in Figure 9b. The data set from this site is shown because it forms two groups, one following the line for branches and the other following the line for grasses. As seen in Figure 10, based on back trajectory analysis using the NOAA ARL (National Oceanic and Atmospheric Administration Air Resources Laboratory) HYSPLIT trajectory model [Draxler and Rolph, 2003; Rolph, 2003], this corresponds with a change in the middle of the study period at this site in the source region of the

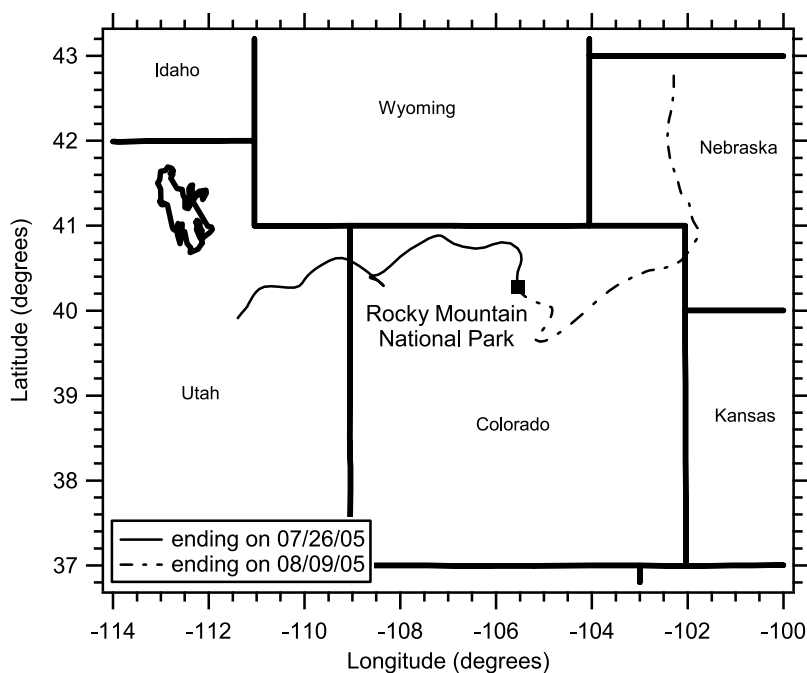


Figure 10. Characteristic 72-hour air mass back trajectories for the Rocky Mountain National Park site. All back trajectories are based on the NOAA ARL HYSPLIT trajectory model. The trajectory ending on 26 July 2005 is typical of the time period for which the data in Figure 9b follows the branches line and the trajectory ending on 9 August 2005 is typical for the data that follows the grasses line.

sampled air mass. Periods when the air masses were coming from west of the site correspond with the data that follows the branches line and periods when the air masses were coming from east of the site correspond with the data that follows the grasses line. This is encouraging considering the area east of CO is dominated by grasses while the region west of Rocky Mountain National Park contains significantly more forest and shrub coverage.

[45] Currently, we have not been able to identify the compounds that elute at these two retention times. This would prevent these compounds from being more generally used in biomass burning profiles. However, it still suggests that by using the HPAEC-PAD method to measure smoke markers in ambient aerosol we could potentially gain extra information about the dominant fuel component burned that can help in choosing the most appropriate source profile for determining the contribution of biomass burning to the total OC.

4. Summary

[46] Hi-Volume filter source samples from the smoke of fuels that are known to burn during prescribed fires and wildfires were collected at the Fire Science Laboratory in Missoula, MT during FLAME I and II. The goal was to obtain source profile information that can be used to assess the contribution of wildfires and prescribed fires to the total organic carbon aerosol concentrations.

[47] In order to do this, levoglucosan (and various other carbohydrates), water-soluble potassium, OC, and EC were determined in these samples. A direct alternative method for measuring levoglucosan using HPAEC-PAD was used. The technique offers numerous advantages over traditional

methods because the filter samples could be extracted directly in DI Water and levoglucosan and other carbohydrates could then be determined directly from the liquid extract.

[48] It was observed that the ratio of levoglucosan to OC for these source samples was fairly well correlated overall. Although the levoglucosan was a small fraction of the OC, there was a definite pattern that emerged based on fuel component burned. This suggests that the creation of a regional source profile may actually help provide a better determination for the contribution of biomass burning to ambient aerosol concentrations. There was no overall correlation between levoglucosan and water-soluble potassium, but some patterns were observed. For example, needle and duff burns emitted the lowest water-soluble potassium. For the burning of straw and branches, levoglucosan was correlated with water-soluble potassium.

[49] It also appears that by using HPAEC-PAD to determine carbohydrates in smoke samples, extra peaks are observed in the chromatograms that provide fingerprint information about the types of fuel involved in the burn. Observations of these extra peak ratios in ambient samples impacted by smoke could help in constraining the choice of the most appropriate source profile and lead to a better determination of the contribution of biomass burning to particulate OC.

[50] **Acknowledgments.** This work was funded by the Joint Fire Science Program and National Park Service. The authors would also like to thank Dr. L. R. Mazzoleni and R. Cullin for help with collecting the samples during FLAME I and Dr. G. Engling for his help during FLAME I and II. We thank Dr. B. A. Schichtel for providing the samples from the IMPROVE Radiocarbon Study. We also thank Dr. J. A. Cox for all her help and advice about the HPAEC-PAD system. Lastly, we want to

acknowledge M. Chandler, J. Chong, D. Davis, Dr. G. Engling, E. Garrell, Dr. G. Gonzalez, S. Grace, J. Hinkley, R. Jandt, R. Moore, S. Mucci, R. Olson, Dr. K. Outcalt, J. Reardon, Dr. K. Robertson, P. Spaine, and Dr. D. Weise for providing the fuels used during FLAME I and II.

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