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Application of high-performance anion-exchange chromatography–pulsed amperometric detection for measuring carbohydrates in routine daily filter samples collected by a national network: 1. Determination of the impact of biomass burning in the upper Midwest

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[1] Biomass burning is one of the major sources of organic carbon aerosols. However, there is limited information on the temporal and spatial variability for the impact of biomass burning in most regions of the United States, including the upper Midwest. In an attempt to obtain information on these variabilities, high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) was employed to measure the smoke marker levoglucosan (and various other carbohydrates) on archived daily Federal Reference Monitor (FRM) Teflon filter samples from the $PM_{2.5}$ NAAQS compliance monitoring network. Levoglucosan data, along with measurements of water-soluble organic carbon (WSOC) and potassium, from the analysis of FRM samples collected at 10 sites in the upper Midwest from March 2004 through February 2005 are presented. Results suggest that WSOC contains a substantial regional component, summer levoglucosan is dependent on both horizontal and vertical transport of fire emissions, and potassium revealed no clear pattern associated with biomass burning impacts. The contribution of organic carbon due to primary biomass burning particle emissions ranged on average from about 5 to 35%, suggesting that for this study in the upper Midwest, >50% of the WSOC is from secondary organic aerosol rather than biomass burning. In a second paper the results from the measurements of the other carbohydrates that HPAEC-PAD analysis can determine are discussed to investigate their sources and trends.

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1. Introduction

[2] Biomass burning has been found to be one of the major sources of atmospheric fine particle organic carbon. This includes smoke from wildfires and prescribed burning as well as from residential wood combustion [*Simoneit*, 2002, and references within]. In order to quantify the contribution of biomass burning to the total organic carbon, the most common method employed is the use of smoke marker measurements. The most commonly used smoke marker is levoglucosan, an anhydrosugar produced during the combustion of cellulose [*Simoneit et al.*, 1999].

[3] Levoglucosan is traditionally measured using gas chromatography–mass spectrometry (GC-MS) [*Nolte et al.*, 1999; *Hays et al.*, 2002; *Zdráhal et al.*, 2002; *Simpson et al.*, 2004]. GC-MS requires chemical derivatization, making it labor intensive and expensive due to the instrumentation, reagents, and solvents needed. For this work, levoglucosan was instead measured using high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) [*Gao et al.*, 2003; *Gorin et al.*, 2006; *Engling et al.*, 2006; *Puxbaum et al.*, 2007; *Sullivan et al.*, 2008]. HPAEC-PAD has the advantages that it is more sensitive, the extraction of the filter can be performed directly in water, the filter extract can be directly analyzed for levoglucosan, and it uses ion chromatography (IC), an analytical technique commonly used by aerosol monitoring

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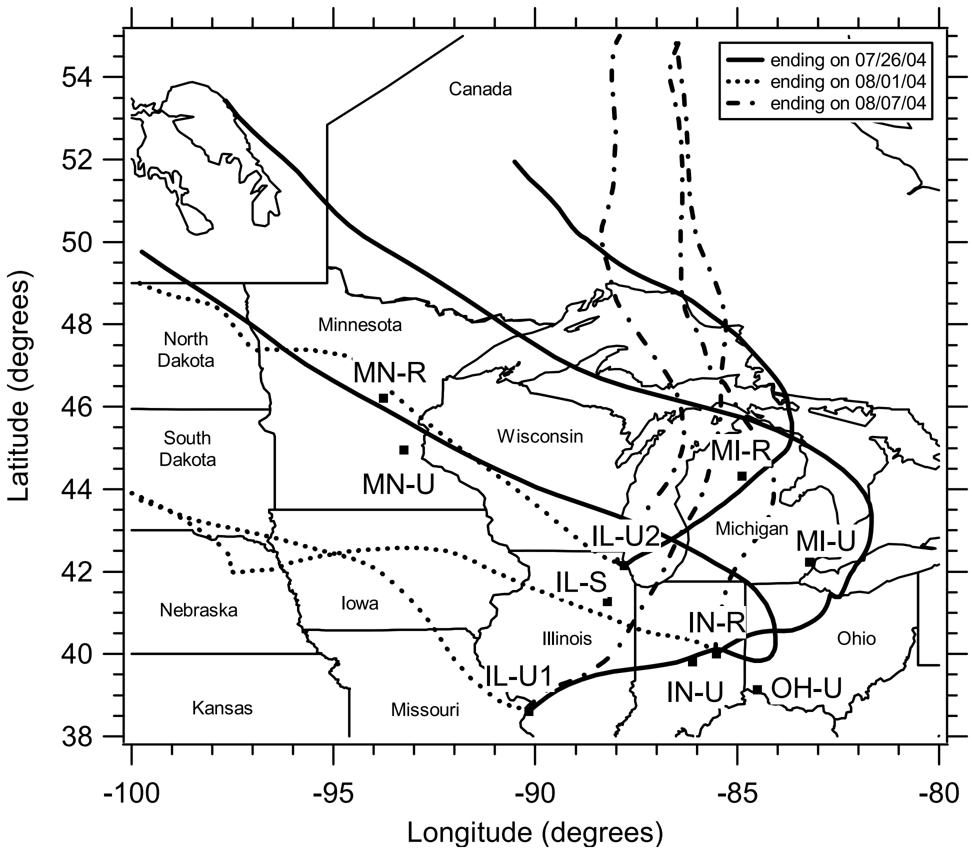

Figure 1. Map of the locations for the 10 sites used for this study. Also included are characteristic 72 h air mass back trajectories ending on 26 July, 1 August, and 7 August 2004 at midnight local time for IL-U1, IL-U2, and IN-R for the event discussed in section 3.1.1. All back trajectories are based on the NOAA ARL HYSPLIT trajectory model.

networks for analysis of the major inorganic aerosol species. This method can also simultaneously detect a variety of other carbohydrates in addition to levoglucosan. Part 2 of this paper [*Sullivan et al.*, 2011] discusses the results from the measurements of these other carbohydrates in an investigation of their sources and trends from the same samples from the upper Midwest presented here.

[4] Previous work in the upper Midwest involving positive matrix factorization (PMF) analysis of CSN (Chemical Speciation Network) filter data from December 2000 to April 2005 found in Detroit, MI that biomass burning contributed 3% of the $PM_{2.5}$ [*Gildemeister et al.*, 2007]. A study in Chicago, also using CSN filter data, found that based on PMF analysis or CMB (chemical mass balance) modeling in 2001–2003 the contribution of biomass burning to $PM_{2.5}$ was 5 or 11% [*Rizzo and Scheff*, 2007]. The routine measurements made on the CSN filters do not include organic markers, such as levoglucosan. However, two other studies in the upper Midwest did determine levoglucosan using GC-MS. In the first study, a comparison of CMB [*Bae et al.*, 2006] and PMF results on filter samples collected at the St. Louis–Midwest Supersite (June 2001 to June 2003) found the biomass burning contribution to OC to be 14% [*Jaeckels et al.*, 2007]. The second investigation, using data from the 2004–2005 Urban Organics Study, found that on an annual average, 15–25% of the organic carbon was due to biomass burning at the five sites where measurements were made (see http://www.ladco.org/reports/rpo/monitoring/urban_organics_study_integration_final_report_sti_uw.pdf for more information). This last study, as well as most previous studies looking at the impact of biomass burning at numerous sites, have been based on the analysis of monthly composited filter samples [e.g., *Zheng et al.*, 2002]. As a result, there is generally a lack of information on the temporal and spatial variability for the impact of biomass burning in the upper Midwest or in other regions. Since it appears that biomass burning can be an important source of organic carbon in this region, daily samples routinely collected by the Federal Reference Monitor (FRM) deployed for the $PM_{2.5}$ NAAQS compliance monitoring network were analyzed to quantify biomass burning impacts on regional fine particle organic carbon concentrations.

[5] The $PM_{2.5}$ NAAQS compliance monitoring network is a national network that consists of over a thousand sites across the United States. As part of the routine measurements made by this network, a 47 mm Teflon filter is collected to obtain a gravimetric measurement of the total $PM_{2.5}$ mass concentration. Once this measurement is completed, the entire filter is archived, generally refrigerated and in a petri dish, providing a filter sample that can be analyzed by additional methods. The main disadvantage of using FRM samples is that the total organic carbon concentration cannot be directly measured from them by thermal-optical techniques because the filters are Teflon. However, the total

Table 1. Details About the Sites Used in This Study Grouped By State From West to East[a]

	Mille Lacs, Minnesota	Minneapolis, Minnesota, at the HC Anderson School Site	Braidwood, Illinois	East St. Louis, Illinois	Northbrook, Illinois	Houghton Lake, Michigan	Detroit, Michigan, at the Allen Park Site	Mechanicsburg, Indiana	Indianapolis, Indiana, at the Washington Park Site	Cincinnati, Ohio, at the Taft St. Site
AQS code	27-095-3051	27-053-0963	17-197-1007	17-163-0010	17-031-4201	26-113-0001	26-163-0001	18-065-0003	18-097-0078	39-061-0040
Latitude, longitude coordinates (deg)	46.21, −93.76	44.95, −93.26	41.28, −88.22	38.61, −90.16	42.12, −87.80	44.31, −84.89	42.23, −83.21	40.01, −85.52	39.81, −86.11	39.13, −84.50
Number of samples analyzed	52	58	54	55	47	47	58	56	61	57
Site type	Rural	Urban	Suburban	Urban	Urban	Rural	Urban	Rural	Urban	Urban
Abbreviation used	MN-R	MN-U	IL-S	IL-U1[b]	IL-U2[b]	MI-R	MI-U	IN-R	IN-U	OH-U
Mass ($\mu g/m^3$)										
Annual	5.67 ± 3.57	8.46 ± 4.52	10.60 ± 6.20	14.65 ± 5.92	10.81 ± 7.64	7.50 ± 6.51	13.12 ± 8.15	11.94 ± 7.23	14.28 ± 7.82	14.30 ± 7.97
Summer	5.48 ± 2.95	7.65 ± 4.12	10.73 ± 6.94	15.97 ± 6.83	9.00 ± 5.44	10.32 ± 8.38	15.02 ± 9.66	13.62 ± 8.38	16.63 ± 9.86	17.35 ± 10.61
Winter	7.01 ± 5.06	10.08 ± 5.44	12.50 ± 7.00	13.98 ± 4.20	16.01 ± 11.10	7.74 ± 6.42	13.58 ± 8.18	12.39 ± 7.60	14.23 ± 7.68	13.47 ± 5.63
t test value	±2.75	±3.03	±4.53	±3.81	±6.38	±5.28	±5.63	±5.18	±5.46	±5.80
Seasonal dependence	no	no	no	no	yes	no	no	no	no	no
OC ($\mu g\ C/m^3$)										
Annual	1.36 ± 0.92	2.62 ± 1.11	NA	3.45 ± 1.79	2.16 ± 1.11	1.37 ± 1.31	2.83 ± 1.43	1.96 ± 1.19	3.15 ± 1.81	2.89 ± 1.31
Summer	2.00 ± 1.05	3.24 ± 1.14	NA	4.07 ± 2.02	2.35 ± 0.83	2.16 ± 1.23	3.80 ± 1.63	2.61 ± 1.32	3.96 ± 1.78	3.33 ± 1.41
Winter	0.99 ± 0.51	2.37 ± 0.73	NA	3.16 ± 1.77	2.47 ± 1.50	0.93 ± 1.41	2.67 ± 1.34	1.50 ± 1.09	2.66 ± 1.74	2.73 ± 1.36
t test value	±0.65	±0.74	NA	±1.48	±0.83	±0.90	±1.04	±0.89	±1.17	±0.91
Seasonal dependence	yes	yes	NA	no	no	yes	yes	yes	yes	no
WSOC ($\mu g\ C/m^3$)										
Annual	1.30 ± 0.44	1.43 ± 0.49	1.48 ± 0.47	1.98 ± 0.68	1.73 ± 0.56	1.68 ± 0.70	1.88 ± 0.83	2.27 ± 0.70	1.84 ± 0.76	1.76 ± 0.69
Summer	1.53 ± 0.57	1.73 ± 0.60	1.76 ± 0.57	2.33 ± 0.82	1.90 ± 0.76	2.31 ± 1.02	2.57 ± 1.10	2.50 ± 0.88	2.27 ± 0.99	2.17 ± 0.88
Winter	1.05 ± 0.13	1.16 ± 0.11	1.29 ± 0.35	1.68 ± 0.40	1.73 ± 0.45	1.48 ± 0.30	1.48 ± 0.33	2.25 ± 0.53	1.60 ± 0.47	1.47 ± 032
t test value	±0.34	±0.33	±0.35	±0.48	±0.47	±0.58	±0.62	±0.49	±0.51	±0.50
Seasonal dependence	yes	yes	yes	yes	no	yes	yes	no	yes	yes
Levoglucosan (ng/m^3)										
Annual	21.26 ± 19.73	25.05 ± 22.84	12.71 ± 11.60	36.68 ± 36.72	12.63 ± 19.54	20.37 ± 17.84	23.63 ± 23.99	39.35 ± 30.62	69.13 ± 53.59	14.53 ± 19.37
Summer	15.78 ± 12.85	16.03 ± 10.58	7.73 ± 6.01	28.86 ± 19.29	4.63 ± 5.35	16.42 ± 11.64	25.55 ± 26.61	26.97 ± 16.16	50.63 ± 42.65	10.48 ± 12.75
Winter	41.73 ± 22.35	39.28 ± 21.78	20.29 ± 14.12	58.61 ± 52.32	30.11 ± 29.20	29.54 ± 23.95	33.87 ± 28.29	66.78 ± 37.51	98.93 ± 53.20	25.70 ± 27.00
t test value	±15.16	±12.64	±8.18	±27.46	±17.68	±14.73	±17.43	±21.87	±32.70	±15.36
Seasonal dependence	yes	yes	yes	yes	yes	no	no	yes	yes	no
Potassium ($\mu g/m^3$)										
Annual	0.020 ± 0.014	0.053 ± 0.039	0.071 ± 0.064	0.085 ± 0.074	0.058 ± 0.047	0.037 ± 0.030	0.057 ± 0.040	0.059 ± 0.053	0.088 ± 0.061	0.091 ± 0.090
Summer	0.015 ± 0.012	0.062 ± 0.048	0.065 ± 0.040	0.111 ± 0.109	0.066 ± 0.049	0.049 ± 0.041	0.065 ± 0.053	0.062 ± 0.072	0.099 ± 0.068	0.130 ± 0.135
Winter	0.022 ± 0.015	0.043 ± 0.019	0.061 ± 0.025	0.055 ± 0.029	0.069 ± 0.059	0.036 ± 0.024	0.058 ± 0.037	0.054 ± 0.024	0.095 ± 0.051	0.080 ± 0.037
t test value	±0.010	±0.024	±0.022	±0.057	±0.038	±0.025	±0.029	±0.036	±0.036	±0.069
Seasonal dependence	no	no	no	no	no	no	no	no	no	no

[a] Included are the Air Quality System (AQS) code, coordinates, number of samples (excluding blanks) analyzed at each site, site type, and the abbreviation used for each site throughout the text. The abbreviations for the sites use the postal abbreviation for the state the site is located in followed by a U for an urban site, R for a rural site, and S for a suburban site. Also included are the annual, summer, and winter average ± standard deviation for $PM_{2.5}$ mass, OC, WSOC, levoglucosan, and potassium for each site, where NA denotes "not available." The results from performing a Student *t* test at the 95% confidence interval on the summer versus winter average and whether this indicated a seasonal dependence is also included. The mass and OC concentrations, except at IL-U1, were obtained from the EPA Air Quality Data Mart. The OC at IL-U1 was measured as part of the St. Louis–Midwest Supersite and at all other sites by the CSN Network with application of the blank correction discussed in section 3.2.

[b] Since there are two urban sites in Illinois, U1 and U2 are used to distinguish the sites in East St. Louis and Northbrook, respectively.

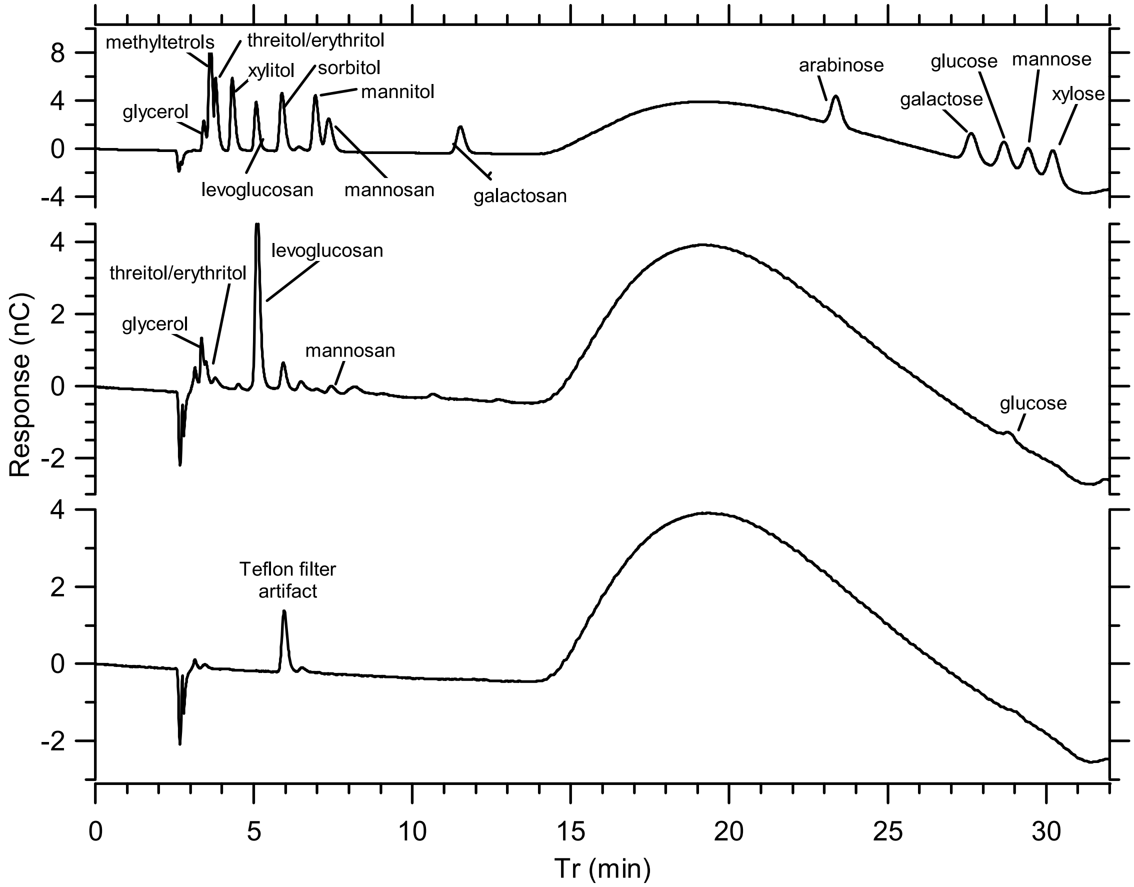

Figure 2. Example chromatograms from using the PA-1 column, where Tr is retention time. The top chromatogram is from the injection of a mixed carbohydrate calibration standard. The sugar alcohols/polyols (labels top left of calibration chromatogram) and anhydrosugars (labels bottom left of calibration chromatogram) elute before 10 min and the sugars elute after 20 min. The middle and bottom chromatograms are from the analysis of an ambient and blank FRM filter sample, respectively.

water-soluble organic carbon (WSOC) can be measured from the same aqueous filter extract as the levoglucosan. WSOC can be a very valuable measurement since it has been found that the two main sources of WSOC are secondary organic aerosol and biomass burning [*Sullivan et al.*, 2006].

[6] Results from the application of HPAEC-PAD to measure levoglucosan on archived FRM Teflon filter samples collected at ten sites in the upper Midwest from March 2004 through February 2005 will be presented. Along with the levoglucosan data, measurements of water-soluble potassium and WSOC will also be shown. These data will be used to investigate the spatial and temporal trends of these various species. A determination of the impact of biomass burning on the total organic carbon (OC) concentration in this region will be provided.

2. Methods

2.1. Filter Samples

[7] The filter samples used for this work were archived 47 mm Teflon filters collected to provide routine $PM_{2.5}$ mass measurements as part of the $PM_{2.5}$ NAAQS compliance monitoring network. These samples are collected on a standard $PM_{2.5}$ NAAQS compliance monitoring sampler, which has a flow rate of 16.7 LPM and uses a 2.5 μm WINS or SCC impactor (http://www.epa.gov/fedrgstr/EPA-AIR/2002/April/Day-02/a7944.htm). The 24 h (starting at midnight) 1-in-6 day samples collected from 4 March 2004 to 27 February 2005 at ten sites in the Midwest United States were analyzed. Figure 1 shows a map with the locations of these ten sampling sites. More details about each of the sites can be found in Table 1.

[8] Any blank samples available at each of the sites on the 1-in-6 day sampling days were also analyzed. The blanks for all measurements were found to be negligible, as no peaks for species of interest were detected (see Figure 2). Therefore, no blank correction has been applied to the data presented.

2.2. Measurement Approach

[9] The entire 47 mm Teflon filter was extracted in 15 mL of deionized water (DI Water) in a Nalgene Amber HDPE bottle, sonicated without heat for 40 min, and then filtered using a 0.2 μm PTFE syringe filter to ensure that only the water-soluble fraction of the aerosol particles was measured. The liquid extracts were analyzed for levoglucosan using high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) the same

Table 2a. Coefficients of Linear Determination From Site to Site Scatterplots Forced Through Zero for $PM_{2.5}$ Levoglucosan[a]

Site	MN-R	MN-U	IL-S	IL-U1	IL-U2	MI-R	MI-U	IN-R	IN-U	OH-U
MN-R	1	0	0	0.30	0	0	0	0	0	0
		0	0	0	0	0	0	0	0	0
MN-U		1	0	0	0	0	0	0	0	0
			0	0	0	0	0	0	0	0
IL-S			1	0	0.55	0.32	0.30	0.43	0	0.35
				0	0.60	0.04	0	0.13	0.21	0
IL-U1				1	0	0	0.24	0	0	0
					0	0	0	0	0.44	0
IL-U2					1	0	0.26	0.26	0.21	0
						0.42	0.58	0.16	0.30	0
MI-R						1	0.05	0.50	0	0
							0.79	0.31	0.34	0.03
MI-U							1	0.28	0.20	0
								0.12	0.13	0
IN-R								1	0	0.04
									0.76	0.40
IN-U									1	0
										0.37
OH-U										1

[a]The value at the top of each box is for summer and at the bottom for winter.

day the filters were extracted. The measurements of water-soluble potassium (K^+) using ion chromatography (IC) and WSOC occurred within 48 h of extraction.

[10] HPAEC-PAD is essentially an electrochemical technique where hydroxyl groups associated with chromatographically resolved compounds are oxidized on the surface of a gold working electrode. More details about this technique and the instrument used are provided by *Sullivan et al.* [2008]. However, the separation method is provided in detail below as a new column, a Dionex CarboPac PA-1 (guard 4 × 50 mm and analytical 4 × 250 mm) column was used. The eluents are 200 mM sodium hydroxide (NaOH) and DI Water. The complete run time is approximately 59 min using a flow rate of 0.5 mL/min and includes isocratic elution for 10 min at 10 mM NaOH to detect anhydrosugars and sugar alcohols/polyols, a 19 min linear gradient from 10 to 70 mM NaOH to detect sugars, a column cleaning at 180 mM NaOH for 14 min, and a reequilibration step for 16 min to return to the starting conditions of 10 mM NaOH. In this method, arabitol, a sugar alcohol/polyol associated with fungi, can overlap with levoglucosan in the chromatogram. This is only a factor for ambient samples collected from approximately May through November as arabitol originates from spores which are not active during winter and spring. The concentration of mannitol, another sugar alcohol/polyol associated with fungi, is used to correct the levoglucosan data as it has been found that the mannitol concentration is equal to 1.5 ± 0.26 times the concentration of arabitol [*Bauer et al.*, 2008]. The correction for this data set was actually quite small, being on average less than 2 ng/m^3 with a mean and range of estimated arabitol/uncorrected levoglucosan ratio of 0.13 and 0.001 to 0.79, respectively. Having to correct the data does increase the propagated uncertainty in reported levoglucosan concentrations from ~10% to 28% for all samples. Although not having to correct the levoglucosan is preferable, the repeatability, precision, and sensitivity of the measurement technique prevent the increased uncertainty from greatly affecting the data interpretation.

Table 2b. Coefficients of Linear Determination From Site to Site Scatterplots Forced Through Zero for $PM_{2.5}$ WSOC[a]

Site	MN-R	MN-U	IL-S	IL-U1	IL-U2	MI-R	MI-U	IN-R	IN-U	OH-U
MN-R	1	0.83	0	0	0	0.08	0	0	0	0.65
		0.25	0	0	0	0	0	0	0	0
MN-U		1	0.37	0	0.32	0.36	0.17	0	0	0.33
			0	0	0	0	0	0	0	0
IL-S			1	0.42	0.80	0.87	0.83	0.71	0.54	0.46
				0.29	0.69	0.11	0.24	0.53	0.53	0.43
IL-U1				1	0.79	0.64	0.70	0.52	0.57	0.20
					0.60	0	0.01	0.61	0.54	0.60
IL-U2					1	0.85	0.77	0.75	0.49	0
						0.70	0.89	0.47	0.42	0.14
MI-R						1	0.70	0.89	0.82	0
							0.45	0.09	0	0
MI-U							1	0.69	0.71	0
								0.25	0.23	0
IN-R								1	0.78	0.77
									0.75	0.86
IN-U									1	0.70
										0.50
OH-U										1

[a]The value at the top of each box is for summer and at the bottom for winter.

[11] Figure 2 shows chromatograms for a calibration standard, ambient sample, and blank sample using this method. Based on using the study's flow rate of 16.7 LPM and sampling time of 24 h, the limit of detection (LOD) for the various carbohydrates is less than approximately 0.10 ng/m^3. Based on analysis of standards, the precision and accuracy are 3% and ±0.0003 μg (0.01 ng/m^3), respectively. The detector is run with a range of 500 nC and the response has been found to be linear over this entire range. In the supporting information, a comparison between determining levoglucosan from archived collocated FRM Teflon filters using the HPAEC-PAD method described above and a traditional GC-MS method [*Simpson et al.*,

Table 2c. Coefficients of Linear Determination From Site to Site Scatterplots Forced Through Zero for $PM_{2.5}$ Potassium[a]

Site	MN-R	MN-U	IL-S	IL-U1	IL-U2	MI-R	MI-U	IN-R	IN-U	OH-U
MN-R	1	0	0	0	0	0	0	0	0	0
		0.37	0	0	0.16	0	0	0	0	0
MN-U		1	0.08	0	0	0	0	0	0	0
			0	0	0	0	0	0	0	0
IL-S			1	0	0.07	0.55	0.54	0	0.15	0.26
				0.08	0.28	0.36	0.10	0.35	0	0
IL-U1				1	0	0	0.60	0	0.06	0
					0.29	0	0	0	0	0.19
IL-U2					1	0.38	0.53	0	0	0
						0	0.25	0	0.13	0
MI-R						1	0.38	0.15	0	0.28
							0.21	0.02	0.10	0
MI-U							1	0.21	0.14	0.30
								0	0	0
IN-R								1	0.06	0.34
									0	0
IN-U									1	0.30
										0
OH-U										1

[a]The value at the top of each box is for summer and at the bottom for winter.

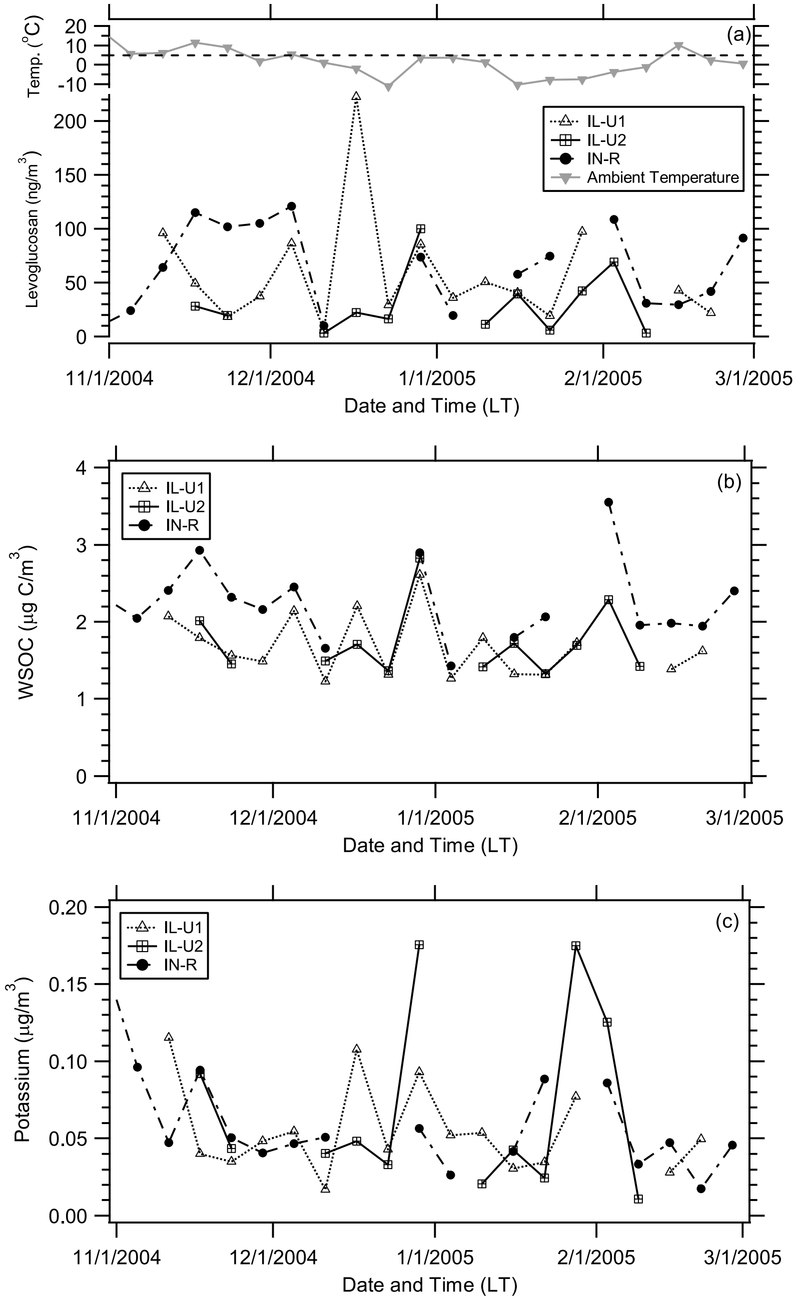

Figure 3. Time series for $PM_{2.5}$ (a) levoglucosan, (b) WSOC, and (c) potassium during the winter at IL-U1, IL-U2, and IN-R. The ambient temperature recorded at IN-R is also included at the top of Figure 3a. The dashed line indicates 5°C. Dates are given as month/day/year.

2004; *Ward et al.*, 2006] is provided (auxiliary material Figure S1).[1] The results from the two methods agree quite well, suggesting the methods are comparable and both effective at analyzing levoglucosan from Teflon filter samples.

[12] Water-soluble potassium was measured in the liquid extract using a Dionex ICS-3000 ion chromatograph which includes an isocratic pump, conductivity detector, self-regenerating cation SRS-ULTRA suppressor, and an eluent generator with a methanesulfonic acid cartridge. A Dionex IonPac CS12A analytical (3 × 150 mm) column with a 20 mM methanesulfonic acid eluent at a flow rate of 0.5 mL/min allowed for separation of the common inorganic cations. The complete run time was 17 min. A sample injection volume of 50 μL was used. The LOD for water-soluble potassium was approximately 0.001 $\mu g/m^3$ (or 1 ng/m^3) for this study.

[13] WSOC was measured using a Sievers Model 800 Turbo Total Organic Carbon (TOC) Analyzer. The TOC analyzer works by converting organic carbon in the sample to carbon dioxide using chemical oxidation by reaction with ammonium persulfate and ultraviolet light. Carbon dioxide

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[1] Auxiliary material data sets are available at ftp://ftp.agu.org/apend/jd/2010jd014166. Other auxiliary material files are in the HTML.

formed was measured by an increase in sample conductivity. The analyzer was run in Turbo mode, providing a 3 s integrated measurement. For this study, the LOD for WSOC was approximately 0.06 μg C/m^3.

3. Results and Discussion

3.1. Spatial and Temporal Patterns for PM$_{2.5}$ Levoglucosan, WSOC, and Water-Soluble Potassium

3.1.1. Overview

[14] The levoglucosan concentrations at all sites are typically higher in the winter than the summer (Table 1), with an all-site winter mean of 44 ± 24 ng/m^3 versus 19 ± 12 ng/m^3 in summer. (Note that, when referring to summer versus winter, summer includes data from June through September and winter from November through February.) It is often observed that levoglucosan concentrations are higher in the winter than summer due to the increase in residential burning that occurs in winter [e.g., *Puxbaum et al.*, 2007; *Zheng et al.*, 2002]. Levoglucosan concentrations in the winter are generally more highly correlated between sites than in summer (Table 2a) and significantly different than summer concentrations (Table 1). WSOC, on the other hand, is higher at all sites in the summer than in winter with an all-site mean of 2.02 ± 0.33 μg C/m^3 in summer and 1.52 ± 0.34 μg C/m^3 in winter (Table 1). Moreover, Table 2b suggests WSOC in summer is correlated even more strongly across sites than in the winter. Unlike levoglucosan or WSOC, potassium exhibits no real pattern between seasons at any of the sites and no significant difference was found between summer and winter concentrations (Table 1). The mean concentration across all sites in summer and winter are quite similar (0.068 ± 0.030 μg/m^3 versus 0.057 ± 0.021 μg/m^3 respectively). There is also generally little correlation in potassium concentrations between sites in either season (Table 2c). Potassium is often considered to be a good inorganic marker for biomass burning so the lack of seasonal variation or site-to-site correlation in potassium is surprising. Data Sets S1–S10 in the auxiliary material provide the concentrations for the various species measured for each filter sample at each site.

[15] To further illustrate the observations described above, the remainder of this section will focus on results from three sites in summer and winter: IL-U1, IL-U2, and IN-R. These three sites include one rural site (IN-R) and two urban sites (one more southern, IL-U1, and one more northern, IL-U2). These sites are about 400 to 480 km away from each other. Observations at these locations have been found to be typical of the other seven study sites.

[16] As seen in Figure 3a, for most of the winter the levoglucosan concentrations at all three sites track each other. The ambient temperature measured at IN-R, which is similar to the temperature profile at all other sites, is also included in Figure 3a. There is little correlation between the levoglucosan concentration and ambient temperature across the full data set. However, levoglucosan concentrations correlate more strongly across the sites once the temperature falls below 5°C (note the difference in the tracking of levoglucosan at all three sites before and after December 1 when the temperature drops below 5°C). For example, the correlation between winter levoglucosan concentrations at IL-U1 versus IN-R is low at R^2 = 0.14. However, the correlation increases to R^2 = 0.39 for times when the temperature is less than 5°C and drops to R^2 = 0.04 for times when the temperature is greater than 5°C. Increased correlation at low temperatures suggests an increase in residential burning at all sites due to uniform cold temperatures across the Midwest. Strong tracking of levoglucosan concentrations across sites during this time may also be related to covariance in the mixing layer depth. Lower mixing heights trap surface emissions near the ground and contribute to elevated surface pollutant concentrations. The mixing layer height, calculated from back trajectory analysis using the NOAA ARL (National Oceanic and Atmospheric Administration Air Resources Laboratory) HYSPLIT trajectory model (R. R. Draxler and G. D. Rolph, HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model, 2003, http://www.arl.noaa.gov/ready/hysplit4.html, and G. D. Rolph, Real-time Environmental Applications and Display sYstem (READY) Web site, 2003, http://www.arl.noaa.gov/ready/hysplit4.html), during winter at IL-UI and IN-R was moderately correlated with R^2 = 0.52. But the correlation is even better (R^2 = 0.98) for times when the temperature is less than 5°C.

[17] In contrast, during summer the levoglucosan concentrations generally do not peak or track together at the three sites (Figure 4a). For example, there are many periods when the levoglucosan concentration at IL-U2 is only a few ng/m^3 and varies little from sample to sample. However, during these same times the concentrations at the other sites are two times higher and vary by at least 5 to 10 ng/m^3 from sample to sample.

[18] It is expected that during the summer levoglucosan is associated with smoke from wildfires and prescribed burning as opposed to residential burning. Based on the NOAA Satellite Fire Detections viewer (http://map.ngdc.noaa.gov/website/firedetects/viewer.htm) and comparisons with other regions in the United States there were few fires occurring in the Midwest suggesting it was not an intense burning season in this region. Also, unlike in other years, the site operators did not note any burning. This of course does not rule out the presence of small local or regional fires, but does suggest they were insignificant.

[19] The Satellite Fire Detections viewer does reveal wildfires burning in Alaska from June through September 2004 that periodically impacted the study region with smoke. One such period is for the samples collected on 26 July, 1 August, and 7 August. On these days, generally the three sites are sampling similar air masses. This conclusion is supported by 72 h back trajectory analysis on these three days using the NOAA ARL HYSPLIT trajectory model (R. R. Draxler and G. D. Rolph, HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model, 2003, http://www.arl.noaa.gov/ready/hysplit4.html, and G. D. Rolph, Real-time Environmental Applications and Display sYstem (READY) Web site, (http://www.arl.noaa.gov/ready/hysplit4.html) (Figure 1). As shown in Figure 4b, the WSOC concentrations at each site on these days are also similar. This is likely related to a high-sulfate region that extends over the entire upper Midwest as indicated by the NAAPS Global Aerosol Model (http://www.nrlmry.navy.mil/aerosol_web/#currentaerosolmodeling). In addition, synoptic weather transitions were not present in the study region during this time. Weather maps (http://www.hpc.ncep.noaa.gov/noaa/

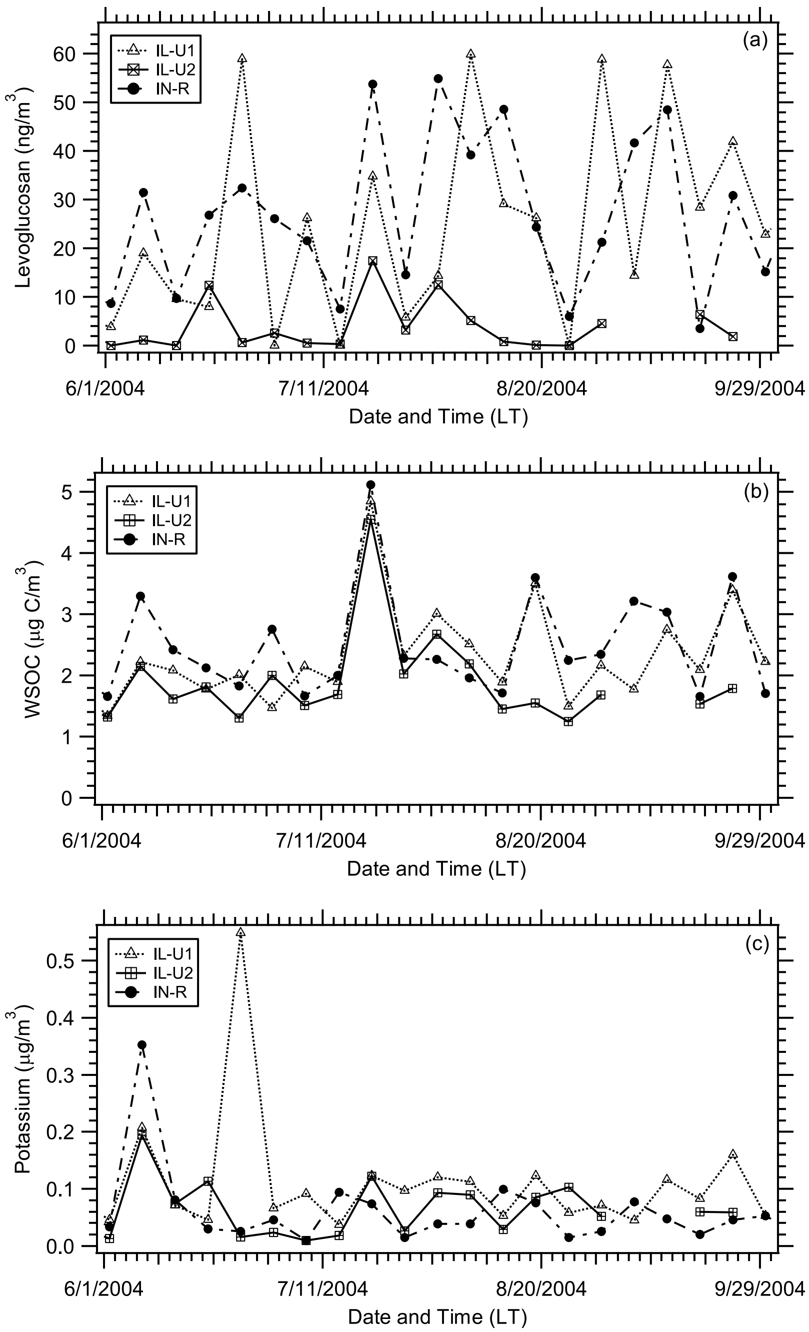

Figure 4. Time series for $PM_{2.5}$ (a) levoglucosan, (b) WSOC, and (c) potassium during the summer at IL-U1, IL-U2, and IN-R.

noaa_archive.php) indicated a high-pressure center sitting over the Midwest on 26 July and 7 August and the study region situated between fronts on 1 August, with cold fronts passing over the sites between sampling days on 29–30 July and 3–4 August.

[20] As shown in Figure 4a, there was no noticeable increase in the levoglucosan concentration at IL-U2. The levoglucosan at IL-U1 spikes on 7 August, not on 1 August as it did at IN-R. If we examine the altitude profiles from the back trajectory analysis seen in Figure 5, we see that the air masses being transported to IL-U2 never go above 2 km (i.e., do not come from aloft), unlike at the other two sites. At IL-U1 and IN-R, the altitude profiles are similar on 26 July. But on 1 August only the air mass arriving at IN-R comes from aloft. The reverse is observed on 7 August. These altitude profiles are consistent with the pattern observed in levoglucosan concentrations at these two sites. It would appear that since the emissions from these fires are being transported long distances, in order for a particular site to be impacted by smoke not only does the horizontal location of the transport for the air mass need to be right, but the air mass needs to come from aloft.

[21] In both the winter and the summer, WSOC concentrations across the study region appear to rise and fall

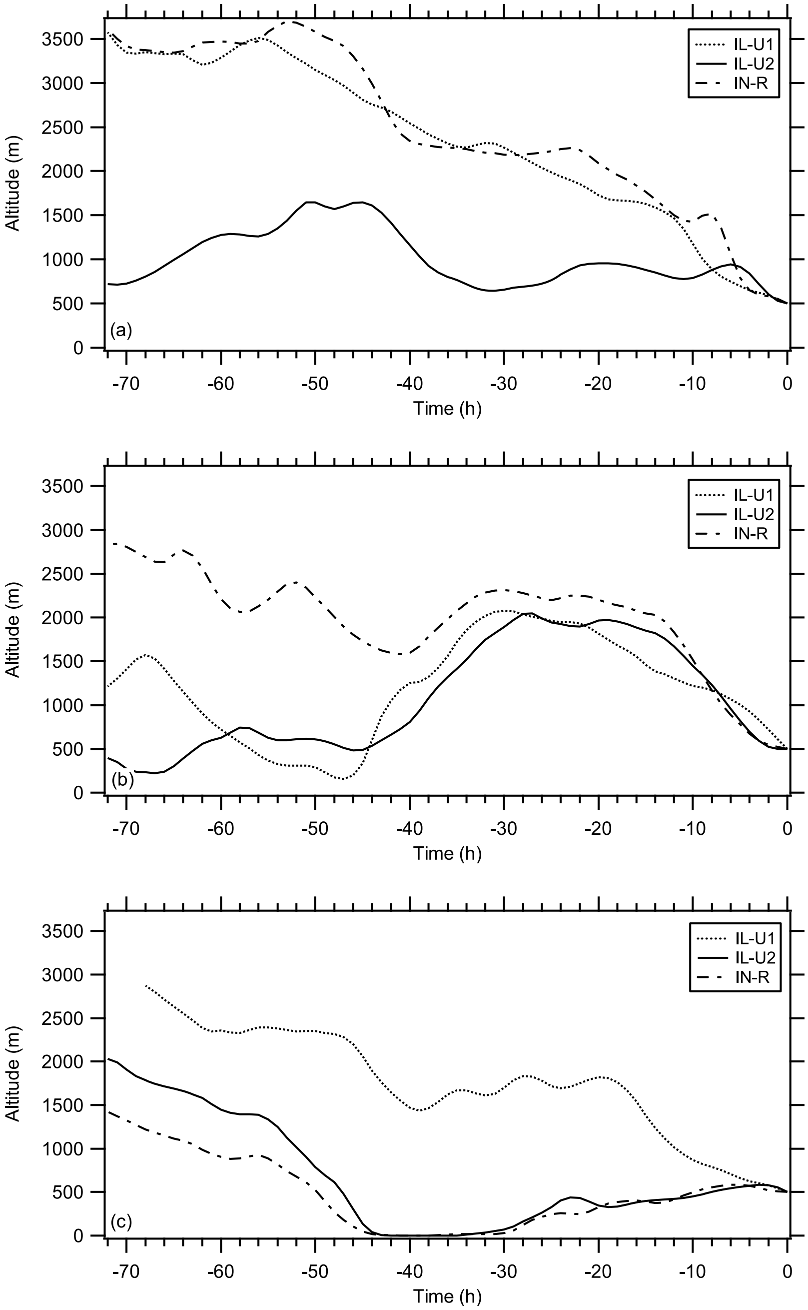

Figure 5. The altitude profiles from the 72 h air mass back trajectory analysis ending on (a) 26 July 2004, (b) 1 August 2004, and (c) 7 August 2004 at midnight local time for IL-U1, IL-U2, and IN-R. The back trajectories were calculated using the NOAA ARL HYSPLIT trajectory model.

together as seen in Figures 3b and 4b. This trend is indicative of the WSOC in summer being regionally influenced. Levoglucosan and WSOC concentrations are highly correlated in the winter (R^2 values from 0.47 to 0.89), but not in the summer (R^2 values from 0.07 to 0.63) as indicated by Figure 6. (Note, since IL-U2 generally has lower WSOC concentrations in the summer than the other two sites, the high correlation at IL-U2 during the summer is due to the one high WSOC point from the filter sample collected on 20 July 2004. If this point is removed, the R^2 value is more similar to the other sites.) This further suggests that during the summer SOA (secondary organic aerosol) production may be a more important source of WSOC than is biomass burning.

[22] As previously mentioned, there is no seasonal pattern for potassium (Figures 3c and 4c). This probably reflects important potassium contributions from multiple source types. In addition to biomass burning, potassium can come from incinerators and fly ash [*Schauer et al.*, 2001].

[23] As seen in Figure 6, potassium has a stronger correlation with WSOC in winter (R^2 values from 0.30 to 0.63) than summer (R^2 values from 0.02 to 0.20). This could suggest that biomass burning becomes a more dominant source of organic carbon in the winter. However, this likely

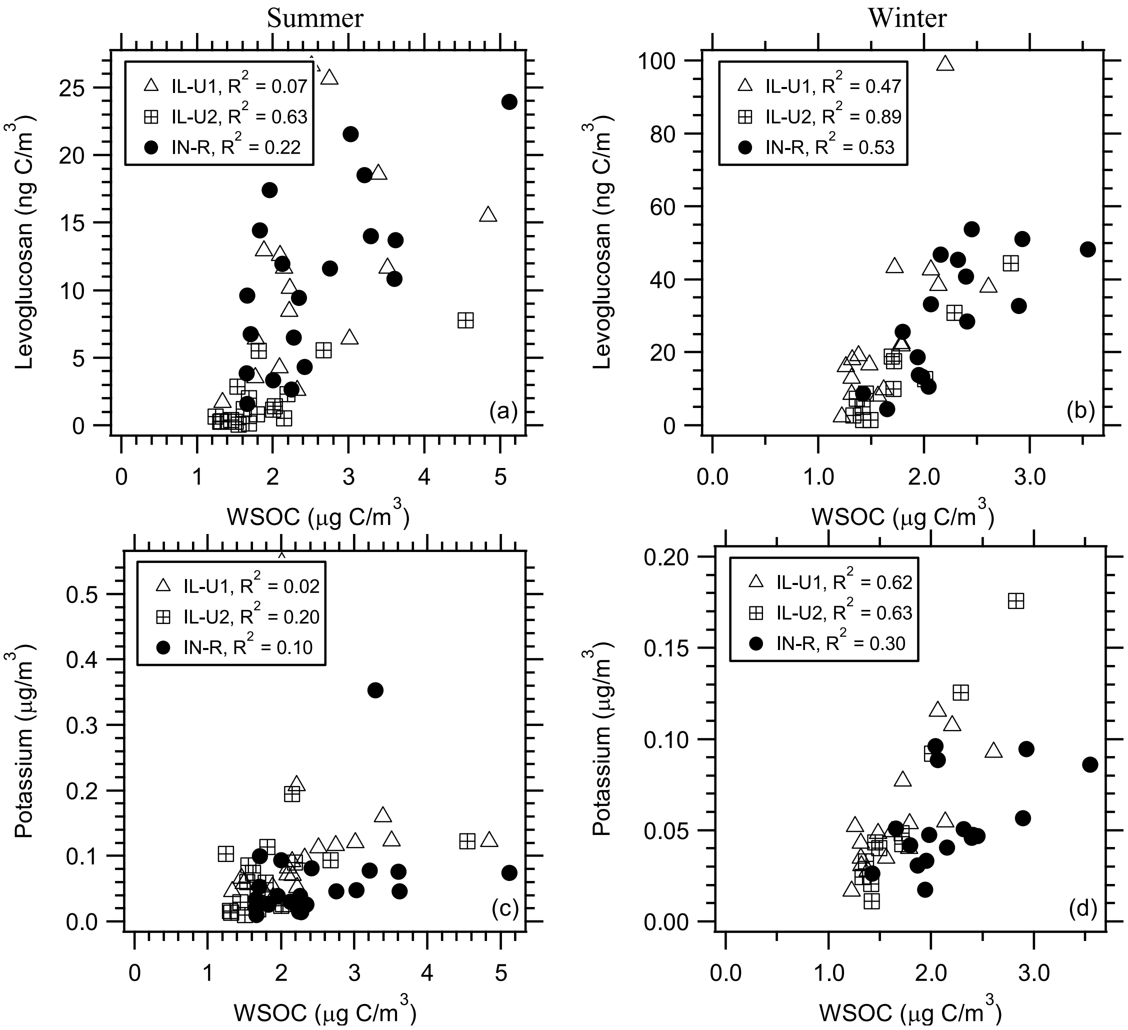

Figure 6. Scatterplots of $PM_{2.5}$ levoglucosan versus $PM_{2.5}$ WSOC for (a) summer and (b) winter and $PM_{2.5}$ potassium versus $PM_{2.5}$ WSOC for (c) summer and (d) winter for the data from IL-U1, IL-U2, and IN-R. The levoglucosan versus WSOC plot is presented on a carbon mass basis (i.e., the units of levoglucosan have been converted from ng/m^3 to ng C/m^3).

is not the case for this particular data set as will be illustrated later in section 3.2. Another possibility is that residential burning, the main source of biomass burning in the winter, produces greater potassium emissions than wildfires or prescribed burning. It has been observed that potassium is predominately emitted during flaming combustion, which is typically what occurs in a fireplace, as opposed to the smoldering phases more typical of wildfires and prescribed fires [*Ward et al.*, 1991; *Echalar et al.*, 1995; *Lee et al.*, 2010].

3.1.2. Urban Versus Rural Sites

[24] From looking only at data for IL-U1, IL-U2, and IN-R (Figures 3 and 4), large differences are not readily apparent between the rural site (IN-R) and the urban sites (IL-U1 and IL-U2). However, also included in this data set are 3 urban/rural site geographical pairs which make for a better comparison. These pairs include rural/urban pairs in Indiana (IN-R and IN-U), Michigan (MI-R and MI-U), and Minnesota (MN-R and MN-U). As can be seen in Table 1, for all of these pairs the average potassium concentration in summer and winter is higher at the urban site than the rural site. This is likely due to a higher density of sources in urban areas. In addition, the non–biomass burning sources of potassium are more likely to be found in urban areas.

[25] As previously discussed, the levoglucosan concentration in summer is more dependent on transport and, therefore, is independent of whether a site is rural or urban. However, during the winter the average levoglucosan concentration is generally slightly higher at the urban site than the rural site for all three pairs (Table 1). Based on population density differences between an urban and rural site, this is not surprising, although the difference might be mitigated by increased frequency of residential wood combustion in rural environments.

[26] The average WSOC concentrations are quite similar during the summer and winter for both the Michigan and Minnesota urban/rural site pairs. In Indiana during winter, however, WSOC concentrations are higher at the rural site. This might be due to the IN-R and IN-U pair being the only set where the rural site is downwind of the urban site.

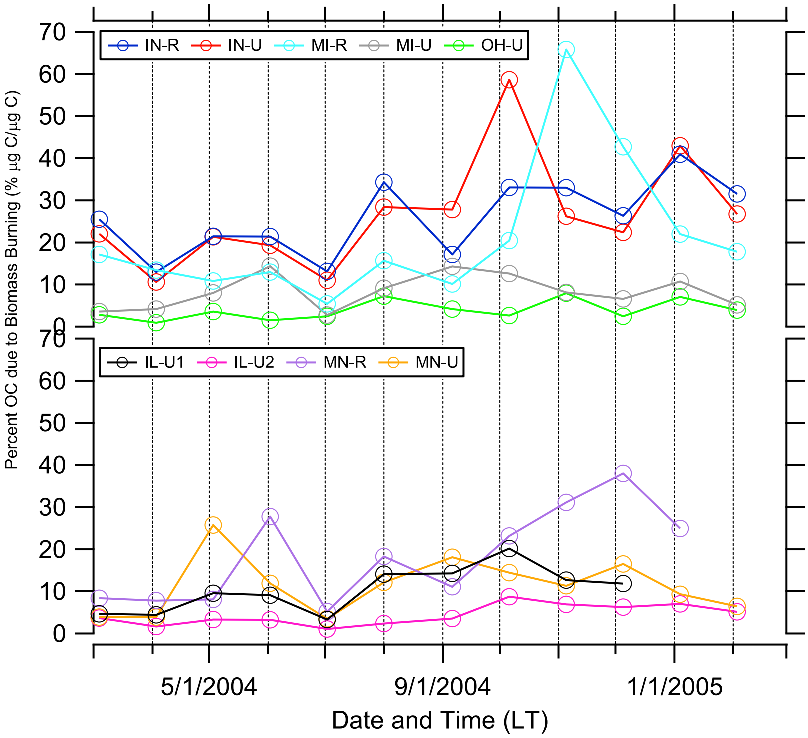

Figure 7. Time series for the monthly averaged percentage of $PM_{2.5}$ OC due to primary biomass burning particle emissions on a carbon mass basis for nine of the FRM sites. For clarity, the top half of the graph shows the data for the more eastern sites of IN-R, IN-U, MI-R, MI-U, and OH-U and the bottom half the more western sites of IL-U1, IL-U2, MN-R, and MN-U.

WSOC is expected to increase downwind of urban areas as urban emissions age and react to form SOA.

3.2. Determination of the Contribution of $PM_{2.5}$ OC due to Primary Biomass Burning

[27] The percentage contribution of $PM_{2.5}$ OC due to primary biomass burning is estimated by dividing the levoglucosan/OC ratio of an ambient sample by the levoglucosan/OC ratio from a source profile and multiplying by 100. Because the sources of biomass burning are different in summer and winter, two different sets of source profiles are needed. For the winter data, the source profiles come from the work of *Fine et al.* [2004]. In this work, the emissions of fireplace combustion for ten different woods from the western and midwestern United States were examined. The average levoglucosan/OC ratio determined, 0.071 ± 0.045 μg C/μg C, is used. For the summer data, the source profiles come from the work of *Sullivan et al.* [2008], which provides data from a series of open burns conducted at the Fire Science Laboratory in Missoula, MT that examined the emissions of fuels known to burn during prescribed fires and wildfires. The most appropriate source profile to use for each sample is determined by employing a combination of the peak ratios in the carbohydrate chromatogram and back trajectory analysis. More details about using the ratio of peaks in the chromatogram can be found in section 3.2 of *Sullivan et al.* [2008]. From applying this method to this data set, it was found that for a majority of the samples, the average levoglucosan/OC ratio for the combustion of leaves (0.023 ± 0.009 μg C/μg C) should be used. *Munchak et al.* [2010] found that for combustion of most typical U.S. fuelbeds, levoglucosan/OC ratios are expected to vary by less than a factor of 2.

[28] The ambient levoglucosan concentration comes from our measurement made off of the Teflon filters. As previously mentioned, OC cannot be measured on a Teflon filter. However, for nine of the sites, collocated OC measurements made by another network are available. All but 2 of the sampling sites (IL-S and IL-U1) are collocated CSN sites. The IL-U1 site was collocated with the St. Louis–Midwest Supersite. Both collocated networks routinely collect a quartz filter sample to determine the $PM_{2.5}$ OC concentration using thermal-optical transmittance (TOT) [*Birch and Cary*, 1996].

[29] The OC data from the St. Louis–Midwest Supersite were reported and downloaded blank corrected with each individual sample having an uncertainty assigned to it (http://www.engineering.wustl.edu/STLSupersite/MeasurementsData.htm). The CSN OC data are reported and downloaded through the Environmental Protection Agency's (EPA) Air Quality System Data Mart with no blank correction applied. However, it has been suggested that the CSN OC data should be corrected for sampling artifacts. A recent study by *Chow et al.* [2010] examining the blanks across different U.S. networks found, that based on 238 CSN sites and 2335 samples collected in 2005, the average blank OC concentration is 0.87 ± 0.32 μg C/m^3. The OC data presented in Data Sets S1–S10 were corrected using this average blank value. Of course using a single-valued OC artifact correction has severe limitations when trying to

examine individual day samples. This would be especially true if the artifact correction is a large fraction of the ambient OC concentration. As can be seen in Table 1, the average OC at all three rural sites are lower than their average WSOC concentrations suggesting the above can be a factor. This also suggests that the correction factor is too large at these sites. Based on the standard deviation of the average blank value determined by *Chow et al.* [2010] it is also likely that there would be samples where the correction is too low. The blank correction should really only be used when looking at a parameter averaged over several samples. Therefore, in Data Sets S1–S10 the biomass burning contribution for each sample at each site has been reported along with a range determined using the ± uncertainty of the average artifact correction or in the case of IL-U1 the individual ± uncertainty determined for each OC filter sample. The discussion below on the calculated biomass burning contribution will only focus on the monthly average.

[30] The time series for the monthly averaged contribution of $PM_{2.5}$ OC due to biomass burning for nine of the FRM sites is shown in Figure 7. These values as well as the ones in Data Sets S1–S10 represent only primary particle emissions from biomass burning. Additional biomass burning contributions due to SOA production in aging fire emissions are not quantified. This would be more of a factor in summer since during this period there is more time for the aging of transported emissions from wildfires and prescribed fires and there is greater photochemical activity. Underestimates of primary smoke emission contributions are also possible if levoglucosan decays during smoke transport [*Hennigan et al.*, 2010]. This effect is also expected to be greater in summer when smoke sources appear to be more distant and photochemical activity increases.

[31] Overall, the estimated OC contribution from biomass burning is generally similar in winter and summer for all but IN-U and the three rural sites, where the contribution is higher in winter. Only at the Minnesota and Michigan urban sites is the average contribution in summer slightly higher than in winter (MI-U 10% versus 8%, MN-U 11% versus 10%). Based on all the sites the annual average OC contribution from biomass burning for the Midwest appears to range from about 5 to 35%. The contribution is at the low end of this range for sites with the lowest levoglucosan concentrations, such as IL-U2 and OH-U. During summer, the contributions at IN-R and IN-U are on average higher than the other sites. For the pairs in MI and MN, at times during the winter the rural site has a larger contribution from biomass burning compared to the urban site (MI-R versus MI-U and MN-R versus MN-U). For the pair in MN, this might be due to the MN-R site being on tribal land where there can be significant outdoor burning occurring during the winter.

[32] For the conditions sampled in this study, more than 50% of the WSOC, in both summer and winter, appears to come from sources other than biomass burning. Based on findings from previous studies [*Sullivan et al.*, 2006], it is likely that SOA accounts for much of this WSOC. Since 1-in-6 day samples were analyzed from a single study year, more variability in the contributions of biomass burning to Midwest United States OC is probably present, however, than characterized here. This is especially likely in summer when smoke impacts of long-range transport are expected to vary strongly with burn activity, burn location, and prevailing transport patterns.

4. Summary

[33] Archived 1-in-6 day FRM Teflon filters collected at ten sites in the upper Midwest from March 2004 though February 2005 were analyzed for levoglucosan, water-soluble potassium, and WSOC. The main goals of this work were to demonstrate the ability to measure smoke marker concentrations using filter samples collected from routine monitoring networks and to use the data obtained to better understand the impact of biomass burning on fine particle organic carbon concentrations both spatially and temporally in this region.

[34] It was shown that HPAEC-PAD has sufficient sensitivity to be able to determine levoglucosan from daily 47 mm filter samples collected with a low flow rate (i.e., 16.7 LPM). This means smoke marker measurements could potentially be made on a more routine basis, which would help in better constraining biomass burning estimates in models and understanding its impacts on air quality.

[35] WSOC in the Midwest United States appears to contain a substantial regional component. Regional levoglucosan concentrations were higher during winter than summer, consistent with an increase in biomass burning due to residential wood burning. Summer peaks in levoglucosan concentrations were observed at some locations, when conditions appeared favorable for transport from distant wildfires in Alaska. Potassium concentrations exhibited no clear association with biomass burning impacts for this region.

[36] Based on the monthly average, the contribution to $PM_{2.5}$ OC from primary particle emissions from biomass burning was similar in the winter and summer at six sites. The other four sites (IN-R, IN-U, MI-R, and MN-R) had higher contributions in winter. The contribution from biomass burning was highest at the Indiana study sites (IN-R and IN-U), being on average 20% in summer and 30% in winter. The contribution was generally around 10% at sites IL-U1, MI-U, and MN-U during summer and winter. In summer, the contribution was similar at the rural Michigan and Minnesota sites, but higher in winter, being 31% and 37% at MN-R and MI-R, respectively. The lowest contributions, generally less than 5%, were observed at urban sites in Illinois (IL-U2) and Ohio (OH-U). The range in estimated contributions of biomass burning is due to differences in the levoglucosan concentrations observed, as OC and WSOC were fairly similar at all of the sites. Additional biomass burning contributions through secondary organic aerosol formation were not accounted for and could be possible, especially during summer. Recent evidence of levoglucosan decay [*Hennigan et al.*, 2010] suggests that primary contributions of biomass burning may also be underestimated, especially in summer when photochemical activity increases and smoke sources are generally more distant.

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