

Biomass Burning Impacts on Air Quality in the Upper Midwest

Final Report

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Executive Summary

Biomass burning is a major contributor to atmospheric emissions. Smoke from biomass burning can be derived from both prescribed fires and wildfires as well as from residential wood burning. This smoke has been found to be an important source of fine particles, suggesting it is important to assess the contribution of biomass burning to the total fine particle organic carbon concentration.

The most common method employed to determine the contribution of the smoke from biomass burning to particulate organic carbon is through the use of smoke marker measurements. The most commonly used smoke marker is levoglucosan, a sugar anhydride produced during the combustion of cellulose.

A previous study that used smoke marker measurements, the Urban Organics Study, conducted at five sites in the Upper Midwest in 2004-2005, suggested that 15-25% of the organic carbon was due to biomass burning. The goal of the current study is to use smoke marker measurements to further examine the impact of biomass burning in this region.

Hi-Volume quartz filter samples were collected at five sites in the Upper Midwest. These sites included Ely, MN at the Boundary Waters Canoe (BWC) site, Mayville, WI, Chicago, IL at the ComEd site, Detroit, MI at the Allen Park site, and Cleveland, OH at the 14th and Orange site. Six week sampling campaigns were conducted in the summer from July to August 2007 and in the winter from January to February 2008. Two sampling campaigns were carried out since it is expected that during the summer biomass burning would be associated with prescribed fires and

wildfires whereas in the winter the biomass burning would be due to residential wood burning.

Each of the Hi-Volume filter samples collected was analyzed for $PM_{2.5}$ OC (organic carbon), EC (elemental carbon), levoglucosan, and potassium. OC and EC were determined by thermal/optical transmission (TOT) using a Sunset Laboratories EC/OC analyzer. High-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) was used to determine the levoglucosan concentration. Potassium, a potential inorganic marker for biomass burning, was measured using cation-exchange chromatography.

In addition, radiocarbon analysis was performed on a subset of the filter samples. This measurement can be used to determine the relative contributions of fossil and contemporary carbon. The contemporary carbon fraction is expected to include emissions from biomass burning. The analysis was performed at Lawrence Livermore National Laboratory (LLNL) using an accelerator mass spectrometer (AMS).

Study observations suggest that the fine particle OC concentrations contain a substantial regional component. However, EC concentrations are much higher at the urban sites than at the rural sites. Levoglucosan concentrations also appear to be fairly regional during the summer, consistent with an absence of local burning during this period. Greater spatial variability in levoglucosan concentrations observed in winter is consistent with there being a more local, residential wood burning source during this season. In contrast to levoglucosan, potassium really exhibited no clear pattern in the summer or winter although periods of more locally elevated potassium concentrations were sometimes observed.

Estimated contributions of primary emissions from biomass burning to fine particle OC concentrations were higher in winter than in the summer at all sites. The average contribution for the summer was found to be 12% in BWC, 7% in Chicago, 7% in Cleveland, 10% in Detroit, and 11% in Mayville. During the winter, the average contribution was found to be 16% in BWC, 17% in Chicago, 18% in Cleveland, 19% in Detroit, and 28% in Mayville. These estimates do not include possible contributions of biomass burning to production of secondary organic aerosol.

The contemporary carbon fraction of OC determined from the radiocarbon analysis was found to be generally greater than 50% and largest at the rural sites. The fraction of contemporary carbon in winter was generally higher than in summer, consistent with the increase in biomass burning contributions. As with OC concentrations, a substantial regional component of contemporary carbon was present in summer. Primary particle emissions from biomass burning comprised typically < 10% of the contemporary carbon fraction in summer, but in winter were determined to comprise 20-35% of the contemporary carbon fraction.

1. Introduction

One of the major sources of atmospheric fine particle organic carbon is biomass burning. Smoke from wild and prescribed fires can have a significant impact on $PM_{2.5}$ concentrations, affecting air quality from local to regional and global scales. Smoke can be a significant contributor in causing visibility impairment and affecting the Earth's radiation balance. Additionally, in populated areas, residential wood combustion can be an important source of fine particles.

This has been found to be true for the Upper Midwest. For example, during the Urban Organics Study 2004-2005 it was found that 15-25% of the organic carbon was due to biomass burning at the five sites where the measurements were made (see http://ladco.org/reports/rpo/MWRPOprojects/Monitoring/Integration_FinalReport.pdf for more information). This suggests that biomass burning is an important source of organic carbon in this region and that it is important to be able to assess the contribution of biomass burning to the total organic carbon concentration. This provides the motivation behind the work presented here, to better understand the impact of biomass burning in the Upper Midwest.

The most common method used, and the one used here, to quantify the contribution of biomass burning to the total organic carbon is through the use of smoke marker measurements. In this approach, a compound produced as part of the smoke emitted from a fire is used as a marker to track the plume as it is transported downwind and diluted. If the mass ratio of the marker to the total organic carbon is known at the source and the marker is conserved during transport, then the marker concentration

measured at a downwind location can be used to determine the ambient aerosol fraction associated with primary emissions of smoke.

The most commonly used marker for biomass burning is levoglucosan, a sugar anhydride produced during the combustion of cellulose [Simoneit *et al.*, 1999]. Traditionally, levoglucosan in aerosol samples is measured using Gas Chromatography-Mass Spectrometry (GC/MS). However, this method requires chemical derivatization, making it quite labor intensive and expensive due to the solvents, reagents, and instrumentation needed. Therefore, these analyses are generally conducted only on composited filter samples or for selected filter samples from special studies.

An alternative method that can be used for measurement of levoglucosan couples high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD). This approach offers many advantages such as extraction of the filter directly in water, the ability to directly analyze the filter extract for levoglucosan, and the use of ion chromatography (IC), an analytical technique commonly used by aerosol monitoring networks for analysis of the major inorganic aerosol species. This technique has previously been applied to studies of biomass combustion contributions to fine particles in source samples and ambient samples collected in rural and urban locations [Gao *et al.*, 2003; Gorin *et al.*, 2006; Engling *et al.*, 2006; Puxbaum *et al.*, 2007].

In addition to quantifying the contribution of biomass burning, it is also useful to know the contribution of fossil fuel combustion to fine particle organic carbon. This is especially true since the EPA (Environmental Protection Agency) has required states to develop emission reduction plans in order to meet National Ambient Air Quality standards for PM_{2.5} and to comply with the visibility improvement requirements of the

regional haze rule [USEPA, 1999]. It becomes difficult to craft optimal implementation plans unless the contribution of anthropogenic versus biogenic sources is known. One approach that has been applied to ambient aerosols in order to help distinguish modern from fossil sources involves radiocarbon analysis. Because ^{14}C has been depleted from fossil fuels, measurements of the $^{14}\text{C}/\text{C}$ ratio in ambient $\text{PM}_{2.5}$ aerosols can be used, along with knowledge about the ^{14}C content of modern carbon emissions, to determine the relative contributions of contemporary (including biogenic and biomass combustion emissions) and fossil (emissions from fossil fuel-derived materials such as from industry or transportation) carbon sources [Bench and Herckes, 2004].

Presented here will be the application of this alternative method to measure levoglucosan, along with measurements of water-soluble potassium, organic carbon (OC), and elemental carbon (EC), to filter samples collected at five sites in the Upper Midwest in the summer of 2007 and winter of 2008. This data will be used to investigate the spatial and temporal trends of these various species and to determine the impact of biomass burning on fine particle concentrations in this region. In addition, results from radiocarbon analysis for a subset of the filter samples will be discussed.

2. Methods

2.1. Particulate Collection

To collect ambient particles onto quartz filters for off-line analysis a Thermo Anderson Hi-Volume Air Sampler was used. An identical sampler was placed at each of the five following sites: Ely, MN at the Boundary Waters Canoe (BWC) site, Mayville, WI, Chicago, IL at the ComEd site, Detroit, MI at the Allen Park site, and Cleveland, OH

at the 14th and Orange site (Figure 1). The BWC site is an IMPROVE (Interagency Monitoring of Protected Visual Environments) site whereas the other four sites are EPA sites. These five sites consist of two rural sites (BWC and Mayville) and three urban sites (Chicago, Detroit, and Cleveland). More details about the sites can be found in Table 1.

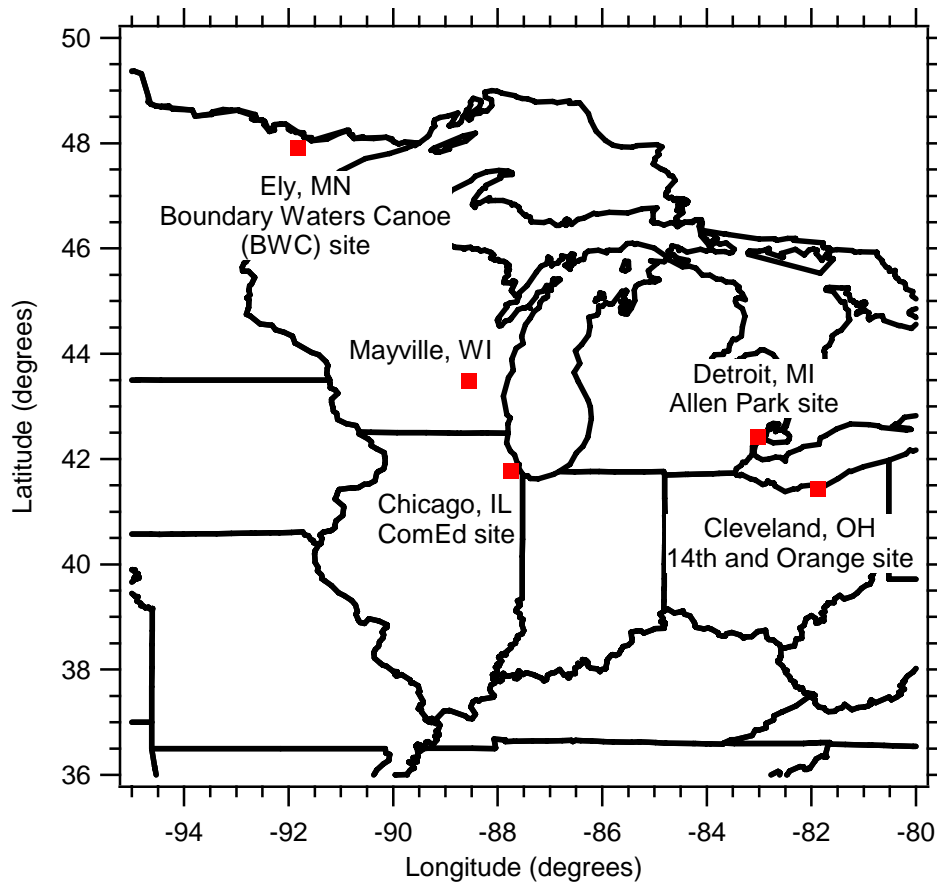


Figure 1. Map of the sampling site locations.

Table 1. Details about the sites used in this study including the Air Quality System (AQS) code, sampling frequency, and coordinates.

Sites	Ely, MN at Boundary Water Canoe (BWC) site	Chicago, IL at ComEd site	Cleveland, OH at 14 th and Orange site	Detroit, MI at Allen Park site	Mayville, WI
AQS Code	27-075-9000	17-031-0076	39-035-0060	26-163-0001	55-027-0007
Sampling Frequency	seven day integrated with the filter changed on Tuesdays to follow the IMPROVE schedule	three day integrated with the filter changed on the day after the 1- in-3 day sample was collected	three day integrated with the filter changed on the day after the 1- in-3 day sample was collected ^a	three day integrated with the filter changed on the day after the 1- in-3 day sample was collected	three day integrated with the filter changed on the day after the 1-in-3 day sample was collected
Latitude, Longitude Coordinates (degrees)	47.9466, -91.4955	41.7514, -87.7134	41.4939, -81.6785	42.2286, -83.2082	43.4350, -88.5277

^aThis was the case unless the filter was scheduled to be changed on a Saturday or Sunday. The filter was changed one day early (i.e., only a two day integrated sample was collected) if the change was scheduled for Saturday and one day late (i.e., a four day integrated sample was collected) if the change was scheduled for Sunday.

Three day integrated filter samples were collected at all of the sites, except BWC where seven day integrated filter samples were collected. Blank filter samples were collected every two weeks for the Sunset EC/OC and radiocarbon analysis by letting a filter sit inside the sampler while it was not operating for 2 minutes. Both the samples and blanks were collected by the local site operator after being trained by Colorado State University personnel and being provided a SOP (Standard Operating Procedure).

Two sampling campaigns were conducted since it is expected that during the summer biomass burning would be coming from prescribed fires and wildfires whereas in the winter the biomass burning would be attributed to residential wood burning. The summer campaign was conducted for 6 weeks from July to August 2007 and the winter campaign was conducted for 6 weeks from January to February 2008.

The Hi-Volume Samplers used draw ambient air at nominally 1.13 m³/min through a two-filter assembly to isolate and collect size fractions of the ambient aerosol. An impactor in combination with a slotted filter collects coarse particles, followed by a 20.3 cm x 25.4 cm filter to collect PM_{2.5}. Only the PM_{2.5} filters were analyzed. The quartz filters were wrapped in aluminum foil and pre-baked in an oven at 550°C for 12 hours before using them for sampling. After baking, the filters were stored in plastic bags in a sealed box until loaded into the filter holder. The filter holder was cleaned with isopropanol before a new filter was loaded. The sampled filters were stored in a freezer.

The samplers were calibrated at the beginning of the summer campaign, between the two campaigns, and after completion of the winter campaign using the manufacturer supplied calibration kit. This calibration kit essentially allows the pressure to be changed going into the sampler and the corresponding flowrate is recorded. For these particular samplers a flowchart recorder with removable flowrate charts (that were changed between each sample) records the flow information.

2.2. Measurement Approach

Each of the Hi-Volume filters collected was analyzed individually for PM_{2.5} levoglucosan, water-soluble potassium, OC, and EC. These analyses are described in detail below.

Typically, ten 25 mm diameter punches of the PM_{2.5} filter were extracted in 20 ml of deionized water (DI Water) in a Nalgene Amber HDPE bottle, sonicated with heat [Baumann *et al.*, 2003] for 1.25 hours, and then filtered using a 0.2 µm PTFE syringe filter to remove any quartz filter fibers. The liquid extracts were analyzed for

levoglucosan using high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) the same day the filters were extracted. The extracts were stored at room temperature in the amber bottles and were not refrigerated until they were measured for water-soluble potassium (K^+) using ion chromatography (IC).

The levoglucosan measurement was made using a Dionex DX-600 series ion chromatograph with a Dionex ED-50 electrochemical detector operating in integrating amperometric mode using waveform A and a Dionex GP-50 gradient pump. The electrochemical detector was connected to a Dionex ED-50/ED-50A electrochemical cell, which contained a pH-Ag/AgCl (silver/silver chloride) reference electrode and a “standard” gold working electrode.

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

Separation was completed on Dionex CarboPac PA-1 guard (4 x 50 mm) and analytical (4 x 250 mm) columns. The eluents are DI Water and 200 mM sodium hydroxide (NaOH). Each run has an eluent flowrate of 0.5 ml/min and takes approximately 59 minutes. For the first 10 minutes isocratic elution with 10 mM NaOH is performed to detect anhydrosugars, such as levoglucosan, and sugar alcohols. Next, a

linear gradient from 10 to 70 mM NaOH is run for 19 minutes to detect sugars. Since carbonate ions can bind to the active sites of the resin and affect the chromatography, the column is cleaned for 14 minutes with 180 mM NaOH. Finally, a 16 minute re-equilibration step is performed to return to the starting conditions. A sample volume of 50 μL is injected onto the column. The limit of detection (LOD) for the various carbohydrates is less than approximately 1 ng/m^3 for the air volumes sampled in this study.

A sample calibration chromatogram using this method is shown in Figure 2. This method is able to separate mannitol, a sugar alcohol associated with fungi, from mannosan, an anhydrosugar associated with biomass combustion. This is important because if mannitol is present then arabitol, another fungi-related sugar alcohol, is also present and arabitol can overlap with levoglucosan in the chromatogram, biasing the levoglucosan quantitation. This is only a factor in the summer campaign as mannitol and arabitol originate from spores which are not active during winter. The summer levoglucosan data can be corrected for any arabitol interference using the mannitol concentrations as it has been found that the mannitol concentration is equal to 1.5 times the concentration of arabitol [Bauer *et al.*, 2008].

Water-soluble potassium was measured in the liquid extract using a Dionex DX-500 series ion chromatograph with a Dionex IP-20 isocratic pump, Dionex CD-20 conductivity detector, and self-regenerating cation SRS-ULTRA suppressor. A Dionex IonPac CS12A analytical (3 x 150 mm) column with a run time of 15 minutes allowed for separation of the common inorganic ions. A 20 mM methanesulfonic acid eluent at a

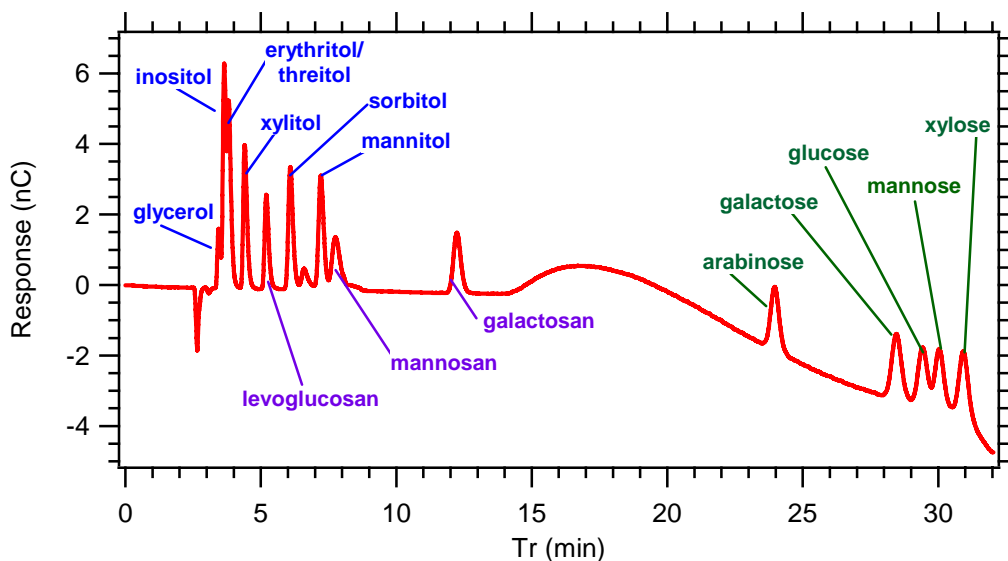


Figure 2. Calibration chromatogram for the injection of a mixed carbohydrate standard on the PA-1 column, where Tr is retention time. The sugar alcohols are labeled in blue, anhydrosugars in purple, and sugars in green.

flowrate of 0.5 ml/min with a sample volume injection of 25 μ L was used. The LOD for water-soluble potassium is about 0.02 μ g/m³ for the air volumes sampled in this study.

Organic and elemental carbon were determined on each Hi-Volume filter using a Sunset Labs EC/OC analyzer (Forest Grove, Oregon). OC and EC carbon mass are quantified in this technique by thermal/optical transmission (TOT) [Birch and Cary, 1996]. The instrument was operated following the NIOSH Method 5040 [Eller and Cassinelli, 1996]. For each filter the average of two 1.4 cm² filter punches was used. The study LOD, based on analysis of the blank filters, for OC and EC are 0.4 μ g C/m³ and 0.01 μ g C/m³ respectively.

Radiocarbon analysis was performed on a subset of the filter samples at Lawrence Livermore National Laboratory (LLNL) to determine the fraction of fossil and

contemporary carbon. Forty samples, 20 from the summer campaign and 20 from the winter campaign, including blanks, were analyzed. Samples were selected so a high and low OC day from the summer, a high OC day from the winter, and transport events from both the summer and winter would be analyzed. Transport events include times when all sites analyzed were sampling similar air masses based on back trajectory analysis.

A 25 cm² (5 x 5 cm) piece of each of the filter samples chosen for radiocarbon analysis was sealed under vacuum with CuO (copper oxide) oxidizer in a quartz tube and combusted at 900°C. Carbon dioxide (CO₂) from the combustion was cryogenically isolated from other combustion products and measured manometrically before conversion to graphite by hydrogen reduction using an iron catalyst. ¹⁴C/C ratios in the graphite samples were measured by accelerator mass spectrometry (AMS). The AMS reported the fraction of carbon that was modern (F_M) based on the comparison of the ¹⁴C/C ratio in the sample to that of a modern carbon standard reference material. F_M was corrected for the variability in the past atmospheric ¹⁴C concentrations to provide the fraction of contemporary carbon (F_C). This was done using the equation

$$F_C = F_M/1.05 \quad (1)$$

The value of 1.05 was derived from the average ¹⁴C/C ratio of contemporary material from 2003 to 2008. A two component model was then assumed to determine the fraction of fossil carbon (F_F).

$$F_F = 1 - F_C = 1 - F_M/1.05 \quad (2)$$

3. Results and Discussion

Table 2a shows the OC, EC, levoglucosan, and water-soluble potassium concentrations at each of the five sites during the summer campaign. Table 2b shows the OC, EC, levoglucosan, and water-soluble potassium concentrations during the winter campaign. Levoglucosan and water-soluble potassium were measured in all the samples collected during both campaigns. Generally, water-soluble potassium could be found in higher concentrations than levoglucosan. OC was also observed in all the samples collected. EC was generally detected, however at much lower concentrations than for OC.

3.1. Spatial and Temporal Patterns for PM_{2.5} OC, EC, Levoglucosan, and Water-Soluble Potassium

Figures 3a and b show the time series for OC at all five sites during the summer and winter campaigns, respectively. Generally during both the summer and winter the OC concentration appears to have a large regional component since the concentrations rise and fall together. There are of course a couple of exceptions to this. The first is during the winter at BWC. This difference is likely due to that fact that the BWC area is a summer tourist location and has considerably fewer residents during the winter. The second occurs in Cleveland during the summer. Although the trends in the OC during the summer in Cleveland are similar to the other sites, often the concentration of OC is higher than at the other sites. This is likely due to local emissions of OC on top of the regional component. Since the samples used in this study were three day integrated filter

Table 2a. Concentrations of PM_{2.5} OC, EC, levoglucosan, and water-soluble potassium for each of the five sites during the summer campaign where ND = not detected. Date shown as month/day/year.

Start and End Date/Time (LT) ^a	OC (µg C/m ³)	EC (µg C/m ³)	Levoglucosan (ng/m ³)	Water-Soluble Potassium (µg/m ³)
	Boundary	Waters	Canoe	
07/17/07 10:00 – 07/24/07 9:00	2.71	0.04	21.36	0.04
07/24/07 9:30 – 07/30/07 10:00	3.70	0.05	19.03	0.07
07/30/07 10:40 – 08/07/07 10:15	1.97	0.03	18.08	0.04
08/14/07 10:15 – 08/21/07 10:30	1.17	ND	11.67	0.02
08/21/07 11:00 – 08/28/07 10:00	2.53	0.08	31.58	0.05
	Chicago			
07/18/07 10:35 – 07/21/07 9:58	3.59	0.25	32.00	0.05
07/21/07 10:25 – 07/24/07 10:11	5.67	0.67	78.33	0.10
07/27/07 10:40 – 07/30/07 10:21	4.84	0.48	36.40	0.15
07/30/07 10:42 – 08/02/07 10:43	9.70	1.69	30.00	0.12
08/02/07 11:02 – 08/05/07 10:26	6.20	0.63	29.61	0.08
08/05/07 10:44 – 08/08/07 11:26	3.73	0.46	9.14	0.05
08/11/07 9:57 – 08/14/07 13:55	4.27	0.45	14.74	0.06
08/14/07 14:21 – 08/17/07 10:11	5.62	0.68	37.74	0.08
08/17/07 10:26 – 08/20/07 10:05	4.29	0.62	39.14	0.19
08/20/07 10:32 – 08/23/07 10:31	2.92	0.42	6.79	0.06
08/26/07 10:28 – 08/29/07 10:03	5.23	0.75	17.98	0.06
	Cleveland			
07/18/07 9:45 – 07/20/07 9:48	5.65	0.84	14.64	0.08
07/20/07 10:28 – 07/23/07 8:59	5.68	1.05	35.33	0.21
07/23/07 9:17 – 07/27/07 13:23	7.04	2.21	20.66	0.13
07/27/07 13:44 – 07/30/07 11:10	6.39	0.96	46.11	0.07
07/30/07 11:27 – 08/02/07 11:19	14.76	3.86	21.75	0.23
08/02/07 11:35 – 08/06/07 10:56	8.61	1.67	44.42	0.23
08/08/07 10:33 – 08/10/07 10:25	6.30	1.65	13.69	0.12

08/10/07 11:20 – 08/14/07 11:14	6.32	1.25	24.60	0.49
08/14/07 11:33 – 08/17/07 12:15	7.16	1.53	17.62	0.18
08/17/07 12:34 – 08/20/07 14:15	3.65	0.58	23.78	0.12
08/20/07 14:35 – 08/23/07 10:00	6.04	1.91	9.52	0.13
08/23/07 10:33 – 08/27/07 11:33	5.73	1.39	15.24	0.16
Detroit				
07/18/07 10:00 – 07/21/07 10:00	3.78	0.49	30.00	0.05
07/27/07 10:00 – 07/30/07 10:00	4.56	0.57	51.11	0.07
07/30/07 10:00 – 08/02/07 10:00	7.09	0.89	28.09	0.06
08/05/07 10:00 – 08/08/07 10:00	3.17	0.38	16.34	0.05
08/08/07 10:00 – 08/11/07 10:00	4.32	0.39	57.71	0.05
08/14/07 10:00 – 08/17/07 10:00	5.57	0.63	49.00	0.07
08/17/07 10:00 – 08/20/07 10:00	2.14	0.08	33.57	0.03
08/20/07 10:00 – 08/23/07 10:00	3.27	0.43	8.70	0.05
08/23/07 10:00 – 08/26/07 10:00	3.66	0.32	17.55	0.05
08/26/07 10:00 – 08/29/07 10:00	4.52	0.58	24.20	0.05
Mayville				
07/21/07 9:15 – 07/24/07 10:00	4.13	0.28	44.23	0.06
7/24/07 10:30 – 07/27/07 7:30	4.11	0.19	20.74	0.04
07/27/07 8:00 - 07/30/07 8:00	6.07	0.32	55.48	0.09
07/30/07 8:30 - 08/02/07 8:00	7.79	0.36	16.43	0.07
08/02/07 8:30 – 08/05/07 7:00	4.73	0.25	24.91	0.08
08/05/07 7:30 – 08/08/07 7:00	2.86	0.10	12.93	0.04
08/08/07 8:00 – 08/11/07 15:30	4.05	0.24	11.96	0.05
08/11/07 16:00 – 08/14/07 10:00	3.68	0.14	11.70	0.08
08/14/07 10:30 – 08/17/07 8:30	4.55	0.28	42.86	0.08
08/17/07 9:00 – 08/20/07 7:45	1.86	0.05	25.03	0.04
08/20/07 8:15 – 08/23/07 8:00	1.66	0.09	2.75	0.03
08/23/07 9:00 –	2.93	0.09	42.15	0.06

08/26/07 7:30				
08/26/07 8:00 – 08/29/07 8:00	4.04	0.23	37.57	0.07

^aLT stands for local time. Therefore for Boundary Waters Canoe, Mayville, and Chicago the time is in CDT (Central Daylight Time) and for Detroit and Cleveland the time is in EDT (Eastern Daylight Time).

Table 2b. Concentrations of PM_{2.5} OC, EC, levoglucosan, and water-soluble potassium for each of the five sites during the winter campaign. Date shown as month/day/year.

Start and End Date/Time (LT) ^a	OC (µg C/m ³)	EC (µg C/m ³)	Levoglucosan (ng/m ³)	Water-Soluble Potassium (µg/m ³)
Boundary Waters Canoe				
02/07/08 14:00 – 02/12/08 10:00	1.29	0.03	28.83	0.04
02/12/08 9:00 – 02/19/08 11:00	0.67	0.01	16.77	0.03
02/19/08 10:00 – 02/26/08 9:30	0.89	0.01	24.31	0.03
Chicago				
01/14/08 10:20 – 01/17/08 9:50	3.19	0.45	112.16	0.06
01/17/08 10:15 – 01/20/08 10:35	2.61	0.30	82.34	0.05
01/20/08 11:05 – 01/23/08 10:10	3.25	0.42	96.37	0.05
01/26/08 9:45 – 01/29/08 10:05	3.20	0.29	98.94	0.05
02/01/08 9:55 – 02/04/08 10:35	3.37	0.47	99.08	0.08
02/07/08 10:40 – 02/10/08 10:00	2.72	0.24	54.04	0.03
02/10/08 10:20 – 02/13/08 11:05	4.03	0.48	69.27	0.09
02/13/08 11:35 – 02/16/08 10:05	3.92	0.79	82.01	0.05
02/16/08 10:30 – 02/19/08 11:15	3.00	0.21	75.75	0.05
02/22/08 10:35 – 02/25/08 9:30	3.70	0.58	86.83	0.05
Cleveland				
01/14/08 11:20 – 01/17/08 13:40	3.44	0.79	131.54	0.14
01/18/08 11:10 – 01/23/08 12:14	2.51	0.73	83.45	0.06
01/23/08 11:50 – 01/25/08 13:07	3.71	0.83	113.22	0.17
01/25/08 13:30 – 01/29/08 12:53	4.08	0.91	130.64	0.15
01/29/08 13:05 – 02/04/08 10:50	3.01	0.91	89.00	0.12
02/04/08 11:20 – 02/07/08 12:20	2.21	0.50	69.43	0.06
02/07/08 12:58 – 02/11/08 12:25	2.86	0.72	66.43	0.07

02/11/08 13:00 – 02/13/08 11:04	4.00	0.64	154.88	0.19
02/13/08 11:22 – 02/15/08 11:37	3.88	0.74	95.71	0.19
02/15/08 11:47 – 02/19/08 12:15	3.98	1.10	68.50	0.08
02/19/08 12:50 – 02/22/08 13:23	3.34	1.27	76.21	0.07
02/22/08 13:40 – 02/25/08 12:40	6.15	1.06	96.61	0.09
Detroit				
01/14/08 10:00 – 01/17/08 10:00	2.32	0.32	93.13	0.05
01/17/08 10:00 – 01/20/08 10:00	2.04	0.26	70.99	0.04
01/20/08 10:00 – 01/23/08 10:00	2.28	0.41	79.29	0.05
01/23/08 10:00 – 01/26/08 10:00	2.75	0.56	81.22	0.06
01/29/08 10:00 – 02/01/08 10:00	2.08	0.44	48.79	0.05
02/01/08 10:00 – 02/04/08 10:00	2.88	0.18	111.85	0.07
02/04/08 10:00 – 02/07/08 10:00	1.88	0.55	61.72	0.08
02/10/08 10:00 – 02/13/08 10:00	2.96	0.46	68.20	0.06
02/13/08 10:00 – 02/16/08 10:00	2.72	0.48	78.49	0.05
02/16/08 10:00 – 02/19/08 10:00	2.51	0.26	67.49	0.06
02/22/08 10:00 – 02/25/08 10:00	3.92	0.39	95.10	0.07
Mayville				
01/17/08 8:17 – 01/20/08 10:45	2.47	0.15	114.42	0.28
01/20/08 11:15 – 01/23/08 8:10	2.66	0.15	133.61	0.22
01/23/08 8:35 – 01/26/08 12:55	2.42	0.16	115.27	0.14
01/26/08 13:30 – 01/29/08 9:15	2.69	0.21	110.61	0.13
01/29/08 9:45 – 02/01/08 8:00	1.68	0.09	74.40	0.17
02/01/08 9:00 – 02/04/08 11:30	2.22	0.15	105.74	0.13
02/04/08 12:00 – 02/07/08 10:00	1.16	0.06	59.16	0.04
02/07/08 10:30 – 02/10/08 13:30	1.84	0.07	75.75	0.10
02/10/08 13:45 – 02/13/08 8:30	2.17	0.09	93.07	0.16
02/13/08 9:00 – 02/16/08 14:00	2.43	0.14	91.78	0.11
02/16/08 14:15 –	1.87	0.04	86.74	0.14

02/19/08 9:00				
02/19/08 9:20 – 02/22/08 7:30	2.43	0.12	104.95	0.15
02/22/08 8:45 – 02/25/08 7:30	3.29	0.12	107.89	0.11

^aLT stands for local time. Therefore for Boundary Waters Canoe, Mayville, and Chicago the time is in CST (Central Standard Time) and for Detroit and Cleveland the time is in EST (Eastern Standard Time).

samples it is hard to pin point the source of these local emissions that causes such events.

Real-time data would be better suited for further investigating this.

The OC concentrations are in contrast to what is observed in Figures 4a and b, the time series for the EC concentration during the summer and winter campaigns. As expected with EC being mainly from primary emissions and local sources, the EC is much higher at the urban sites than at the rural sites. This pattern as well as Cleveland having the highest concentrations is observed during both summer and winter.

The levoglucosan concentrations shown in Figure 5a for the summer campaign suggest that during the summer the levoglucosan concentration in the Midwest appears to also be fairly regional like the OC. However, unlike the OC concentration, this does not appear to be the case for winter. Although, with the exception of BWC, the average concentration at each site appears to be similar during the winter (Figure 5b), occasional local events are also observed. The change from a more regional to a more local characteristic from summer to winter is likely due to the difference in the source of biomass burning during winter vs. summer (i.e., residential burning vs. prescribed burning and wildfires).

In contrast to levoglucosan, the potassium has no real pattern at the five sites

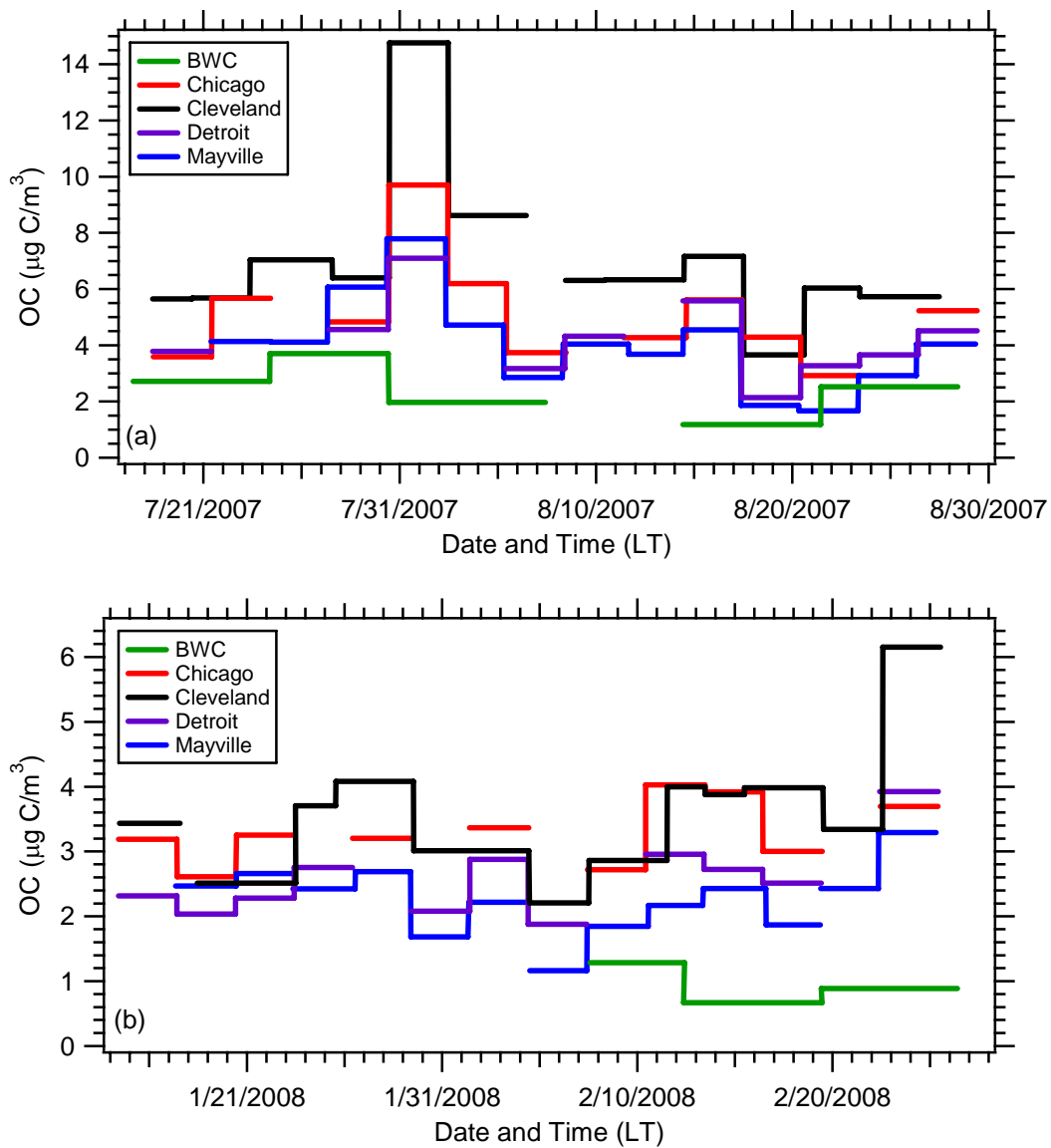


Figure 3. Time series for PM_{2.5} OC concentrations for (a) summer and (b) winter at all five sites.

during either the summer and winter campaigns as seen in Figures 6a and b, respectively. In the summer, generally Cleveland had much higher concentrations of potassium than observed at the other sites, which all exhibited fairly similar concentrations.

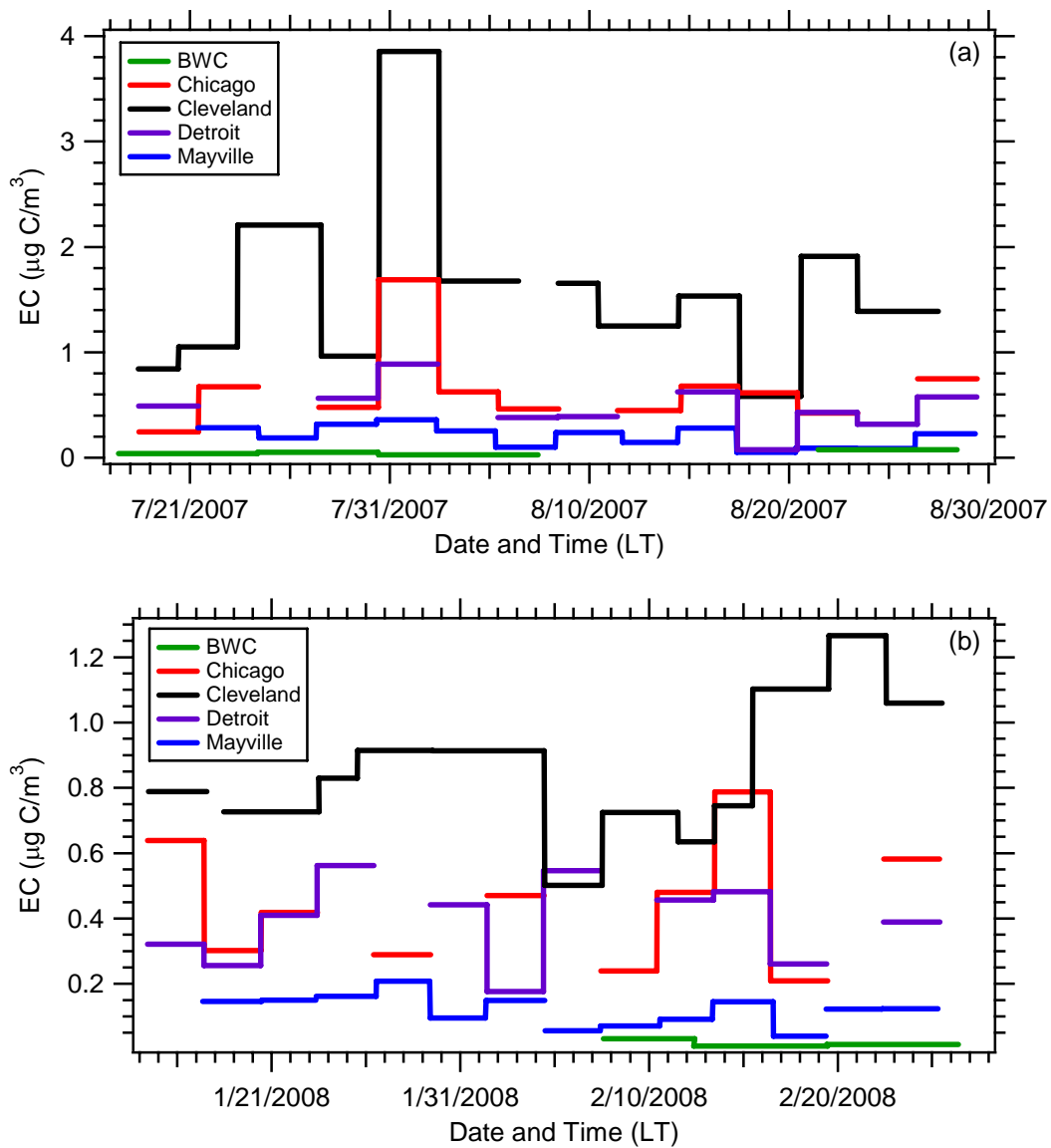


Figure 4. Time series for PM_{2.5} EC concentrations for (a) summer and (b) winter at all five sites.

Interestingly, this was also the case for Cleveland in the winter, but Mayville also observed elevated potassium concentrations during this time (Figure 6b). These elevated concentrations of potassium likely originate from local sources. In addition to being an

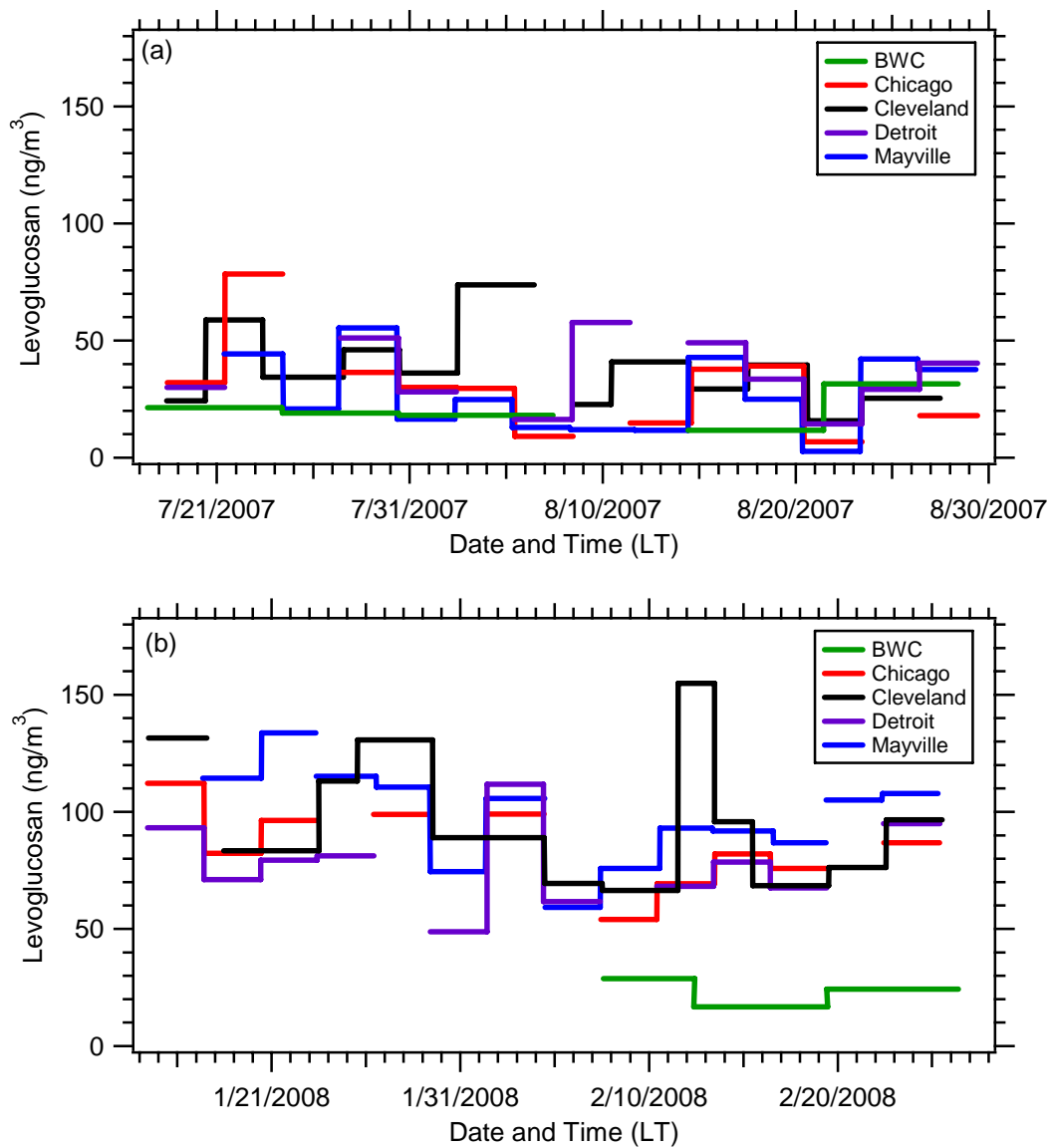


Figure 5. Time series for the PM_{2.5} levoglucosan concentrations for (a) summer and (b) winter for all five sites.

inorganic marker for biomass burning, potassium can also come from fly ash and incinerators. Both of these sources are found in Cleveland and are the likely reason for the high concentrations of potassium. However, in Mayville it is more likely that the

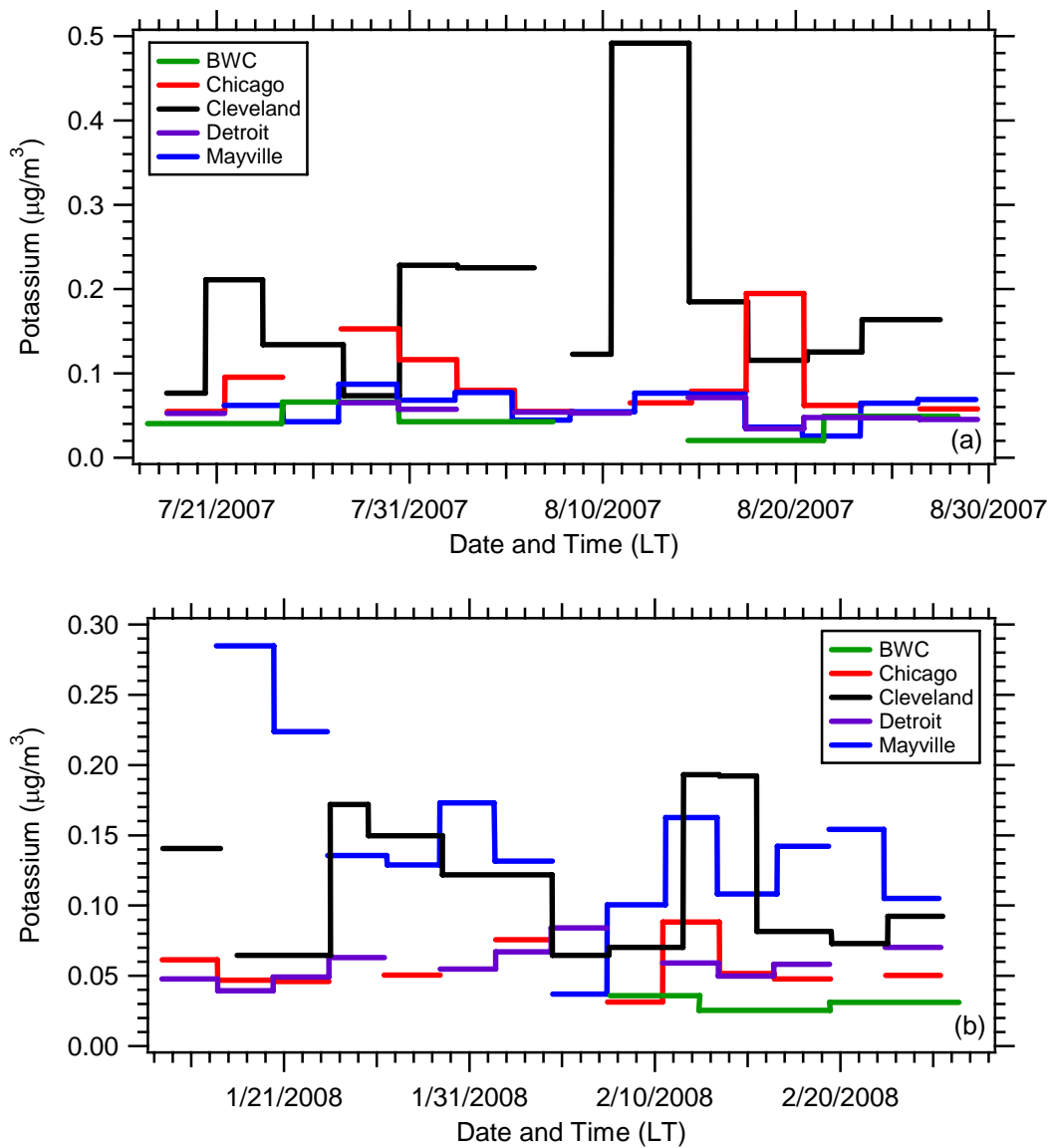


Figure 6. Time series for PM_{2.5} potassium concentrations for (a) summer and (b) winter at all five sites.

elevated potassium came from the salt used for deicing since it is only found during the winter.

Figures 7a and b show the correlation between levoglucosan and potassium for the summer and winter campaigns, respectively. Although potassium is sometimes considered to be a good inorganic marker for biomass burning, in general there is little correlation between levoglucosan and potassium at any of the sites. During the winter in Cleveland there is somewhat of a correlation between levoglucosan and potassium ($R^2 = 0.63$). However, this is really driven by the points with high potassium concentrations. When the high potassium points are removed then the same correlation between levoglucosan and potassium seen at the other sites is observed for winter in Cleveland. There also appears to be a good correlation between levoglucosan and potassium at BWC in winter, but this is based on only 3 points so it is hard to comment further on the robustness of this correlation.

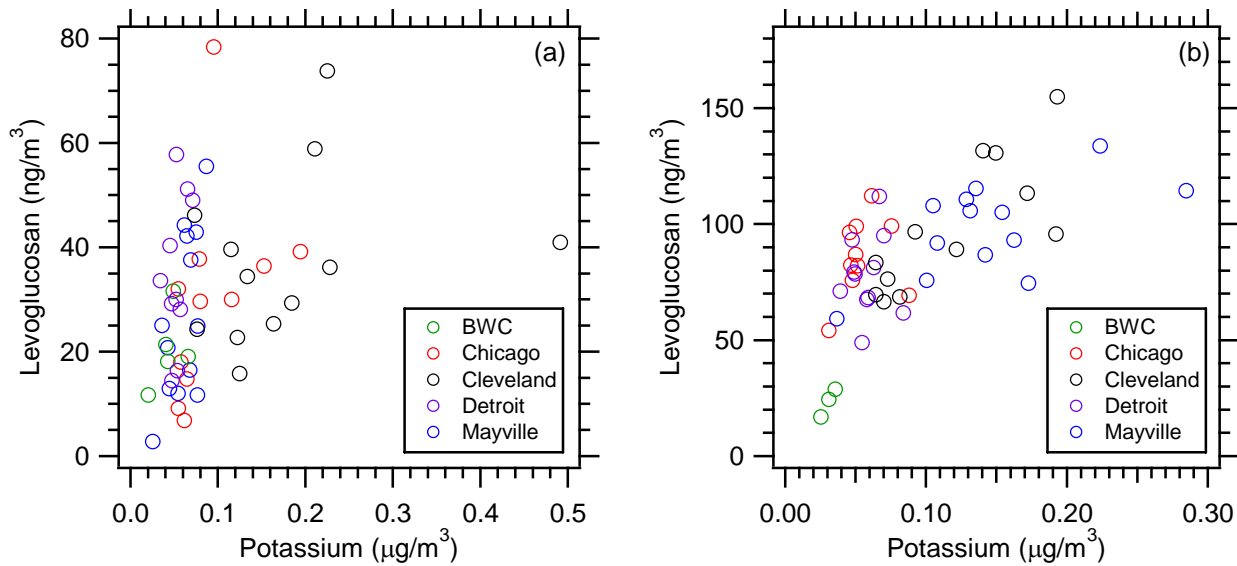


Figure 7. Correlation of PM_{2.5} levoglucosan vs. PM_{2.5} potassium for (a) summer and (b) winter at all five sites.

In Appendix A two panels are provided showing the time series discussed in this section alternatively grouped by campaign. Panel 1 shows the times series for the PM_{2.5} concentrations of OC, EC, levoglucosan, and potassium from during the summer campaign. The time series for these same species measured during the winter campaign are shown in Panel 2.

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

The contribution of PM_{2.5} OC due to biomass burning as a percentage is determined by dividing the levoglucosan/OC ratio of the sample by the levoglucosan/OC ratio from a source profile using the following equation

$$\text{Percentage of PM}_{2.5} \text{ OC due to Biomass Burning} = \frac{\text{levoglucosan/OC}_{\text{sample}}}{\text{levoglucosan/OC}_{\text{source profile}}} \times 100\% \quad (3)$$

Since, as previously mentioned, the sources of biomass burning are different in the summer and winter, two different sets of source profiles are used.

For the summer data, the source profiles come from the work of *Sullivan et al.* [2008]. *Sullivan et al.* [2008] studied the emissions of fuels known to burn during prescribed fires and wildfires through a series of controlled burns conducted at the Fire Science Laboratory in Missoula, MT. The most appropriate source profile is chosen by using a combination of the peak ratios in the carbohydrate chromatogram and back trajectory analysis. This is briefly explained below, but more details can be found in section 3.2 of *Sullivan et al.* [2008].

It has been observed that patterns appear in the HPAEC-PAD carbohydrate chromatograms when burning different types of fuel. A correlation between the response at two retention times, 3.24 and 3.65 min, in the chromatogram has been observed based on the fuel component (e.g., leaves or grasses) burned. This is illustrated in Figure 8, where the lines represent best fits to response ratios observed in source samples. The source profile data create bounds that can be used in analyzing ambient data for determining the fuel component involved in the burn. The ambient data appear to fall on these lines, allowing for the most appropriate source profile to be chosen. As can be seen in Figure 8 for the majority of the summer data the average levoglucosan/OC ratio for combustion of grasses ($0.036 \mu\text{g C}/\mu\text{g C}$) would be used.

For the winter data, the source profiles come from the work of *Fine et al.* [2004]. *Fine et al.* [2004] studied the emissions of fireplace combustion for 10 different woods from the Midwestern and Western U.S. The average levoglucosan/OC ratio determined from this work is $0.071 \mu\text{g C}/\mu\text{g C}$.

The time series for the contribution of $\text{PM}_{2.5}$ OC due to biomass burning for the summer campaign is shown in Figure 9a and for the winter campaign in Figure 9b. Tables 3a and b provide the data shown in Figures 9a and b as well as the concentration of OC due to biomass burning for the summer and winter, respectively. In all cases, these values represent only primary particle emissions from biomass burning. Additional biomass burning contributions due to secondary organic aerosol production in aging fire emissions are unquantified. These are likely to be more important in summer, due to

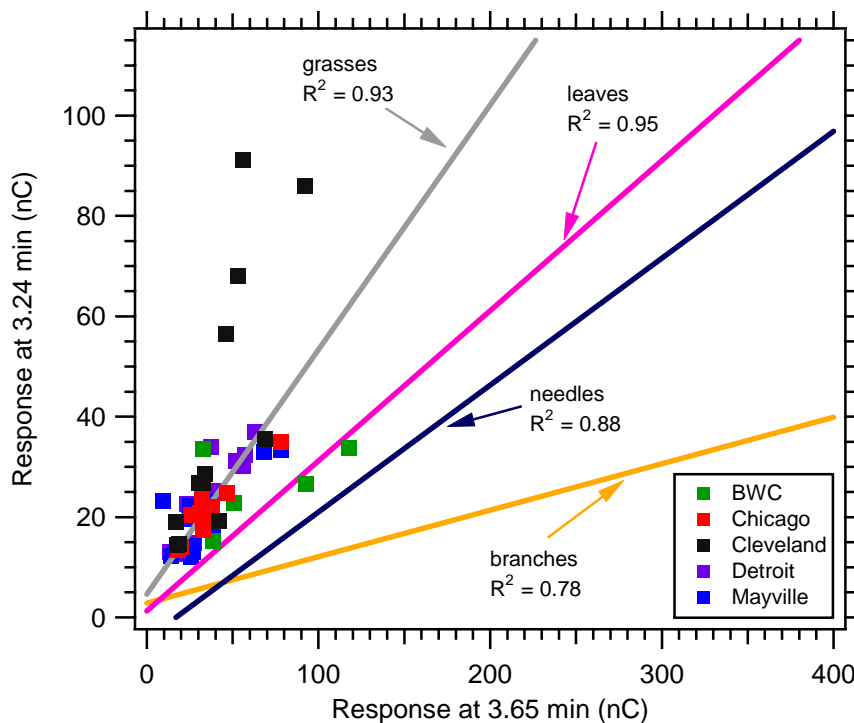


Figure 8. Correlation between the peak response at 3.24 min and 3.65 min for the least square regression fits for the source profile data from *Sullivan et al.* [2008] segregated by fuel component along with the summer data for all five sites.

greater photochemical activity and increased age of transported emissions from wildfires and prescribed fires.

During the summer, the primary particle contribution at the rural sites is only slightly higher than that of the urban sites. On average the contribution from primary biomass burning particle emission is about 10%. However, overall for the winter there is a higher primary contribution from biomass burning at all sites. For the winter, the average contribution from primary biomass burning particle emissions is about 20%.

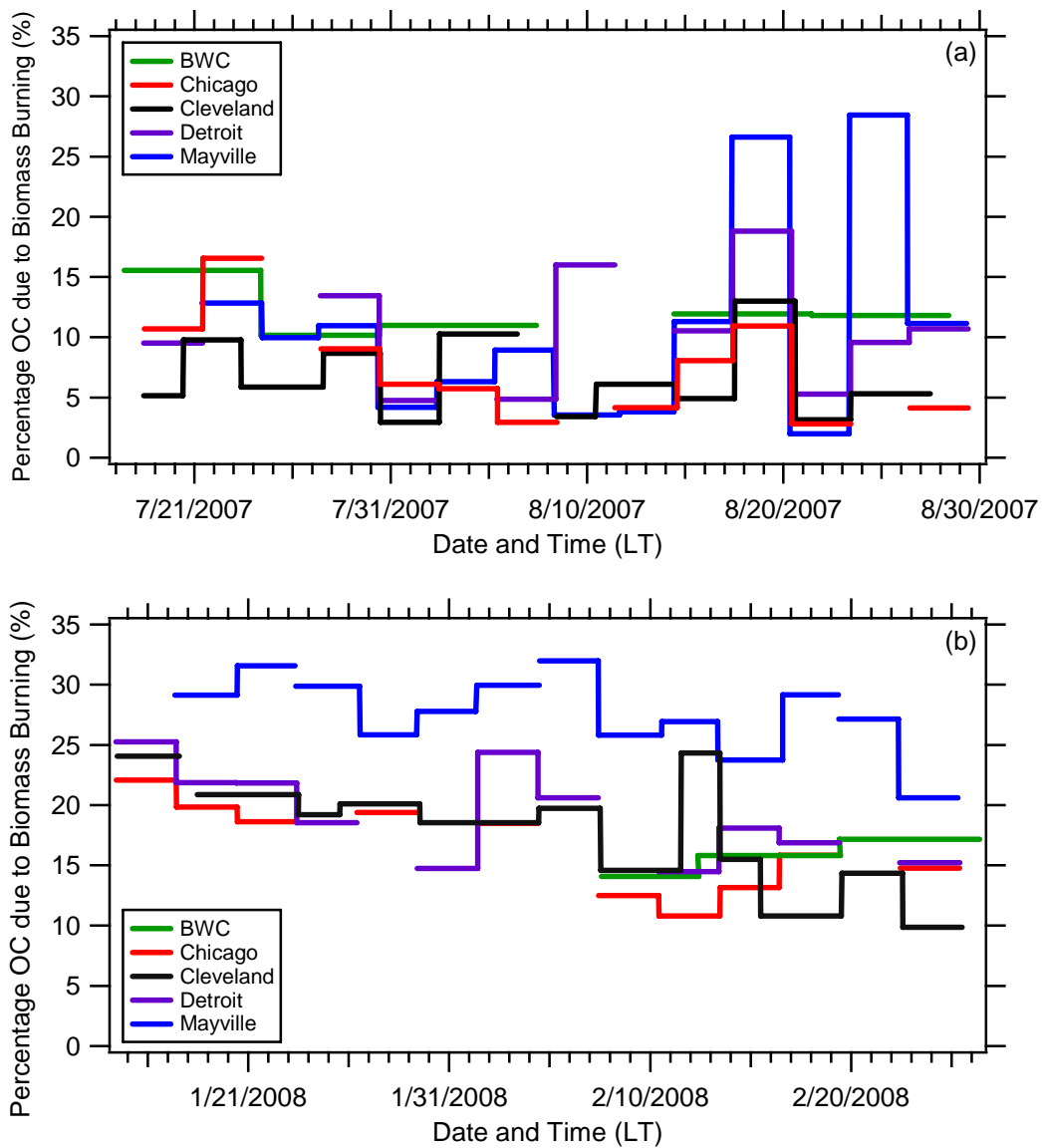


Figure 9. Time series for the percentage of $PM_{2.5}$ OC due to primary biomass burning particle emissions for (a) summer and (b) winter at all five sites.

Figure 10 compares the average contributions of primary biomass burning particle emissions to $PM_{2.5}$ OC across the sites and seasons. During winter, the highest average contribution is observed at Mayville at 28%. This is followed by Detroit, Cleveland,

Table 3a. Percentage and concentration of PM_{2.5} OC due to primary biomass burning particle emissions during the summer campaign. Date shown as month/day/year.

Start and End Date/Time (LT) ^a	Percentage of OC due to Biomass Burning (%)	OC due to Biomass Burning ($\mu\text{g C}/\text{m}^3$)
Boundary Waters Canoe		
07/17/07 10:00 – 07/24/07 9:00	16	0.42
07/24/07 9:30 – 07/30/07 10:00	10	0.38
07/30/07 10:40 – 08/07/07 10:15	11	0.22
08/14/07 10:15 – 08/21/07 10:30	12	0.14
08/21/07 11:00 – 08/28/07 10:00	12	0.30
Chicago		
07/18/07 10:35 – 07/21/07 9:58	11	0.38
07/21/07 10:25 – 07/24/07 10:11	17	0.94
07/27/07 10:40 – 07/30/07 10:21	9	0.44
07/30/07 10:42 – 08/02/07 10:43	6	0.59
08/02/07 11:02 – 08/05/07 10:26	6	0.36
08/05/07 10:44 – 08/08/07 11:26	3	0.11
08/11/07 9:57 – 08/14/07 13:55	4	0.18
08/14/07 14:21 – 08/17/07 10:11	8	0.45
08/17/07 10:26 – 08/20/07 10:05	11	0.47
08/20/07 10:32 – 08/23/07 10:31	3	0.08
08/26/07 10:28 – 08/29/07 10:03	4	0.22
Cleveland		
07/18/07 9:45 – 07/20/07 9:48	3	0.18
07/20/07 10:28 – 07/23/07 8:59	6	0.33
07/23/07 9:17 – 07/27/07 13:23	4	0.25
07/27/07 13:44 – 07/30/07 11:10	9	0.55
07/30/07 11:27 – 08/02/07 11:19	2	0.26
08/02/07 11:35 – 08/06/07 10:56	6	0.53
08/08/07 10:33 – 08/10/07 10:25	2	0.13

08/10/07 11:20 – 08/14/07 11:14	4	0.23
08/14/07 11:33 – 08/17/07 12:15	3	0.21
08/17/07 12:34 – 08/20/07 14:15	8	0.29
08/20/07 14:35 – 08/23/07 10:00	2	0.11
08/23/07 10:33 – 08/27/07 11:33	3	0.18
Detroit		
07/18/07 10:00 – 07/21/07 10:00	10	0.36
07/27/07 10:00 – 07/30/07 10:00	13	0.61
07/30/07 10:00 – 08/02/07 10:00	5	0.34
08/05/07 10:00 – 08/08/07 10:00	5	0.15
08/08/07 10:00 – 08/11/07 10:00	16	0.69
08/14/07 10:00 – 08/17/07 10:00	11	0.59
08/17/07 10:00 – 08/20/07 10:00	19	0.40
08/20/07 10:00 – 08/23/07 10:00	3	0.10
08/23/07 10:00 – 08/26/07 10:00	6	0.21
08/26/07 10:00 – 08/29/07 10:00	6	0.29
Mayville		
07/21/07 9:15 – 07/24/07 10:00	13	0.53
7/24/07 10:30 – 07/27/07 7:30	10	0.41
07/27/07 8:00 - 07/30/07 8:00	11	0.67
07/30/07 8:30 - 08/02/07 8:00	4	0.32
08/02/07 8:30 – 08/05/07 7:00	6	0.30
08/05/07 7:30 – 08/08/07 7:00	9	0.26
08/08/07 8:00 – 08/11/07 15:30	4	0.14
08/11/07 16:00 – 08/14/07 10:00	4	0.14
08/14/07 10:30 – 08/17/07 8:30	11	0.51
08/17/07 9:00 – 08/20/07 7:45	27	0.49
08/20/07 8:15 – 08/23/07 8:00	2	0.03
08/23/07 9:00 –	28	0.83

08/26/07 7:30		
08/26/07 8:00 – 08/29/07 8:00	11	0.45

^aLT stands for local time. Therefore for Boundary Waters Canoe, Mayville, and Chicago the time is in CDT (Central Daylight Time) and for Detroit and Cleveland the time is in EDT (Eastern Daylight Time).

Table 3b. Percentage and concentration of PM_{2.5} OC due to primary biomass burning particle emissions during the winter campaign. Date shown as month/day/year.

Start and End Date/Time (LT) ^a	Percentage of OC due to Biomass Burning (%)	OC due to Biomass Burning ($\mu\text{g C/m}^3$)
Boundary Waters Canoe		
02/07/08 14:00 - 02/12/08 10:00	14	0.18
02/12/08 9:00 – 02/19/08 11:00	16	0.11
02/19/08 10:00 – 02/26/08 9:30	17	0.15
Chicago		
01/14/08 10:20 – 01/17/08 9:50	22	0.70
01/17/08 10:15 – 01/20/08 10:35	20	0.52
01/20/08 11:05 – 01/23/08 10:10	19	0.61
01/26/08 9:45 – 01/29/08 10:05	19	0.62
02/01/08 9:55 – 02/04/08 10:35	18	0.62
02/07/08 10:40 – 02/10/08 10:00	12	0.34
02/10/08 10:20 – 02/13/08 11:05	11	0.44
02/13/08 11:35 – 02/16/08 10:05	13	0.52
02/16/08 10:30 – 02/19/08 11:15	16	0.48
02/22/08 10:35 – 02/25/08 9:30	15	0.55
Cleveland		
01/14/08 11:20 – 01/17/08 13:40	24	0.83
01/18/08 11:10 – 01/23/08 12:14	21	0.52
01/23/08 11:50 – 01/25/08 13:07	19	0.71
01/25/08 13:30 – 01/29/08 12:53	20	0.82
01/29/08 13:05 – 02/04/08 10:50	19	0.56
02/04/08 11:20 – 02/07/08 12:20	20	0.44

02/07/08 12:58 – 02/11/08 12:25	15	0.42
02/11/08 13:00 – 02/13/08 11:04	24	0.97
02/13/08 11:22 – 02/15/08 11:37	16	0.60
02/15/08 11:47 – 02/19/08 12:15	11	0.43
02/19/08 12:50 – 02/22/08 13:23	14	0.48
02/22/08 13:40 – 02/25/08 12:40	10	0.61
Detroit		
01/14/08 10:00 – 01/17/08 10:00	25	0.59
01/17/08 10:00 – 01/20/08 10:00	22	0.45
01/20/08 10:00 – 01/23/08 10:00	22	0.50
01/23/08 10:00 – 01/26/08 10:00	19	0.51
01/29/08 10:00 – 02/01/08 10:00	15	0.31
02/01/08 10:00 – 02/04/08 10:00	24	0.70
02/04/08 10:00 – 02/07/08 10:00	21	0.39
02/10/08 10:00 – 02/13/08 10:00	14	0.43
02/13/08 10:00 – 02/16/08 10:00	18	0.49
02/16/08 10:00 – 02/19/08 10:00	17	0.42
02/22/08 10:00 – 02/25/08 10:00	15	0.60
Mayville		
01/17/08 8:17 – 01/20/08 10:45	29	0.72
01/20/08 11:15 – 01/23/08 8:10	32	0.84
01/23/08 8:35 – 01/26/08 12:55	30	0.72
01/26/08 13:30 – 01/29/08 9:15	26	0.69
01/29/08 9:45 – 02/01/08 8:00	28	0.47
02/01/08 9:00 – 02/04/08 11:30	30	0.69
02/04/08 12:00 – 02/07/08 10:00	32	0.37
02/07/08 10:30 – 02/10/08 13:30	26	0.48
02/10/08 13:45 – 02/13/08 8:30	27	0.58
02/13/08 9:00 –	24	0.58

02/16/08 14:00		
02/16/08 14:15 – 02/19/08 9:00	29	0.54
02/19/08 9:20 – 02/22/08 7:30	27	0.66
02/22/08 8:45 – 02/25/08 7:30	21	0.68

^aLT stands for local time. Therefore for Boundary Waters Canoe, Mayville, and Chicago the time is in CST (Central Standard Time) and for Detroit and Cleveland the time is in EST (Eastern Standard Time).

Chicago, and BWC with average contributions of 19%, 18%, 17%, and 16%, respectively. During summer, the highest average contribution is at BWC with a value of 12%, followed by Mayville, Detroit, Chicago, and Cleveland with average contributions of 11%, 10%, 7%, and 7%, respectively.

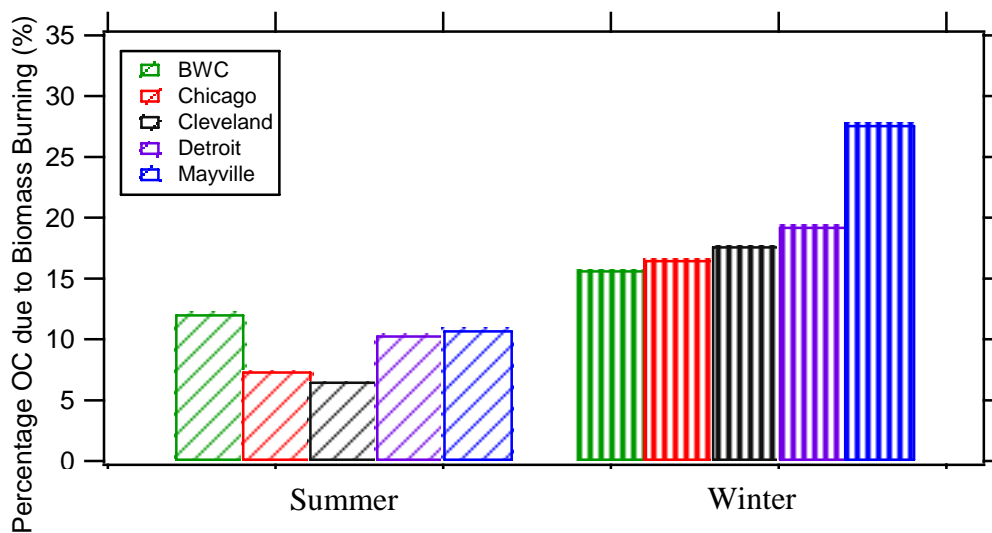


Figure 10. The average percentage of PM_{2.5} OC due to primary biomass burning particle emissions in summer and winter at each of the five sites.

3.3. Radiocarbon Analysis

Tables 4a and b show the fraction of total carbon attributed to fossil and contemporary carbon and the concentrations of the fossil and contemporary carbon for all the samples analyzed by radiocarbon analysis for the summer and winter, respectively. It should be noted that since only a subset of the samples collected were analyzed by radiocarbon analysis some of the sites only have 2 samples that were measured. The values presented could be used to create an overview of fossil and contemporary carbon concentrations in the Upper Midwest, but should not be taken as absolute for a particular site.

As a check for this radiocarbon data, the total carbon (TC) determined by the radiocarbon analysis can be compared to the TC determined from summing the OC and EC concentrations measured by the Sunset EC/OC analyzer. Figure 11 shows this comparison. As indicated by the high R^2 value of 0.92 and slope of 0.89, there appears to be reasonably good agreement between both TC measurements.

Since the BWC filters were collected over a week as opposed to the three day integrated samples collected at the other four sites, the BWC data will be shown separately. Figure 12 shows the fraction of contemporary and fossil carbon to the total carbon for BWC during both the summer and winter. As expected during both seasons the carbon is almost entirely comprised of contemporary carbon, with the fraction of contemporary carbon being only slightly higher in summer than in winter.

The fraction of summer contemporary carbon at the other four sites is not nearly as high as that of BWC (Figure 13a). The fraction of contemporary carbon, however, is

Table 4a. Fraction of contemporary and fossil carbon to the PM_{2.5} total carbon, concentrations of contemporary and fossil carbon, and fraction of contemporary carbon due to biomass burning for the set of summer samples measured by radiocarbon analysis.

Date shown as month/day/year.

Start and End Date/Time (LT) ^a	Fraction of Contemporary Carbon to Total Carbon (µg C/µg C)	Fraction of Fossil Carbon to Total Carbon (µg C/µg C)	Contemporary Carbon (µg C/m ³)	Fossil Carbon (µg C/m ³)	Fraction of Contemporary Carbon due to Biomass Burning (µg C/µg C)
Boundary Waters Canoe					
07/24/07 9:30 – 07/30/07 10:00	0.96	0.04	3.75	0.15	0.10
08/14/07 10:15 – 08/21/07 10:30	0.98	0.02	1.45	0.03	0.10
Chicago					
07/30/07 10:42 – 08/02/07 10:43	0.50	0.50	5.51	5.47	0.11
08/02/07 11:02 – 08/05/07 10:26	0.64	0.36	3.88	2.15	0.09
08/11/07 9:57 – 08/14/07 13:55	0.55	0.45	2.53	2.06	0.07
08/14/07 14:21 – 08/17/07 10:11	0.59	0.41	3.67	2.54	0.12
Cleveland					
07/30/07 11:27 – 08/02/07 11:19	0.39	0.61	6.49	10.12	0.07
08/14/07 11:33 – 08/17/07 12:15	0.47	0.53	4.16	4.68	0.08
Detroit					
07/30/07 10:00 – 08/02/07 10:00	0.55	0.45	4.57	3.69	0.07
08/14/07 10:00 – 08/17/07 10:00	0.56	0.44	3.20	2.50	0.18
Mayville					
07/30/07 8:30 - 08/02/07 8:00	0.81	0.19	5.72	1.36	0.06
08/02/07 8:30 – 08/05/07 7:00	0.87	0.13	4.30	0.66	0.07
08/11/07 16:00 – 08/14/07 10:00	0.85	0.15	3.51	0.62	0.04
08/14/07 10:30 – 08/17/07 8:30	0.86	0.14	4.09	0.67	0.13
08/20/07 8:15 – 08/23/07 8:00	0.72	0.28	1.35	0.52	0.02

^aLT stands for local time. Therefore for Boundary Waters Canoe, Mayville, and Chicago the time is in CDT (Central Daylight Time) and for Detroit and Cleveland the time is in EDT (Eastern Daylight Time).

Table 4b. Fraction of contemporary and fossil carbon to the PM_{2.5} total carbon, concentrations of contemporary and fossil carbon, and fraction of contemporary carbon due to biomass burning for the set of winter samples measured by radiocarbon analysis. The values listed in red in the parenthesis are from performing the sensitivity test discussed at the end of section 3.3. Date shown as month/day/year.

Start and End Date/Time (LT) ^a	Fraction of Contemporary Carbon to Total Carbon (µg C/µg C)	Fraction of Fossil Carbon to Total Carbon (µg C/µg C)	Contemporary Carbon (µg C/m ³)	Fossil Carbon (µg C/m ³)	Fraction of Contemporary Carbon due to Biomass Burning (µg C/µg C)
Boundary Waters Canoe					
02/12/08 9:00 – 02/19/08 11:00	0.88 (0.74)	0.12 (0.26)	0.55 (0.46)	0.08 (0.17)	0.19 (0.23)
02/19/08 10:00 – 02/26/08 9:30	0.92 (0.78)	0.08 (0.22)	0.73 (0.62)	0.06 (0.18)	0.21 (0.25)
Chicago					
02/07/08 10:40 – 02/10/08 10:00	0.87 (0.74)	0.13 (0.27)	1.92 (1.62)	0.28 (0.58)	0.18 (0.21)
02/10/08 10:20 – 02/13/08 11:05	0.36 (0.30)	0.64 (0.70)	1.54 (1.30)	2.72 (2.97)	0.28 (0.34)
02/13/08 11:35 – 02/16/08 10:05	0.64 (0.54)	0.36 (0.46)	2.10 (1.76)	1.16 (1.49)	0.25 (0.29)
02/22/08 10:35 – 02/25/08 9:30	1.34 ^b (1.12) ^b	-0.34 (-0.12)	3.24 (2.73)	-0.81 (-0.30)	0.17 (0.20)
Cleveland					
02/07/08 12:58 – 02/11/08 12:25	0.69 (0.58)	0.31 (0.42)	1.27 (1.07)	0.58 (0.78)	0.33 (0.39)
02/22/08 13:40 – 02/25/08 12:40	0.53 (0.44)	0.47 (0.56)	1.78 (1.50)	1.60 (1.89)	0.34 (0.40)
Detroit					
02/10/08 10:00 – 02/13/08 10:00	0.52 (0.44)	0.48 (0.56)	1.26 (1.06)	1.15 (1.35)	0.34 (0.41)
02/13/08 10:00 – 02/16/08 10:00	0.53 (0.45)	0.47 (0.55)	1.29 (1.08)	1.13 (1.34)	0.38 (0.46)
02/22/08 10:00 – 02/25/08 10:00	1.06 ^b (0.89)	-0.06 (0.11)	3.46 (2.91)	-0.20 (0.35)	0.17 (0.21)
Mayville					
02/07/08 10:30 – 02/10/08 13:30	1.11 ^b (0.93)	-0.11 (0.07)	1.69 (1.42)	-0.17 (0.11)	0.28 (0.34)
02/10/08 13:45 – 02/13/08 8:30	0.79 (0.67)	0.21 (0.34)	1.68 (1.41)	0.44 (0.71)	0.35 (0.41)
02/13/08 9:00 – 02/16/08 14:00	1.10 ^b (0.92)	-0.10 (0.08)	1.88 (1.58)	-0.17 (0.13)	0.31 (0.37)
02/22/08 8:45 – 02/25/08 7:30	2.77 ^b (2.33) ^b	-1.77 (-1.33)	5.64 (4.74)	-3.60 (-2.70)	0.12 (0.14)

^aLT stands for local time. Therefore for Boundary Waters Canoe, Mayville, and Chicago the time is in CST (Central Standard Time) and for Detroit and Cleveland the time is in EST (Eastern Standard Time).

^bContemporary fraction is higher than 100% suggesting that the two component model of the total carbon being composed of contemporary and fossil carbon may not be appropriate for this sample.

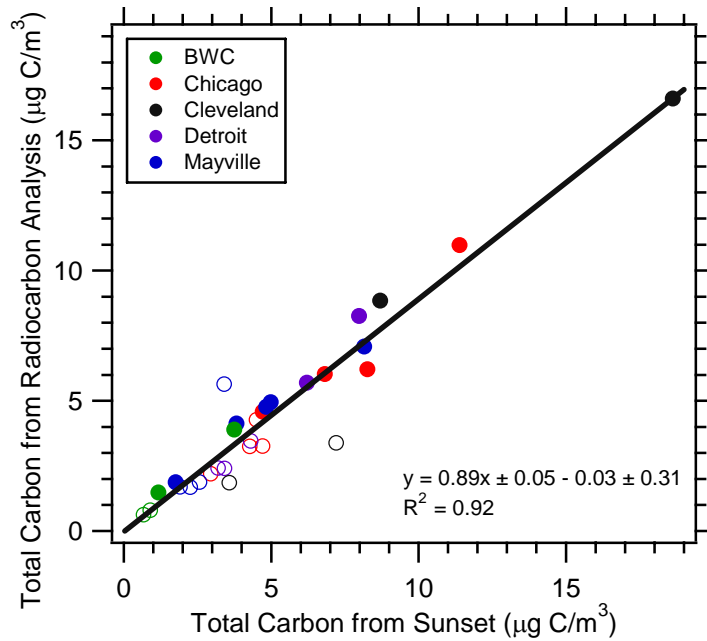


Figure 11. Comparison of the Total Carbon determined from the radiocarbon analysis vs. the Total Carbon measured by the Sunset EC/OC analyzer for all the summer (filled) and winter (unfilled) samples from all five sites analyzed by radiocarbon analysis. The uncertainties associated with the regression are one standard deviation.

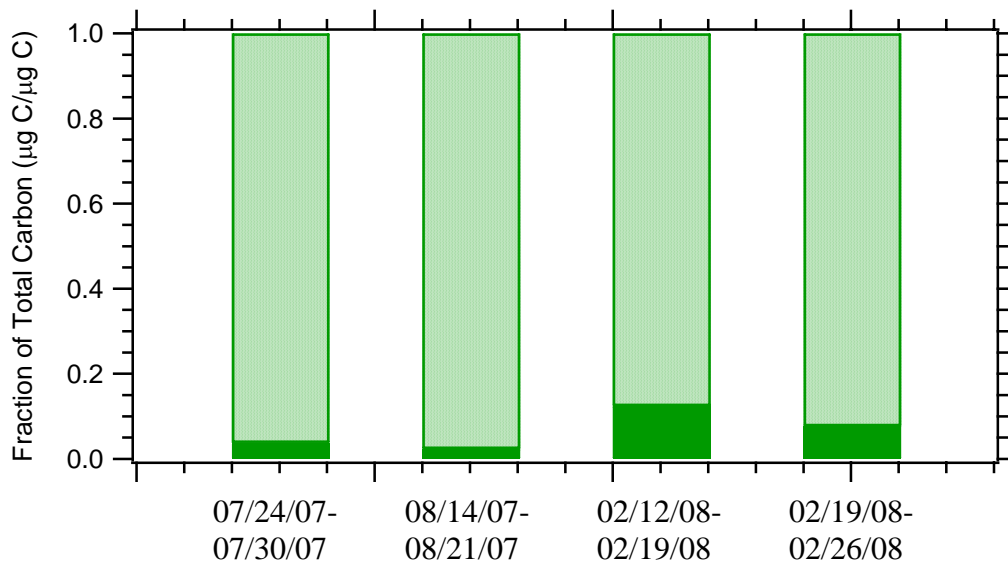


Figure 12. Fraction of contemporary (shaded) and fossil (solid) carbon to the $\text{PM}_{2.5}$ total carbon for the summer and winter samples analyzed by radiocarbon analysis from the Boundary Waters Canoe site.

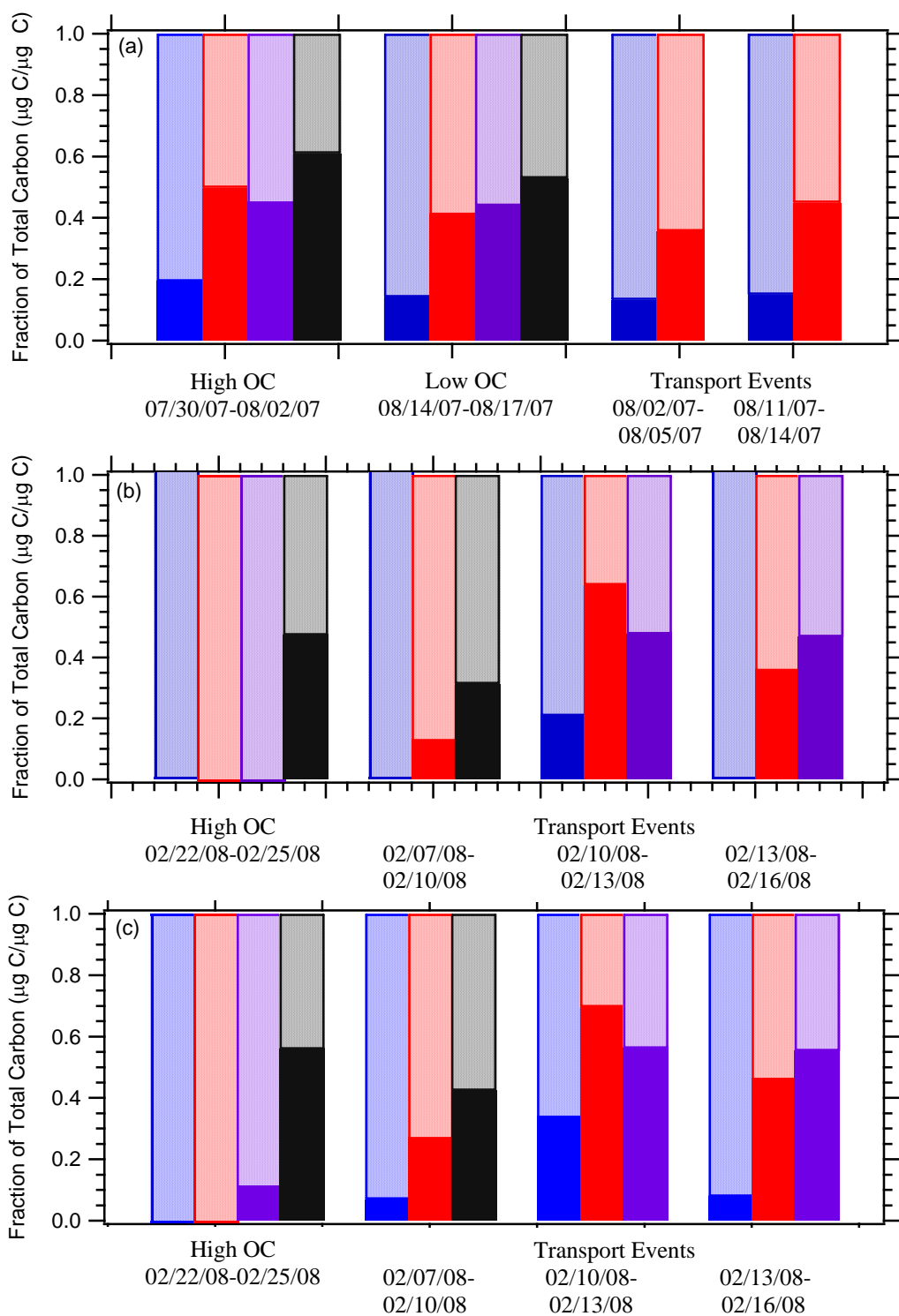


Figure 13. Fraction of contemporary (shaded) and fossil (solid) carbon to the $\text{PM}_{2.5}$ total carbon for the samples analyzed by radiocarbon analysis for (a) summer, (b) winter with a F_M correction of 1.05, and (c) winter with a F_M correction of 1.25 from Mayville (blue), Chicago (red), Detroit (purple), and Cleveland (black).

higher at the rural site of Mayville than at the 3 urban sites. Mayville contemporary carbon fractions range between 72% and 87% for the four summer periods analyzed. The contemporary fractions at the three urban sites (Chicago, Cleveland, and Detroit) range from 39% to 64% in the summer periods analyzed. The fractions at a particular site appear to be fairly independent of where the air mass is being transported from or if the OC concentrations are high or low. Even more interestingly, the absolute concentrations of contemporary carbon are actually fairly similar at each of the four sites (Figure 14), suggesting a fairly similar regional background of contemporary fine particle carbon exists in the region during summer.

During the winter generally the fractions of contemporary carbon at each of the four sites shown in Figure 13b are higher than in the summer. It is also important to note that at times during the winter the calculated fraction of contemporary carbon is actually higher than 100%. The samples from Mayville, Chicago, and Detroit on the high OC day (02/22/08 - 02/25/08) were actually analyzed twice and the same results were obtained both times. This suggests that these results are real and for some of the samples the two component model may not be appropriate. It is not fully understood why this is happening to some of the winter samples. But possible reasons could include that another source of ^{14}C in addition to fossil and contemporary carbon is present or that the wood being burned is several decades older, from a period when ^{14}C concentrations in the atmosphere were higher, due to nuclear bomb testing in the 1950s and 1960s.

In order to evaluate the latter possibility, we conducted a sensitivity test where F_M (see equation 1) was corrected using a value of 1.25 instead. This higher correction factor has been found to be more appropriate for the burning of older vegetation [Szidat

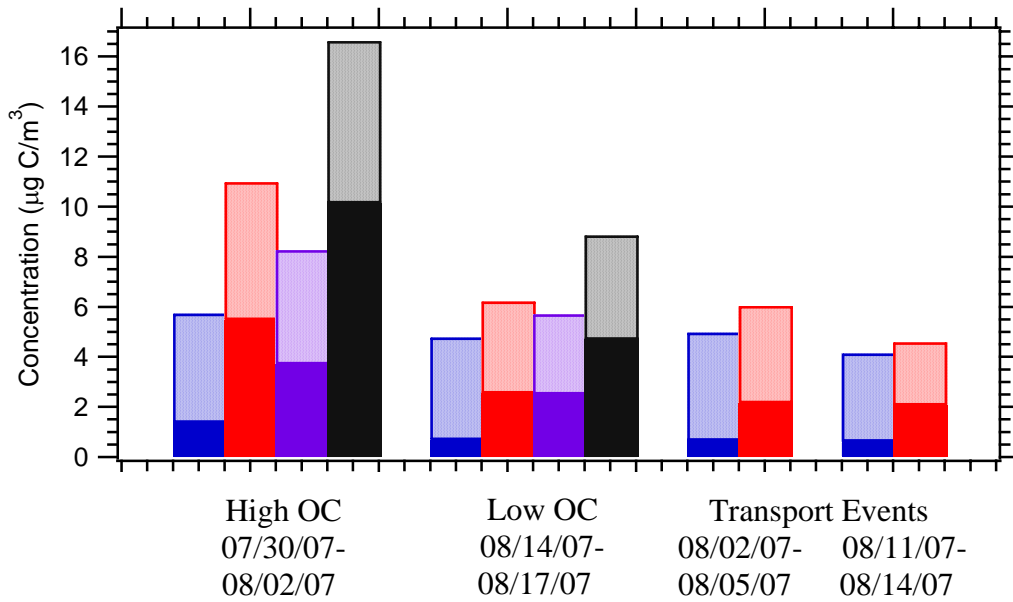


Figure 14. Concentrations for the contemporary (shaded) and fossil (solid) carbon for the summer samples analyzed by radiocarbon analysis for Mayville (blue), Chicago (red), Detroit (purple), and Cleveland (black).

et al., 2006]. When using this alternative factor, the fraction of contemporary carbon is now under 100% for all but two samples (Figure 13c and Table 4b). This suggests that it is possible that older wood may have been used in some of the residential burning that occurred in winter. Since it has been suggested that the range of this correction factor can be from 1.08 to 1.25 [Lewis *et al.*, 2004], the values using the original correction of 1.05 in Table 4b could be considered a lower limit and the ones using the higher factor of 1.25 could be considered the upper limit.

Contributions of carbon from biomass burning should be included in the contemporary carbon fractions. Table 4 also provides the fraction of contemporary carbon due to primary biomass burning particle emissions for all the samples. The

fraction of contemporary carbon due to primary biomass burning emissions is larger in winter than summer, consistent with the importance of residential wood combustion during winter in this region and with an expected decrease in secondary organic aerosol production from biogenic VOC (volatile organic carbon) emissions in winter.

4. Summary

Hi-Volume PM_{2.5} filter samples were collected at five sites in the Upper Midwest in July to August 2007 and January to February 2008. The goal was to better understand the impact of biomass burning on fine particle concentrations in this region during the summer and winter.

In order to do this, levoglucosan, water-soluble potassium, OC, and EC were determined in these samples. A direct alternative method for measuring levoglucosan using HPAEC-PAD was used. The technique offers numerous advantages over traditional methods because the filter samples could be extracted directly in DI Water and levoglucosan could then be determined directly from the liquid extract. From using this method it was found that during the summer the levoglucosan concentrations ranged from 3 to 78 ng/m³ and during the winter from 17 to 163 ng/m³.

From looking at the various time series of each of the species measured, it was observed that OC appears to contain a substantial regional component. However, for EC the concentrations are much higher at the urban sites than the rural sites. During the summer, the levoglucosan appears to also be regional, consistent with transport from distant wildfires and/or prescribed fires. During the winter some local influences are observed on levoglucosan concentrations, consistent with a more local, residential wood

burning source at this time of year. In contrast to this, potassium really exhibited no clear pattern in the summer or winter suggesting in this case potassium was not a useful marker for biomass burning. However, periods of more locally elevated potassium concentrations were observed.

The contribution to OC from primary particle emissions from biomass burning was calculated for both the summer and winter. The contribution of biomass burning to PM_{2.5} OC was higher in winter than in the summer at all sites. The average contribution for the summer was at BWC 12%, Chicago 7%, Cleveland 7%, Detroit 10%, and Mayville 11%. In the winter, the average contribution was at BWC 16%, Chicago 17%, Cleveland 18%, Detroit 19%, and Mayville 28%. Additional biomass burning contributions through secondary organic aerosol formation are also possible, especially during summer.

Radiocarbon analysis showed that the contemporary carbon fraction of OC was generally greater than 50% and largest at the rural sites. A substantial regional component of contemporary carbon was present in summer, with similar levels across study sites and values typically in the 3-5 $\mu\text{g C}/\text{m}^3$ range. The fraction of contemporary carbon in winter was generally higher than in summer. Primary particle emissions from biomass burning comprised only a small fraction of contemporary carbon in summer samples (typically < 10%) but increased in winter, with many samples in the 20-35% range.

Since this study focused only on one particular source of OC, biomass burning, our ability to suggest appropriate and effective control strategies for OC in the Upper Midwest is limited. From the perspective of our study, biomass burning does not appear

to be a huge source of OC in this region during the summer period studied. Biomass burning does become a bigger influence in the winter, so limiting residential wood combustion on stagnation days or installing cleaner burning fireplaces or woodstoves could help. But, again, even in the winter biomass burning still does not comprise a majority of the OC or even of the contemporary carbon.

The radiocarbon data suggests that generally the contemporary fraction accounts for more than 50% of the total carbon and is, therefore, a larger contributor than fossil carbon sources. Since the contemporary fraction is assumed to come from biogenic sources (including biomass combustion) and appears to have a large regional component one might anticipate that regional strategies may be required for control. However, there is some evidence (e.g., [Weber *et al.*, 2007]) that suggests that even if the carbon contained in the particles is of biogenic origin the oxidation of biogenic volatile organic compounds to a point where they condense to form secondary organic aerosol may actually be strongly linked to anthropogenic precursors. More data would be necessary to assess this possibility and to determine whether local strategies (e.g., through NO_x emissions reductions) could be effective in regional contemporary fine particle carbon control.

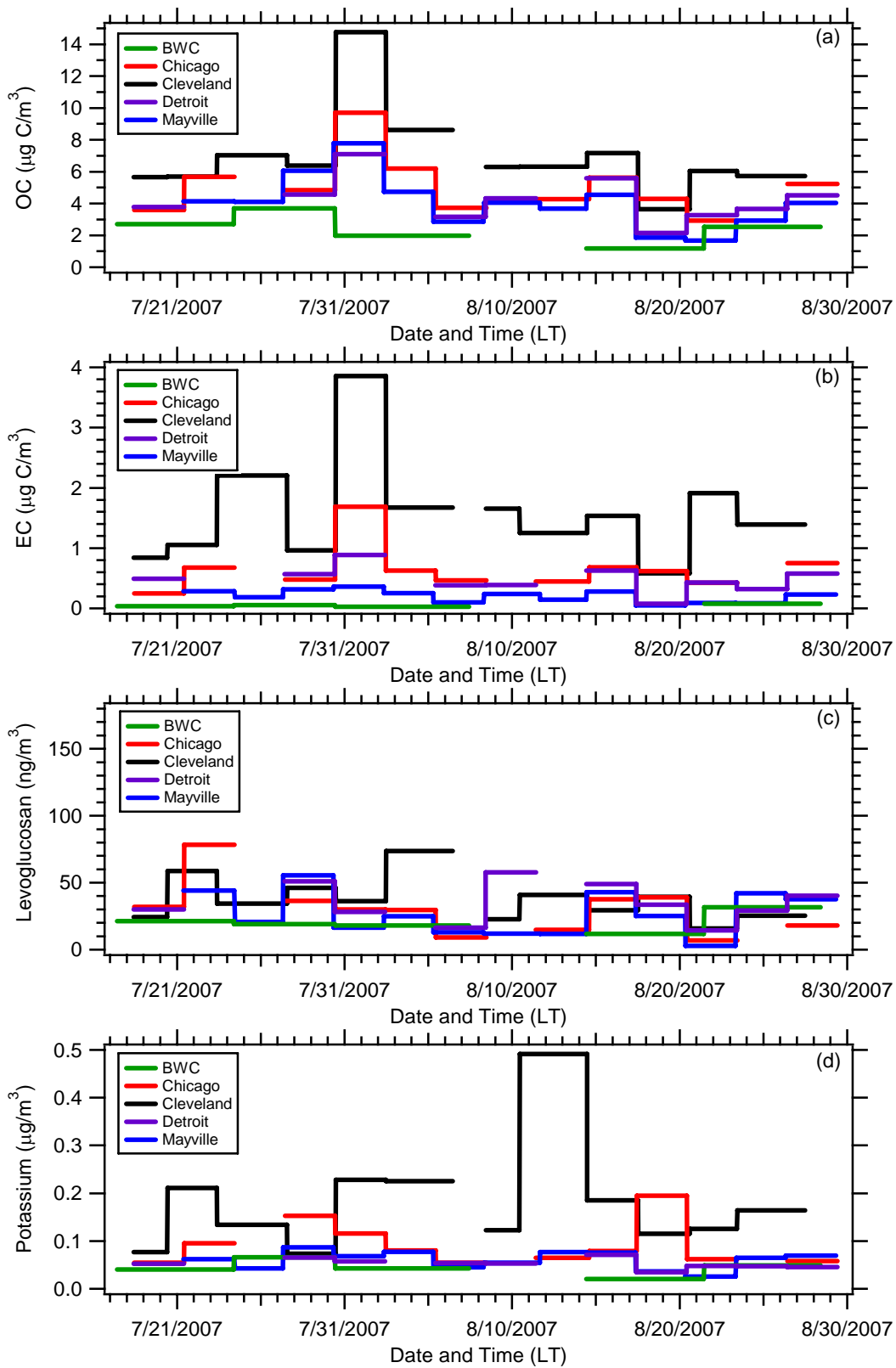
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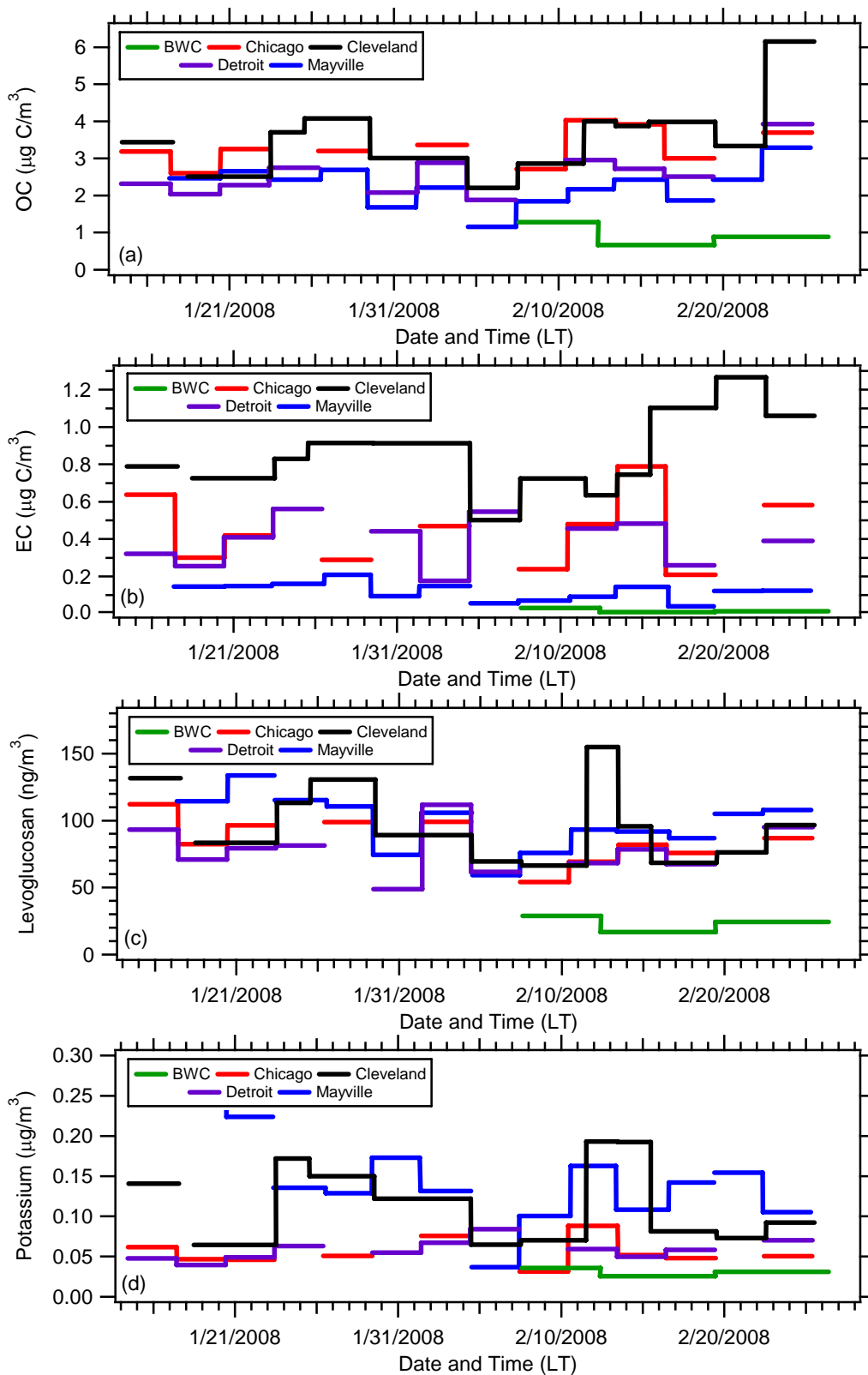
assistance in setting-up and transporting the samplers. Lastly, we would like to acknowledge the state representatives from IL, MI, MN, OH, and WI and the site operators from BWC, Chicago, Cleveland, Detroit, and Mayville for all their help in collecting the samples.

Appendix A

Figures 3a, 3b, 4a, 4b, 5a, 5b, 6a, and 6b have been regrouped to provide a panel with all the time series showing the concentrations for the various species measured for the summer (Panel 1) and winter (Panel 2) campaigns. Each panel contains the data for the PM_{2.5} concentrations of OC, EC, levoglucosan, and potassium measured at each of the five sites.



Panel 1. Time series for the summer PM_{2.5} concentrations for (a) OC, (b) EC, (c) levoglucosan, and (d) potassium at all five sites.



Panel 2. Time series for the winter PM_{2.5} concentrations for (a) OC, (b) EC, (c) levoglucosan, and (d) potassium at all five sites.

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