



## Comparison and Evaluation of Methods to Apportion Ambient PM<sub>2.5</sub> to Residential Wood Heating in Fairbanks, AK

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### ABSTRACT

Biomass burning for residential heating significantly contributes to ambient PM<sub>2.5</sub> burdens in many areas, making source apportionment to wood heater emissions an important issue. This study compares and evaluates Chemical Mass Balance (CMB), levoglucosan analysis, and <sup>14</sup>C analysis methods for apportionment. Results suggest that the CMB method appears to overestimate the contribution of residential wood heating in Fairbanks, perhaps due to non-representativeness of emissions source profiles. Carbon-14 analysis allows for apportionment to biomass sources, but must be corrected for non-carbon PM<sub>2.5</sub> content. Levoglucosan analysis has the advantage of being relatively inexpensive, but there is considerable uncertainty in determining conversion factors to calculate wood smoke levels from measured levoglucosan concentrations. Conversion factors in the range of 9.1 to 13.3 are calculated from previously published and experimental mass fractions of levoglucosan in wood smoke PM<sub>2.5</sub>. Conversion factors in the range of 10.7 to 12.9 are determined from analysis of independent field measurements of <sup>14</sup>C and levoglucosan in Fairbanks. The calculated and measured conversion factors are consistent and are similar to previously-reported values. The three apportionment methods (focused on residential wood smoke contributions) are complementary and collectively provide a means to evaluate or confirm apportionment results.

**Keywords:** Wood smoke; Levoglucosan; Chemical mass balance; Carbon-14; Source apportionment.

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### INTRODUCTION

Globally, biomass burning for residential heating plays an important role in both indoor and outdoor particulate matter (PM) exposures and associated adverse health effects. In mountainous regions of the northwestern United States, fine particulate matter less than 2.5 μm in diameter (PM<sub>2.5</sub>) can be a major air pollutant of concern, with the majority of ambient PM<sub>2.5</sub> during the winter often resulting from residential wood combustion (Conner and Stevens, 1991; Rogge *et al.*, 1998; Ward and Smith, 2005; Ward *et al.*, 2006b). Reliable means to apportion PM<sub>2.5</sub> to various sources, including residential wood heating, is an essential first step in efforts to implement PM<sub>2.5</sub> control measures.

Exposure to elevated levels of PM<sub>2.5</sub> from wood combustion is known to cause adverse effects on human health (Smith *et al.*, 2000; Naeher *et al.*, 2007). These include chronic obstructive pulmonary diseases, asthma, lung cancer, tuberculosis, negative birth outcomes (e.g., low birth weight,

stillbirth), eye disease (Ezzati and Kammen Daniel, 2002), and an elevated risk of lower respiratory tract infections (LRTI) among children (Kossove, 1982; Pandey *et al.*, 1989; Collings *et al.*, 1990; Armstrong and Campbell, 1991; Mishra, 2003). In vitro human immune cell exposures to wood smoke have been shown to induce significant increases in the pro-inflammatory response, with effects dependent on the stove type and combustion conditions (Kocbach *et al.*, 2008; Boelling *et al.*, 2012).

The United States Environmental Protection Agency (USEPA) has set National Ambient Air Quality Standards (NAAQS) to protect public health and welfare. NAAQS are reviewed every five years and are periodically revised to take into consideration advancements in the knowledge of adverse effects. Current Primary NAAQS for PM<sub>2.5</sub> include an annual standard of 12 μg m<sup>-3</sup> (annual mean averaged over three years) and a 24-hour standard of 35 μg m<sup>-3</sup> (annual 98<sup>th</sup> percentile averaged over three years) (USEPA, 2012). Populated areas that exceed NAAQS are designated as nonattainment, requiring local and state environmental agencies to identify major PM<sub>2.5</sub> sources and then reducing emissions from these sources.

Several methods for quantitative and reliable source apportionment of PM<sub>2.5</sub> to residential wood stove use have been developed and implemented in recent years - each

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with significant advantages and limitations. Over the past several decades the Chemical Mass Balance (CMB) model has been commonly employed for comprehensive source apportionment (Vega *et al.*, 1997; Paode *et al.*, 1999; Chen *et al.*, 2001; Ward, 2001; Li *et al.*, 2003; Ward and Smith, 2005; Olson *et al.*, 2008; Yin *et al.*, 2010; Ward and Lange, 2010; Larson *et al.*, 2011; Herich *et al.*, 2014). CMB requires comprehensive chemical analysis of at least as many constituents of ambient PM<sub>2.5</sub> as there are potential sources, as well as reliable source profiles including the same constituents in PM<sub>2.5</sub> from all potential sources. CMB analysis identifies a linear combination of source profiles that best matches the composition of the ambient PM<sub>2.5</sub>. CMB assumes that the source profiles are representative of the sources impacting the measurement site and are constant throughout the sampling period. It is also assumed that the source profiles are independent and the chemical constituents do not react with one another. CMB is relatively expensive because it requires comprehensive chemical analysis of ambient and often source-specific PM<sub>2.5</sub> as well as careful application of the mass balance model.

Carbon-14 analysis, also referred to as radiocarbon analysis or carbon dating, has also been used extensively to apportion particulate matter carbon to biomass vs. fossil fuel sources (Szidat *et al.*, 2004; Jordan *et al.*, 2006; Ward *et al.*, 2006b; Szidat *et al.*, 2007; Gustafsson *et al.*, 2009; Szidat, 2009; Ward and Lange, 2010; Buchholz *et al.*, 2013). The <sup>14</sup>C content in emissions from the combustion of carbonaceous fuels mirrors that of the fuel. Carbon-14 is a cosmogenic isotope that is continually being produced in the upper atmosphere. Once produced, the carbon oxidizes to form CO<sub>2</sub>, and enters the terrestrial carbon cycle through several different avenues, including photosynthesis in plant life. The amount of <sup>14</sup>C found in a plant thus reflects the amount of <sup>14</sup>C present in the atmosphere when that plant grew. Over time after death, the <sup>14</sup>C fixed in an organic sample will decay, and if enough time is allowed to pass no <sup>14</sup>C will be detectable. Thus, analyzing the PM<sub>2.5</sub> samples for <sup>14</sup>C allows determination of the PM<sub>2.5</sub> emitted by biomass combustion ('modern' carbon – known <sup>14</sup>C) versus that emitted by fossil fuel combustion ('old' carbon – no <sup>14</sup>C), such as petroleum diesel exhaust or exhaust from coal burning sources. This approach is also relatively expensive due to the specialized instrumentation and expertise required, and the method is applicable to the carbon fraction of the particulate only.

Both inorganic and organic markers have been used in PM<sub>2.5</sub> source apportionment. Potassium is a recognized inorganic marker of PM<sub>2.5</sub> from wood combustion, and has been used to apportion PM<sub>2.5</sub> e.g., (Ward *et al.*, 2006a; Caseiro *et al.*, 2009). This is a relatively cost effective approach, but can over-estimate wood smoke contribution if additional sources of potassium are not considered or accounted for.

Levoglucosan, a sugar anhydride from the incomplete combustion of cellulose, has been identified as a selective organic marker of biomass combustion (Schauer *et al.*, 2001; Jordan *et al.*, 2006; Ward *et al.*, 2006a, b; Bergauff *et al.*, 2008; Schmidl *et al.*, 2008; Caseiro *et al.*, 2009). Multiple

approaches have been developed for relatively cost-effective and even field-based analysis of the levoglucosan content of PM<sub>2.5</sub>, e.g., (Engling *et al.*, 2006; Jordan *et al.*, 2006; Ward *et al.*, 2006a; Bergauff *et al.*, 2008; Ma *et al.*, 2010; Piazzalunga *et al.*, 2010; Saarnio *et al.*, 2010; Harrison *et al.*, 2012). A review and comparison of levoglucosan analytical methods has recently been published (Yttri *et al.*, 2015).

However, levoglucosan has not often been used for quantitative apportionment of PM<sub>2.5</sub> to residential wood burning because the mass fraction of levoglucosan in wood smoke PM must be known for it to be used as a quantitative tracer species. Several attempts have been made to quantitatively estimate wood smoke PM from levoglucosan or to measure and report conversion factors from levoglucosan to wood smoke PM. Hedberg *et al.* (2006) found that there was too much uncertainty or variation in the mass fraction of levoglucosan in wood smoke to allow quantitative estimates. Schmidl *et al.* (2008) and Caseiro *et al.* (2009) measured, reported and used a conversion factor of 10.7 to calculate wood smoke particulate from levoglucosan. Herich *et al.* (2014) compared results for multiple studies in alpine regions of Europe and found that wood smoke PM to levoglucosan ratios varied from 10.7 to 25.2. The positive matrix factorization (PMF) method has also been applied to develop quantitative conversion of levoglucosan to PM. Zhang *et al.* (2010a) used PMF to obtain a conversion factor of 18.3 for the southeastern US, while Piazzalunga *et al.* (2011) generated conversion factors of 10.4 using literature values and 16.9 using PMF in Italy. Others have used levoglucosan to quantitatively or semi-quantitatively apportion PM organic carbon to biomass burning in general (Zhang *et al.*, 2010b; Sang *et al.*, 2013; Zhu *et al.*, 2015). Quantitative apportionment was limited in these latter studies by the lack of source- and region- specific mass fractions of levoglucosan in organic carbon from biomass combustion, requiring the use of an estimate calculated from published values.

An additional complication with the use of levoglucosan for quantitative apportionment is that it has been shown in laboratory studies to have limited stability in the presence of common photochemically-generated atmospheric free radicals (Hennigan *et al.*, 2010; Hoffmann *et al.*, 2010). This suggests that PM to levoglucosan ratios measured on "fresh" emissions from wood burning devices may not be representative of the values for aged wood smoke PM. However, levoglucosan is relatively stable in the winter months, which are the focus of this study (Hoffmann *et al.*, 2010; Zhang *et al.*, 2010a). Limited stability would thus be of greatest concern to efforts to use levoglucosan to source-apportion PM that has been transported on a continental scale over a period of days, or in summer months when photochemical activity is relatively high.

In the current study we have used results from studies in Fairbanks Alaska PM<sub>2.5</sub> to obtain estimates for the quantitative levoglucosan to wood smoke PM<sub>2.5</sub> conversion ratio in that region. Fairbanks, Alaska has experienced elevated levels of PM<sub>2.5</sub> and was designated a nonattainment area due to frequent exceedance of 24 hour NAAQS standards during several heating seasons. Comprehensive chemical analyses

and subsequent modeling of Fairbanks ambient PM<sub>2.5</sub> has included CMB, carbon-14, potassium, and levoglucosan analyses. These data present a rare opportunity to compare and evaluate these approaches to source apportionment in a single airshed. In the current study we evaluate and compare the <sup>14</sup>C, levoglucosan and CMB approaches to apportion PM<sub>2.5</sub> to residential wood combustion. We also utilize the correlations between levoglucosan and wood smoke PM<sub>2.5</sub> determined by the <sup>14</sup>C and CMB methods to gain estimates of field-relevant levoglucosan to wood smoke PM<sub>2.5</sub> conversion factors.

## EXPERIMENTAL

### Methods

During the winters of 2008/2009, 2009/2010, and 2010/2011, a research study was conducted to identify the major sources of ambient PM<sub>2.5</sub> in Fairbanks, Alaska.

### Sampling Program

PM<sub>2.5</sub> sampling was conducted every three days following the EPA's fixed monitoring schedule at the State Building, North Pole, and Peger Road (also known as the Transit Yard) sites during the aforementioned winters. The State Building site (64.840833°N, -147.723056°W) is located in central Fairbanks and is a State and Local Air Monitoring Site (SLAMS) for PM<sub>2.5</sub> as well as a Speciation Trend Network (STN) site. The other sites are Special Purpose Monitoring (SPM) sites. The Peger Road site (64.818871°N, -147.775955°W) is located in Fairbanks, while North Pole (64.752336°N, -147.347208°W) is a town located approximately 20 km to the southeast of Fairbanks in a more rural setting. A total of 332 samples were collected from 11/8/09–4/16/09 (n = 56), 11/3/09–3/15/2010 (n = 50) and 11/1/2010–3/16/2011 (n = 46) at the State Building site; from 1/23/2009–4/7/2009 (n = 28), 11/3/2009–3/15/2010 (n = 43) and 1/9/2011–3/7/2011 (n = 20) at North Pole; and from 1/25/2009–4/7/2009 (n = 27), 11/3/2009–3/15/2010 (n = 42) and 1/9/2011–3/7/2011 (n = 20) at Peger Road. Not all samples were analyzed by all techniques: 161 samples were analyzed for both CMB and levoglucosan, while 40 samples were analyzed for both <sup>14</sup>C and levoglucosan.

Twenty-four hour PM<sub>2.5</sub> sampling was conducted using a MetOne (Grants Pass, OR) Spiral Ambient Speciation Sampler (SASS) at each site. During each 24-hour sampling event, the SASS collected ~9.7 m<sup>3</sup> of air through Teflon, nylon, and two quartz filter media. In addition to traditional speciation analyses, one of the quartz filters was later analyzed for <sup>14</sup>C and chemical markers of wood smoke. Quality assurance and control procedures (USEPA, 2013) were followed throughout the sampling program. Following sampling, all filter samples were kept cold until their respective analyses described in the following sections.

### PM<sub>2.5</sub> Speciation

Exposed SASS filter samples were analyzed by the Research Triangle Institute (RTI, Research Triangle Park, NC). From the Teflon filter, a gravimetric analysis (RTI, 2008) was initially performed followed by an elemental

analysis (RTI, 2009d) using energy-dispersive X-ray fluorescence (EDXRF) where 33 elements were quantified. From the nylon filter, ions (including ammonium, potassium, sodium, nitrate, and sulfate) were measured by ion chromatography (IC) (RTI, 2009a, b). From the first quartz filter, Elemental Carbon and Organic Carbon (EC/OC) concentrations were quantified by Thermal Optical Transmittance following NIOSH protocol (RTI, 2009c). Following the analyses, sample results (including analyte concentrations and uncertainties) were provided for use in the CMB source apportionment model.

### Carbon-14 (<sup>14</sup>C) Analyses

For a random subset of the samples collected throughout the three-winter programs (and from each of the three sites), one half of the second quartz filter was analyzed for <sup>14</sup>C at the University of Arizona's (UA) Accelerator Mass Spectrometry Laboratory Facility. Carbon was extracted from each sample independently via combustion in an oxygen rich environment. The analysis yields the fraction of carbon in the PM<sub>2.5</sub> that is <sup>14</sup>C. Assuming no carbon on the blank filter and that the fraction of <sup>14</sup>C in old carbon is zero, the fraction of modern carbon can be calculated from (Ward and Lange, 2010):

$$\%(\text{modern}) = \frac{F_{C14}(\text{measured})}{F_{C14}(\text{modern})} \times 100 \quad (1)$$

where  $F_{C14}(\text{measured})$  is the measured fraction of <sup>14</sup>C and  $F_{C14}(\text{modern})$  is the modern atmospheric fraction of <sup>14</sup>C. Several points need to be taken into account in assigning  $F_{C14}(\text{modern})$ . Nuclear testing in the 1950s and 1960s caused a significant increase of <sup>14</sup>C in the atmosphere, with a peak fraction of 1.85 parts per trillion (ppt) being reached in 1965. Since that time, the fraction has dropped to the present day level of approximately 1.075 ppt. With atmospheric concentrations changing yearly, the exact fraction for a piece of wood will be the integration of all <sup>14</sup>C incorporated over the period of growth. A complete survey of the wood harvesting methods, locations and average wood age, as well as the relative size and lifespan of the trees cut, was not possible to determine for this project. An examination of yearly atmospheric <sup>14</sup>C values over the last 130 years was conducted and decadal averages were calculated to obtain a high estimate of  $F_{C14}(\text{modern})$  of 1.294 ppt, while the current value of 1.075 ppt was used as a low estimate of  $F_{C14}(\text{modern})$ . Using these values results in low and high estimates of  $\%(\text{modern})$ .

### Levoglucosan

Levoglucosan analysis was conducted using a previously-published method (Bergauff et al., 2008). This method was used for all samples except the Fairbanks source-specific filters. Because the PM loading of these filters was relatively high, it was necessary to adjust the filter fraction analyzed, amount of D-levoglucosan internal standard added, and the final dilution factors to obtain final analysis concentrations within the linear range of the original method.

### Fairbanks Source-Specific Biomass $PM_{2.5}$

To support the CMB modeling, source emission testing was conducted by OMNI Environmental Services (Portland, OR). The goal of the OMNI testing was to generate emission profiles for the following types of heating appliances and fuel types commonly used in Fairbanks: pellet stoves, USEPA qualified wood stoves (birch, spruce), conventional wood stoves (birch, spruce), USEPA qualified hydroponic heaters (birch, spruce), non qualified outdoor hydroponic heaters (spruce, birch, wet stoker coal), oil burners (No. 1 fuel oil, No. 2 fuel oil), waste oil burning, coal stoves (dry stoker coal, wet stoker coal, wet lump coal, dry lump coal), and coal hydroponic heaters (wet stoker coal and coal-typical moisture).

Wood heating appliances were operated following USEPA method 28 (USEPA, 2014a), except that Alaskan cordwood was used in place of dimensional lumber. Particulate sampling was carried out in accordance with applicable portions of USEPA method 201A (USEPA, 2014b). The particulate sampling system relied on a cyclone head attachment on the sample probe in order to sample only particulate smaller than 2.5 microns in diameter ( $PM_{2.5}$ ). The cyclone head was placed in the dilution tunnel and the sample flow was split into 5 branches, each with a respective filter (one Teflon, three quartz, and one glass fiber). The flow rate in each branch was individually controlled. From the Teflon filter,  $PM_{2.5}$  mass, ions (potassium, sodium, ammonium, nitrate, and sulfate), and elements (33 in total) were quantified by the Research Triangle Institute. A single quartz filter sample for each of 41 trials with different devices, burn rates and wood species was shipped to the University of Montana for levoglucosan analysis.

### Source Apportionment Modeling

The most recent version of the USEPA Chemical Mass Balance (CMB) computer model (Version 8.2) was utilized to apportion the sources of  $PM_{2.5}$  in Fairbanks. The CMB receptor model (Hidy and Venkataraman, 1996; Friedlander, 1973; Cooper and Watson, 1980; Gordon, 1980, Watson, 1984; Watson *et al.*, 1984; Gordon, 1988; Watson *et al.*, 1990) is based on an effective-variance least squares method, and consists of a solution to linear equations that expresses each receptor chemical concentration as a linear sum of products of source fingerprint abundances and contributions.

A more complete description of the CMB modeling program (as well as experimental and analytical details) is provided in (Ward *et al.*, 2012). Briefly, for each sample day, the CMB modeling process began by selecting from a combination of 91 sources and 43 chemical species (36 elements, 5 ions, OC and EC) in an effort to reconstruct the measured Fairbanks ambient  $PM_{2.5}$  mass and chemical composition. Source profiles were either taken directly from the most recent version of SPECIATE 4.0 (USEPA, 2006) or from previous Missoula Valley CMB applications (Carlson, 1990; Schmidt, 1996; Ward and Smith, 2005). The types of source profiles included street sand and road dust, pure secondary source emissions, gasoline and diesel exhaust emissions, tire and brake wear, meat cooking, residential wood combustion, and other local sources/industry

in Fairbanks.

### Data Analysis

All results are reported as the means and 95% confidence intervals. Method intercomparisons are conducted using matched sample pairs. Distributions are compared using *t*-tests with significance reported for the 95% confidence level. Results for wood smoke  $PM_{2.5}$  by either CMB or  $^{14}C$  analysis are plotted and regressed against measured levoglucosan  $PM_{2.5}$  concentrations using Microsoft® Excel to obtain slopes and statistics. All plots and regressions are through the origin.

## RESULTS AND DISCUSSION

### Chemical Mass Balance – Wood Smoke Contribution

The results of CMB source apportionment modeling are presented and discussed in detail elsewhere (Ward *et al.*, 2012). Residential wood smoke was the major source of  $PM_{2.5}$  identified by CMB modeling throughout the three-winter study in Fairbanks, contributing between 60% and 80% of the measured  $PM_{2.5}$  at the three sites (see Table 1). The wood smoke source identified by the CMB model should be viewed as a general source predominantly composed of wood stove emissions. A source profile developed in Missoula, Montana in the late 1980s served as the best statistically fitting wood smoke profile for each of the three sites when conducting the Fairbanks CMB analyses. It should also be noted that many other residential wood combustion source profiles from the USEPA SPECIATE database gave good statistical fits throughout the computer modeling process for each of the sites. Note that the OMNI wood heating source profiles were not used for CMB modeling in this study.

### Carbon-14

Throughout the 3-year program, OC concentrations averaged between 10.6 and 15.4  $\mu g m^{-3}$ , with EC concentrations between 1.4 and 2.3  $\mu g m^{-3}$ .  $PM_{2.5}$  mass was composed of 43–58% OC and 6–9% EC, respectively, at each of the sites. The  $^{14}C$  analyses return estimates of the fraction of total carbon attributable to biomass combustion. The CMB apportionment of Fairbanks  $PM_{2.5}$ , however, suggests high non-carbon fractions, primarily of secondary sulfate. This causes some complications for quantitative apportionment of Fairbanks  $PM_{2.5}$  using the  $^{14}C$  method. To account for this we estimated the portion of total ambient  $PM_{2.5}$  attributable to biomass from the mass fraction of biomass-generated carbon on the filter using Eq. (2):

$$PM_{2.5} (\% \text{ biomass}) = \frac{(X_{C \text{ biomass}})(TC_{\text{measured}})}{(y_{C \text{ biomass}})(PM_{2.5 \text{ gravimetric}})} \times 100\% \quad (2)$$

where  $PM_{2.5} (\% \text{ biomass})$  is the percent contribution of biomass burning  $PM_{2.5}$  to the ambient  $PM_{2.5}$ ,  $X_{C, \text{biomass}}$  is the mass fraction of carbon on the filter that originates from biomass combustion as determined by  $^{14}C$  analysis,  $y_{C, \text{biomass}}$

**Table 1.** Wood smoke (WS) contributions to ambient PM<sub>2.5</sub> as determined by <sup>14</sup>C analysis, levoglucosan (LG) analysis, and CMB modeling.

Site and Period	Wood Smoke Contribution (%) to Ambient PM <sub>2.5</sub> Mass Concentration by the Indicated Apportionment Method							
	<sup>14</sup> C Minimum	<sup>14</sup> C Maximum	n	Levoglucosan (CF <sub>1</sub> = 9.01)	Levoglucosan (CF <sub>2</sub> = 13.3)	n	CMB Model	n
State Bldg								
2008/2009	31.6 ± 8.0	38.0 ± 9.6	8	28.1 ± 10.0	34.7 ± 5.9	24	64.2 ± 9.0	47
2009/2010	36.7 ± 7.5	44.2 ± 9.1	8	21.0 ± 5.6	31.0 ± 8.3	19	67.9 ± 10.0	40
2010/2011	28.7 ± 4.3	34.5 ± 5.1	2	26.7 ± 2.9	39.4 ± 4.3	22	71.5 ± 13.3	15
3-yr avg	33.6 ± 7.7	40.4 ± 9.3	18	25.6 ± 4.1	35.2 ± 3.5	65	68.5 ± 8.6	102
North Pole								
2008/2009	42.9 ± 9.8	51.7 ± 11.8	2	36.8 ± 10.0	54.3 ± 14.7	14	79.6 ± 6.1	21
2009/2010	56.7 ± 6.3	68.3 ± 7.6	8	43.3 ± 4.6	63.8 ± 6.8	38	80.7 ± 11.1	35
2010/2011	58.4 ± 6.9	70.4 ± 8.3	3	43.7 ± 4.8	64.3 ± 7.0	14	77.2 ± 11.8	10
3-yr avg	55.0 ± 8.3	66.2 ± 10.0	13	42.0 ± 3.4	61.8 ± 5.1	58	79.2 ± 9.7	66
Peger Road								
2008/2009	23.6	28.4	1	14.3 ± 3.7	21.1 ± 5.4	15	65.3 ± 9.4	26
2009/2010	33.9 ± 4.8	40.9 ± 5.8	8	21.5 ± 2.9	31.7 ± 4.3	35	62.2 ± 14.9	38
2010/2011	28.7 ± 6.6	34.6 ± 8.0	3	22.5 ± 3.4	33.1 ± 5.0	14	68.7 ± 10.8	10
3-yr avg	31.8 ± 5.6	38.3 ± 6.7	12	20.0 ± 2.0	29.5 ± 3.0	64	65.4 ± 11.7	74

**Table 2.** Average levoglucosan (LG) mass concentrations and mass percentages in PM<sub>2.5</sub> for three sites over three years.

Season	State Building		Peger Road		North Pole	
	LG Conc. (ng m <sup>-3</sup> )	LG/PM <sub>2.5</sub> (%)	LG Conc. (ng m <sup>-3</sup> )	LG/PM <sub>2.5</sub> (%)	LG Conc. (ng m <sup>-3</sup> )	LG/PM <sub>2.5</sub> (%)
2008–09	573 ± 203	3.1 ± 1.1	628 ± 120	2.18 ± 0.24	833 ± 480	3.8 ± 1.2
2009–10	671 ± 288	2.33 ± 0.63	312 ± 131	1.60 ± 0.41	1720 ± 470	4.80 ± 0.51
2010–11	671 ± 157	2.96 ± 0.32	763 ± 195	2.30 ± 0.36	1150 ± 490	4.85 ± 0.53
3 yr avg	632 ± 118	2.80 ± 0.46	628 ± 120	2.18 ± 0.24	1400 ± 300	4.59 ± 0.40

is the typical mass fraction of carbon in biomass emissions from an emission source profile, TC<sub>measured</sub> is the PM<sub>2.5</sub> total carbon (TC) concentration from the speciation sampler, and PM<sub>2.5</sub><sub>gravimetric</sub> is the gravimetric mass of PM<sub>2.5</sub> from the speciation sampler. The numerator in Eq. (2) represents the amount of biomass-generated carbon in the sample. That, divided by y<sub>C,biomass</sub>, yields an estimate for the total biomass PM<sub>2.5</sub> in the sample. Finally, division by PM<sub>2.5</sub><sub>gravimetric</sub> yields the biomass fraction. For y<sub>C,biomass</sub>, we used the measured average mass fraction of carbon (0.837) in the Fairbanks-specific wood stove emissions generated from the heating device combustion trials, which is not substantially different from the mass fractions generated from the Missoula wood smoke profile or the other USEPA wood smoke profiles from the SPECIATE database.

When using the values for fraction of modern carbon for each of the sample days, the percent wood smoke component of the PM<sub>2.5</sub> can be calculated. For the filter samples analyzed, ~32% to ~66% of the measured ambient PM<sub>2.5</sub> came from a new carbon source (in this case wood smoke). The % biomass PM<sub>2.5</sub> over all samples analyzed for <sup>14</sup>C are presented in Table 1. The results are reported as a minimum and maximum value based on high and low estimates of <sup>14</sup>C in modern biomass, respectively.

### Levoglucosan

Detection of levoglucosan in the ambient PM<sub>2.5</sub> filter

samples supports that wood smoke-related particles are present in the Fairbanks airshed. Table 2 presents averages (with 95% confidence intervals) for levoglucosan levels and PM<sub>2.5</sub> mass fractions by sampling site and year. The variability in these data reflects actual variations in levoglucosan concentrations and mass fractions as well as variations due to analytical reproducibility. Variability in the levoglucosan concentrations, expressed as relative 95% confidence intervals, is high, often exceeding 40%. This variation reflects that levoglucosan concentrations increase and diminish with PM<sub>2.5</sub> concentrations, which also vary significantly. Relative variations in levoglucosan as mass fractions of PM<sub>2.5</sub> are lower, and are typically 15% or less. Significant differences (Student t-test, p < 0.05) are observed between sampling sites, with the North Pole showing higher concentrations and mass fractions compared to the State Building and Peger Road sites. This is evidence that residential wood smoke accounts for a greater fraction of the PM<sub>2.5</sub> in the more rural North Pole location, consistent with the results of the CMB modeling. There are no significant differences or trends in levoglucosan concentrations or fractions for any given site as a function of heating season.

A recent study (Caseiro *et al.*, 2009) generated a quantitative apportionment of ambient PM<sub>10</sub> to biomass combustion in Austria by dividing the levoglucosan fraction of ambient PM<sub>10</sub> by the levoglucosan fraction of PM<sub>10</sub> from biomass combustion. The levoglucosan fraction of wood

smoke was established by analysis of PM<sub>10</sub> from wood heaters burning wood species used in the region of Austria studied (Schmidl *et al.*, 2008). The levoglucosan mass fraction is generally observed to vary between wood species (Fine *et al.*, 2001, 2002a, b, 2004a, b; Schmidl *et al.*, 2008; Caseiro *et al.*, 2009), so a representative value for the Austrian region was calculated as a weighted average based on a survey of the amount or fraction of each wood species consumed (Schmidl *et al.*, 2008; Caseiro *et al.*, 2009). The equation used to calculate a weighted conversion factor (CF) to convert levoglucosan mass fraction to biomass portion is as follows (Schmidl *et al.*, 2008):

$$CF = \frac{1}{f_1L_1 + f_2L_2 + f_3L_3 + \dots + f_nL_n} \quad (3)$$

where the fractional consumption ( $f_n$ ) and mass fraction of levoglucosan in PM ( $L_n$ ) is respective of each wood species ( $n$ ) burned in the area of study.

A survey of wood fuel use in Fairbanks conducted by OMNI Environmental Services under contract to the Fairbanks North Star Borough found that residents used 43% aspen, 52% birch, and 6% spruce. Adaptation of the Eq. (3) to Fairbanks using survey data for wood species consumption yields:

$$CF = \frac{1}{0.43L_A + 0.52L_B + 0.06L_S} \quad (4)$$

where  $L_A$ ,  $L_B$ , and  $L_S$  are the levoglucosan mass fractions for aspen, birch and spruce wood smoke respectively. We have investigated various approaches to calculating a conversion factor for Fairbanks using experimentally-generated and published levoglucosan fraction values for aspen, birch and spruce.

Fairbanks-specific levoglucosan mass fractions in PM<sub>2.5</sub> from biomass combustion were determined using PM<sub>2.5</sub> samples from the heating device combustion trials. The results for levoglucosan fraction in PM<sub>2.5</sub> for these filters are presented in Table 3. In general, these results indicate a relatively low fraction of levoglucosan in the wood smoke (avg. = 3.7%) compared to published values (Fine *et al.*, 2001, 2002a, b, 2004a, b; Schmidl *et al.*, 2008; Caseiro *et al.*, 2009). No significant differences were observed in levoglucosan fraction across wood species based on Student t-test analysis, which is also not consistent with previous studies (Fine *et al.*, 2001, 2002a, b, 2004a, b; Schmidl *et al.*, 2008; Caseiro *et al.*, 2009). Significant differences were observed as a function of burner type and within burner types as a function of burn rate, as has been previously reported by (Jordan and Seen, 2005).

The results of this study demonstrate the substantial challenges in obtaining reliable experimental levoglucosan mass fraction results for use in quantitative source apportionment studies. Although this study was conducted by experienced contractors and followed approved USEPA methods and procedures, the results obtained deviate significantly from previously-published results. Due to cost

and time limitations, the data are limited to single samples for each device, burn rate and wood species, and include results for spruce and birch, but not aspen. The average levoglucosan fractions reported in Table 3 are significantly lower than typical ambient PM<sub>2.5</sub> levoglucosan fractions at the North Pole site, implying unreasonable apportionments in excess of 100% wood smoke for this site and further eroding confidence in the experimental results. The stove burn rate is clearly an important factor, and burn rate data are difficult to collect in the field and are seldom available.

An alternative approach is to use levoglucosan mass fraction data reported in the literature. Significant variation in the published values complicates this approach (Hedberg *et al.*, 2006; Herich *et al.*, 2014). No published results specific for appliances and practices in Fairbanks are available, which may introduce significant error. Experimental levoglucosan fractions of PM<sub>2.5</sub> are reported in the literature for wood smoke from aspen, birch and spruce (Fine *et al.*, 2004a). Other published results for levoglucosan fractions do not include the same species as those burned in Fairbanks and/or are for PM<sub>10</sub> rather than PM<sub>2.5</sub> (Fine *et al.*, 2001, 2002a, b, 2004a, b; Schmidl *et al.*, 2008). The reported experimental levoglucosan fractions in each case are based on relatively few measurements, and their reliability is thus of concern. An additional concern is that the values are measured for “fresh” wood smoke PM and may not be valid for application to aged PM for which levoglucosan levels may be reduced via reaction with atmospheric free radicals (Hennigan *et al.*, 2010; Hoffmann *et al.*, 2010).

We used a combination of the experimental and published values for  $L_A$ ,  $L_B$  and  $L_S$  to establish a low and a high estimate of the conversion factor. Using only the most relevant published results (Fine *et al.*, 2004a) gives a  $CF_1 = 9.01$ , which is used here as a lower limit. An upper limit CF was calculated using the average experimental values for  $L_B$  and  $L_S$  from Table 3 over all burn conditions and the published value of  $L_A$ . The resulting  $CF_2 = 13.3$  is strongly influenced (43%) by the published value for aspen. Finally, device type data by zip code was utilized together with wood species survey data to generate site-specific CF values weighted for both wood species and device type. These conversion factors, calculated using  $L_B$  and  $L_S$  from Table 3 and the published value for  $L_A$ , ranged from 12.2–12.4. There was significant concern about these site-specific results because of the combined uncertainties in L values, wood species usage, and stove type usage. Because of this, and because they are bracketed by  $CF_1$  and  $CF_2$ , they were not used for additional calculations. Our values for  $CF_1$  and  $CF_2$  also bracket those reported by Caseiro *et al.* (Caseiro *et al.*, 2009) and are at the low end of the range reported by Herich *et al.* (Herich *et al.*, 2014).

Using  $CF_1$  and  $CF_2$  we calculated low and high estimates of the wood smoke percent contribution to ambient PM<sub>2.5</sub> in Fairbanks. Table 1 presents these results by site and season. The high end estimates are nearly 48% higher than the low end estimates, representing considerable uncertainty.

### Overall Comparison

Table 1 presents the residential wood smoke apportionment

**Table 3.** Levoglucosan shares for various devices, fuels and burn rates.

Burner Type <sup>a</sup>	Fuel Type	Burn Rate	Levoglucosan Mass Fraction (%) <sup>b</sup>
Pellet Stove	Pellet	single	0.24
Conventional WS	Birch	high	1.08
Conventional WS	Spruce	high	0.88
Conventional WS	Birch	low	1.18
Conventional WS	Spruce	low	0.35
EPA Certified WS	Birch	high	0.27
EPA Certified WS	Spruce	high	1.80
EPA Certified WS	Birch	low	6.12
EPA Certified WS	Spruce	low	6.05
Nonqualified OWHH	Spruce	high	5.86
EPA Certified OWHH	Birch	high	7.46
EPA Certified OWHH	Spruce	high	2.48
EPA Certified OWHH	Birch	low	5.73
EPA Certified OWHH	Spruce	low	11.73

<sup>a</sup> WS = wood stove; OWHH = outdoor wood hydronic heater.

<sup>b</sup> Relative uncertainty in analysis is  $\pm 10\%$ .

results using all CMB,  $^{14}\text{C}$  and levoglucosan analyses. Levoglucosan data were eliminated for a few low PM days with levoglucosan concentrations near or below the detection limit. No more than two data points were eliminated for any heating season. Levoglucosan and CMB results are each large datasets with considerable overlap. Carbon-14 results are from a relatively small random subset of samples.

Average apportionment results by site are presented in Fig. 1, with error bars indicating 95% confidence intervals. The results from  $^{14}\text{C}$  and levoglucosan analysis are generally in good agreement. There are no significant differences between the average results at the State Building or Peger Road sites based on a Student t-test at  $p = 0.05$ . The lower levoglucosan estimate at the North Pole site shows a significant difference from the  $^{14}\text{C}$  estimates, but the upper levoglucosan estimate does not. At the more centrally-located State Building and Peger Road sites, the CMB analysis suggests a significantly higher apportionment to wood smoke than do either the  $^{14}\text{C}$  or levoglucosan approaches. The results converge at the North Pole site, where all three approaches suggest a higher proportion from biomass combustion.

Given the challenges in calculating a representative levoglucosan conversion factor from experimental or published data, we chose to use the results from different apportionment methods to obtain average CF values for Fairbanks. This was accomplished by analysis of observations in which paired data for both levoglucosan and either CMB or  $^{14}\text{C}$  were available.

#### **Levoglucosan vs. CMB**

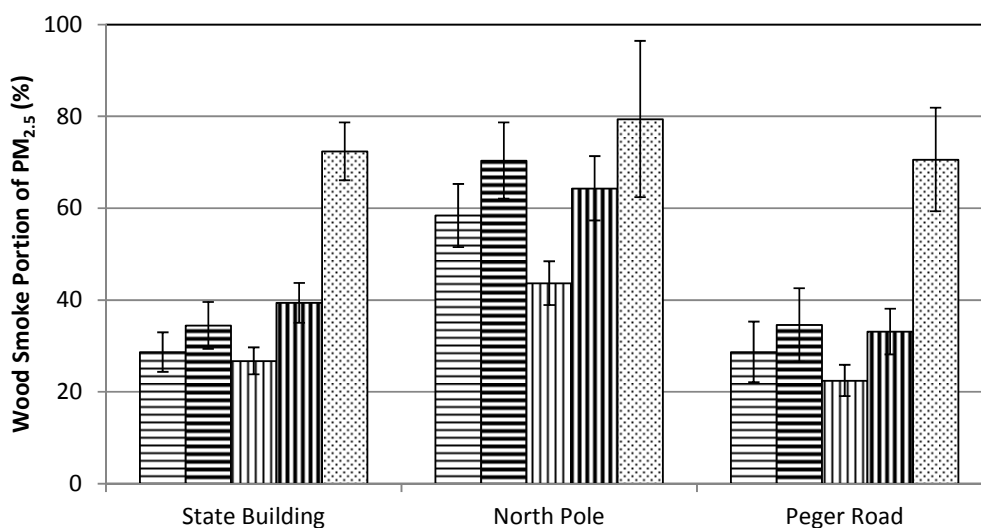
Using the subset of data for which both CMB and levoglucosan analyses were performed, the wood smoke  $\text{PM}_{2.5}$  concentration estimated from CMB is plotted vs the measured levoglucosan levels in Fig. 2(a). Inspection of this plot suggests a different relationship between CMB and levoglucosan results at the State Building and Peger Rd sites compared to the North Pole site. Separate regression of the results at the three sites yields slopes of  $15.12 \pm 0.39$  ( $r^2 = 0.96$ ,  $F = 1470$ ,  $n = 57$ ),  $23.3 \pm 2.2$  ( $r^2 = 0.89$ ,  $F = 464$ ,

$n = 58$ ) and  $19.8 \pm 2.5$  ( $r^2 = 0.84$ ,  $F = 245$ ,  $n = 46$ ) at the North Pole, Peger Rd., and State Building sites, respectively. The slopes are estimates of the CF values assuming that CMB modeling provides an accurate estimate of wood smoke  $\text{PM}_{2.5}$ . Each of these values is significantly higher than the calculated upper limit of  $\text{CF}_2 = 13.3$ .

Although no organic tracers (such as levoglucosan) were used in this CMB application to apportion the wood smoke component, we did consistently utilize 43 “common” chemical species including elemental potassium and the potassium ion. The ambient  $\text{PM}_{2.5}$  in Fairbanks was heavily influenced by elevated concentrations of OC and EC, as well as high concentrations of sulfur and sulfate. A source profile developed in Missoula, Montana in the late 1980s served as the best statistically fitting wood smoke profile for the Fairbanks CMB. However, it is important to note this wood smoke profile was not representative of the specific types/models of wood burning devices used in Fairbanks, nor the sources of fuels (birch and spruce) that are typically combusted. We also hypothesize that the sulfur component was not correctly apportioned in this CMB application, and likely influences the amounts apportioned to other sources in our modeling (including wood combustion). We suspect there is a missing source (such as fuel oil combustion) that was not identified. This is supported by the especially high wood smoke proportions and CF values from CMB modeling for the State Building and Peger Road sites. Through the OMNI combustion trials described above, we have developed Fairbanks-specific profiles for various emissions and will report the results of the updated CMB modeling with those profiles in a subsequent publication.

#### **Levoglucosan vs. Carbon-14**

The wood smoke  $\text{PM}_{2.5}$  mass contribution estimates from the  $^{14}\text{C}$  data are plotted vs. ambient  $\text{PM}_{2.5}$  levoglucosan concentrations on a sample by sample basis in Fig. 2(b). Results for  $^{14}\text{C}$  presented in this figure are based on the arithmetic mean of the minimum and maximum contribution estimates. The plot suggests that the relationship is



**Fig. 1.** Three year average (95% CI) values of wood smoke apportionment using  $^{14}\text{C}$  analysis (horizontal pattern, minimum light and maximum dark), levoglucosan analysis (vertical pattern, low estimate light and high estimate dark), and CMB modeling (stippled pattern).

independent of site and all of the data were pooled across sites for subsequent analyses. Fig. 2(b) demonstrates a high correlation between the levoglucosan and  $^{14}\text{C}$  measures with a slope (CF) of  $11.82 \pm 0.67$  ( $r^2 = 0.97$ ,  $F = 1257$ ,  $n = 40$ ). This CF value is less than 10% higher than that published by Caseiro *et al.* (2009) for  $\text{PM}_{10}$  (10.7). Regression analysis after eliminating the highest point ( $\text{CF} = 11.31 \pm 0.62$ ,  $r^2 = 0.97$ ,  $F = 1374$ ,  $n = 39$ ) and four highest points ( $\text{CF} = 11.46 \pm 0.70$ ,  $r^2 = 0.97$ ,  $F = 1121$ ,  $n = 36$ ) from North Pole yielded no significant differences in the CF values or regression statistics. Using all data and the minimum and maximum wood smoke  $\text{PM}_{2.5}$  estimates from the  $^{14}\text{C}$  data yielded  $\text{CF} = 10.72 \pm 0.61$  and  $12.91 \pm 0.74$ , respectively. Another approach is to calculate and average the ratios of wood smoke  $\text{PM}_{2.5}$  to levoglucosan for each sample. Using minimum and maximum estimates for wood smoke  $\text{PM}_{2.5}$  from the  $^{14}\text{C}$  data yielded mean CF values of  $11.45 \pm 0.89$  and  $13.8 \pm 1.1$ , respectively. These estimates are slightly higher than the regression slope estimates because of a non-zero regression intercept. All of these values are within the range of estimates of  $\text{CF}_1 = 9.01$  and  $\text{CF}_2 = 13.3$  calculated and presented above within 95% confidence, and fall within but at the lower end of the range published by (Herich *et al.*, 2014).

## CONCLUDING REMARKS

Source apportionment of ambient  $\text{PM}_{2.5}$  to residential wood heater use is an important issue in many areas. Our results suggest that this can be done reliably using a variety of means. Each method has its strengths and limitations. Each relies, at least to some extent, on knowledge of local emission profiles.

In the current study, the CMB method appears to overestimate the contribution of residential wood heating. The method relies on the availability of representative emission profiles which may be difficult to obtain in areas like Fairbanks with unique climate and atmospheric chemistry.

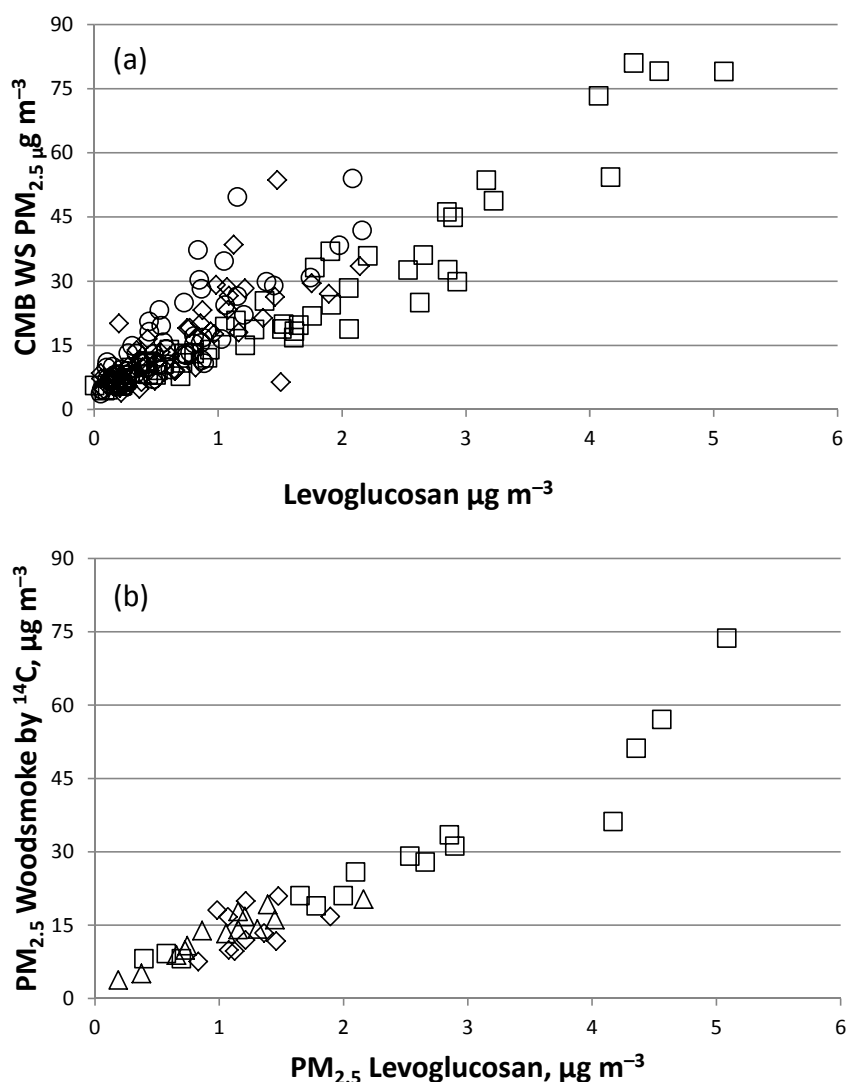
The method is relatively expensive and time consuming, as it requires comprehensive chemical analysis of filter samples as well as considerable experience, time and effort with the model.

Apportionment through  $^{14}\text{C}$  analysis is based on well understood and accepted principles, and thus allows good confidence in the results. The method only allows apportionment of the carbon in the PM, however. In situations like Fairbanks, where non-carbon species make up a significant fraction of the PM, the results must be corrected for the expected carbon content of biomass combustion emissions. This approach is also expensive as it utilizes costly and dedicated instrumentation.

The use of levoglucosan  $\text{PM}_{2.5}$  mass fractions for apportionment has the advantage of being relatively inexpensive. The uncertainty in this approach is primarily in the conversion from levoglucosan fraction to wood smoke PM portion. The cost advantage is not real if location-specific conversion factors must be measured for each study because this is both expensive and, in our experience, not necessarily reliable. Efforts in this study indicate that an appropriate conversion factor lies in the range of 9.1 to 13.3. Using values in this range results in wood smoke apportionment consistent with that obtained from  $^{14}\text{C}$  analysis.

To our knowledge, this is the first report with extensive results correlating levoglucosan levels to wood smoke  $\text{PM}_{2.5}$  levels from  $^{14}\text{C}$  analysis. These correlations result in conversion factors in the range of 10.7 to 12.9. These conversion factor values come from field data, and are as accurate and reliable as the  $^{14}\text{C}$  apportionment results. Similarity of the measured values to those calculated from levoglucosan emission factors for fresh wood smoke PM also suggest a limited or negligible effect of levoglucosan instability on the conversion factor, at least during the relatively cold and dark winter months in Fairbanks and in a localized airshed where wood smoke  $\text{PM}_{2.5}$  is continuously emitted.





**Fig. 2.** (a) Wood smoke PM<sub>2.5</sub> as determined by CMB analysis vs ambient levoglucosan concentration in PM<sub>2.5</sub>. (b) Wood smoke PM<sub>2.5</sub> as determined by <sup>14</sup>C analysis vs ambient levoglucosan concentration in PM<sub>2.5</sub>. <sup>14</sup>C wood smoke levels are the mean of minimum and maximum values.  $\diamond$  State Building,  $\square$  North Pole,  $\circ$  Peger Road.

Previous studies have suggested conversion factors in the range of 10.7 to 25.2. The convergence of the current values and those for studies in different regions suggests that reasonable wood smoke apportionment estimates can be obtained using levoglucosan mass fractions and a conversion factor in the range of 9.1 to 13.3, and likely in the narrower range of 10.7 to 12.9.

CMB is intended to complement rather than replace other data analysis and modeling methods. Results from this study show that alternative approaches can be used to evaluate results from CMB modeling, as well as provide a less expensive alternative to source apportionment of residential wood smoke contributions.

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