Final Report for Task #J2350-08-6023 (February 2008 – June 2009)

Analysis of Levoglucosan, K$^+$, and Water-Soluble Organic Carbon in Archived Filter Samples

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Project Deliverables

Deliverables for this project include this final report. Included in the report are tables with the concentrations for the key species measured in this study from the archived filter samples.

Project Publications and Presentations

Sullivan, A.P.[1], N. Frank[2], and J.L. Collett, Jr.[1], "An Alternative Method for Determining the Impact of Biomass Burning", poster presented at the American Association for Aerosol Research Annual Conference, Orlando, Florida, October 2008.

Sullivan, A.P.[1], D.M. Kenski[3], N. Frank[2], and J.L. Collett, Jr.[1], "Spatial and Temporal Impacts of Biomass Burning (and More) on the Upper Midwest", oral presentation at the American Association for Aerosol Research Annual Conference, Orlando, Florida, October 2008.

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1. Introduction

Biomass burning has been found to be one of the major sources of atmospheric fine particle organic carbon. Smoke from wildfires and prescribed burning can have a significant impact on $PM_{2.5}$ concentrations. This in turn can affect air quality from local to regional and global scales. Biomass burning smoke can also be a significant contributor in affecting the Earth's radiation balance and causing visibility impairment. In addition, residential wood combustion can also be an important source of organic carbon.

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.

In order to quantify the contribution of biomass burning to the total organic carbon, the most common method used and the one used in the above study, is through 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. If the ratio of the marker to the total organic carbon is known at the source and the marker is conserved during transport, then a measurement of the concentration of the smoke marker at a downwind location can be used to determine the contribution of primary aerosols emitted by biomass burning to the total organic carbon concentration.

The most commonly used smoke marker is levoglucosan, a sugar anhydride produced during the combustion of cellulose [*Simoneit et al.*, 1999].

Levoglucosan is traditionally measured using Gas Chromatography-Mass Spectrometry (GC-MS). GC-MS requires chemical derivatization, making it quite labor intensive and expensive due to the instrumentation, reagents, and solvents needed. However, there is an alternative method available for measuring levoglucosan that could be used. It couples high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD). 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 networks for analysis of the major inorganic aerosol species.

The results mentioned above for the Upper Midwest used GC-MS to determine the levoglucosan concentration. Therefore, these results, as well as most previous studies looking at the impact of biomass burning, have been based on the analysis of composited filter samples. This often limits determination of temporal and/or spatial variability in the impact of biomass burning in the Upper Midwest as well as other regions. Since it appears that biomass burning can be an important source of organic carbon, in order to better understand its impact it would really be very useful if the levoglucosan analysis and the smoke marker method could be applied to daily samples routinely collected as part of a network, such as from the FRM (Federal Reference Monitor) network.

As part of the routine measurements made at each of the FRM sites, a 47 mm Teflon filter sample is collected. From this filter the concentration of the total $PM_{2.5}$ mass

is obtained. Once this measurement is completed then the entire filter is archived, generally refrigerated and in a Petri dish, providing a filter sample that can later be analyzed by additional methods. The only disadvantage of using these samples is that the total organic carbon concentration can not be directly measured from them because the filters are Teflon. However, the total water-soluble organic carbon (WSOC) can be measured from the same aqueous extract as the levoglucosan. WSOC can be a very interesting measurement since it has been found that the two main sources of WSOC are secondary organic aerosol and biomass burning [*Sullivan et al.*, 2006].

Presented here will be the application of the alternative HPAEC-PAD method to measure levoglucosan, along with measurements of water-soluble potassium and WSOC, on archived FRM Teflon filter samples collected at ten sites in the Upper Midwest from March 2004 through February 2005. These data will be used to investigate the spatial and temporal trends of these various species. A determination of the impact of biomass burning to the total organic carbon concentration in this region will also be provided.

2. Methods

2.1. Filter Samples

The filter samples used for this work were archived 47 mm Teflon filters collected to provide the routine $PM_{2.5}$ mass measurement as part of the FRM network. These samples are collected on the standard FRM sampler, which has a flowrate of 16.7 LPM and uses a 2.5 µm cyclone. The 24 hour (starting at midnight) 1-in-6 day samples collected from March 4, 2004 to February 27, 2005 at 10 sites in the Midwest were analyzed. Figure 1 shows a map with the locations of these ten sampling sites. There are
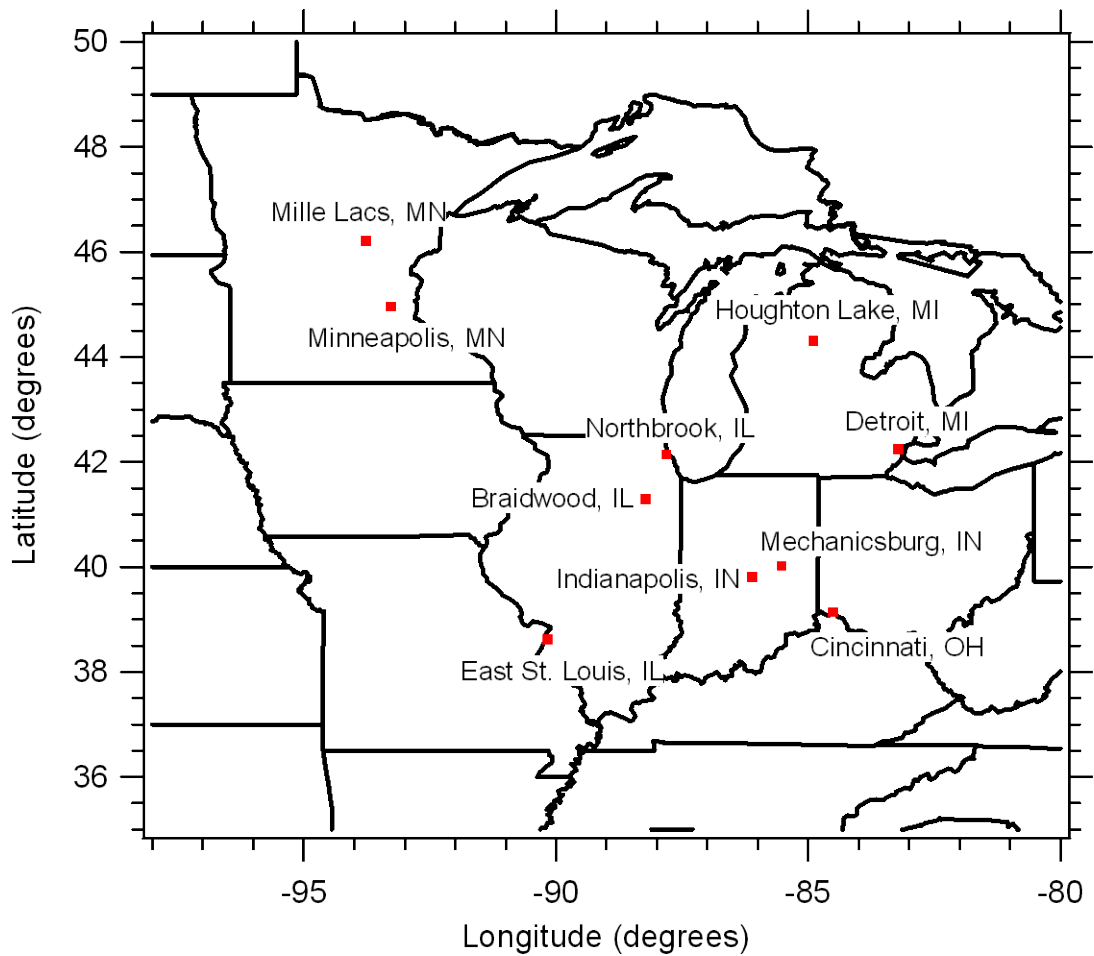
Figure 1. Map of the locations for the 10 sites used for this study.

six urban sites (Indianapolis, IN at the Washington Park site, Cincinnati, OH at the Taft St. site, East St. Louis, IL, Northbrook, IL, Detroit, MI at the Allen Park site, and Minneapolis, MN at the HC Anderson School site), one suburban site (Braidwood, IL), and three rural sites (Mechanicsburg, IN, Houghton Lake, MI, and Mille Lacs, MN). For ease the site names will be abbreviated from this point on throughout the text. The

abbreviations used for each site and more details about each of the sites can be found in Table 1.

2.2. Measurement Approach

Each of the Teflon filters was analyzed individually for $PM_{2.5}$ levoglucosan, water-soluble potassium, and water-soluble organic carbon (WSOC). These analyses are described in detail below.

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 is measured. 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 WSOC, which occurred within 48 hours of extraction, and 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. The electrochemical cell contained a "standard" gold working electrode and a pH-Ag/AgCl (silver/silver chloride) reference electrode.

Table 1. Details about the sites used in this study including the Air Quality System (AQS) code, coordinates, and abbreviation used for each site throughout the text.

Sites	Indianapolis, IN at the Washington Park site	Mechanicsburg, IN	Cincinnati, OH at the Taft St. site	Braidwood, IL	East St. Louis, IL	Northbrook, IL	Detroit, MI at the Allen Park site	Houghton Lake, MI	Minneapolis, MN at the HC Anderson School site	Mille Lacs, MN
AQS Code	18-097-0078	18-065-0003	39-061-0040	17-197-1007	17-163-0010	17-031-4201	26-163-0001	26-113-0001	27-053-0963	27-095-3051
Latitude, Longitude Coordinates (degrees)	39.81, -86.11	40.01, -85.52	39.13, -84.50	41.28, -88.22	38.61, -90.16	42.12, -87.80	42.23, -83.21	44.31, -84.89	44.95, -93.26	46.21, -93.76
Abbreviation Used	WP	Mech	Cinc	BW	ESL	NB	AP	HL	And	ML

Once the analytes are eluted from the column they enter the electrochemical cell. Here they are electroanalytically oxidized on the surface of the gold working electrode by applying a positive potential. However, continuing to do this can cause the surface of the electrode to become poisoned and therefore an entirely different potential has to be applied to clean the surface of the electrode. PAD is essentially the repeated application of a waveform, a series of potentials, to the electrode surface.

This method uses Dionex CarboPac PA-1 guard (4 x 50 mm) and analytical (4 x 250 mm) columns. The eluents are 200 mM sodium hydroxide (NaOH) and DI Water. The complete run time is approximately 59 minutes and includes 4 steps. The first step is isocratic elution with 10 mM NaOH to detect anhydrosugars, such as levoglucosan, and sugar alcohols in the first 10 minutes. Next is a 19 minute linear gradient from 10 to 70 mM NaOH to detect sugars. Since carbonate ions can bind to the active sites of the resin and affect the chromatography, the third step is a column cleaning with 180 mM NaOH for 14 minutes. This of course then requires a re-equilibration step, the fourth step, to return to the starting conditions of 10 mM NaOH. This last step lasts 16 minutes. The flowrate during each step is 0.5 ml/min. A sample injection volume of 50 μL is used. Based on using the study's flowrate of 16.7 LPM and sampling time of 24 hour, the limit of detection (LOD) for the various carbohydrates is less than approximately 0.10 ng/m^3.

Figure 2 shows a sample calibration chromatogram using the method described above. This method is able to separate mannosan, an anhydrosugar associated with biomass combustion, from a sugar alcohol associated with fungi, mannitol. This is important because if mannitol is present then arabitol, another sugar alcohol associated with fungi, is also present. It turns out that arabitol can overlap with levoglucosan in the
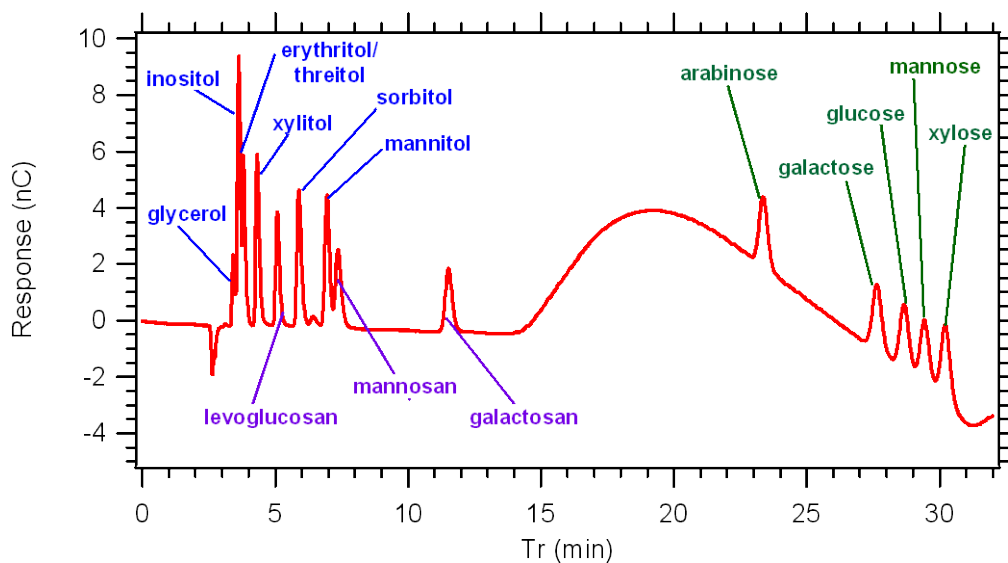
Figure 2. Calibration chromatogram for the injection of a mixed carbohydrate standard on the PA-1 column, where Tr is retention time. The sugar alcohols are labeled in blue, anhydrosugars in purple, and sugars in green.

chromatogram, biasing the levoglucosan quantitation. This is only a factor from May through November as mannitol and arabitol originate from spores which are not active during winter and spring. (Note, additionally in Appendix A is a discussion about the contribution of OC from spores derived from the mannitol concentration.) The mannitol concentration is used to correct the levoglucosan data 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 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 x 150 mm)

column with a 20 mM methanesulfonic acid eluent at a flowrate of 0.5 ml/min allowed for separation of the common inorganic ions. The complete run time was 17 minutes. A sample injection volume of 50 µL was used. The LOD for water-soluble potassium is approximately 0.001 µg/m^3 (or 1 ng/m^3) for this study.

WSOC was measured using a Sievers Model 800 Turbo Total Organic Carbon (TOC) Analyzer. The TOC analyzer works by converting the organic carbon material in the sample to carbon dioxide using chemical oxidation via ammonium persulfate and ultraviolet light. The carbon dioxide formed is then measured by conductivity. The organic carbon is the difference in two channels: an inorganic carbon channel and total carbon channel. The oxidation only occurs in the total carbon channel. The analyzer was run in Turbo mode, providing a 3 s integrated measurement. For this study, the LOD for WSOC is approximately 0.06 µg C/m^3.

3. Results and Discussion

Table 2a shows the WSOC concentrations at all 10 sites. The levoglucosan data for all 10 sites are shown in Table 2b. Table 2c contains the data for the potassium concentrations for all 10 sites. Levoglucosan and water-soluble potassium concentrations were above the detection limit in almost all samples analyzed. Generally, if levoglucosan was below the detection limit this occurred in summer, whereas for potassium it was more variable. WSOC was detected in all the samples.

Table 2a. Concentrations for $PM_{2.5}$ WSOC in units of $\mu g\ C/m^3$ from the 1-in-6 day 24 hour midnight to midnight archived Teflon filter samples analyzed at each of the ten sites where NA = not available and ND = not detected. Date shown as month/day/year.

Date	And	AP	BW	Cinc	ESL	HL	Mech	ML	NB	WP
3/4/04	1.18	2.11	NA	1.55	NA	1.67	1.72	1.13	2.04	1.26
3/10/04	1.20	1.81	1.35	1.26	1.74	1.58	1.89	1.04	1.63	1.55
3/16/04	1.09	1.47	1.33	1.16	NA	1.15	1.83	1.06	1.27	1.06
3/22/04	1.18	1.36	1.21	1.00	1.37	1.18	1.32	1.15	1.42	1.03
3/28/04	1.12	1.60	1.46	2.28	1.58	1.63	2.60	0.99	1.49	2.04
4/3/04	1.12	1.43	1.26	1.39	1.88	1.25	1.74	1.03	NA	1.14
4/9/04	1.26	1.49	1.43	1.74	2.05	1.46	2.06	1.00	1.38	1.50
4/15/04	2.72	1.56	2.25	1.60	2.25	NA	2.29	1.90	2.15	1.98
4/21/04	1.10	1.70	1.11	1.47	1.55	NA	2.17	1.07	1.28	1.68
4/27/04	1.12	1.37	1.29	1.16	1.31	1.16	1.38	1.22	1.27	1.04
5/3/04	1.33	1.39	1.55	1.21	1.43	1.30	1.62	1.19	1.41	1.13
5/9/04	1.75	2.39	1.84	2.39	3.32	2.06	2.96	1.90	2.21	2.67
5/15/04	1.61	1.37	1.04	1.04	1.31	1.04	1.43	1.02	1.20	1.05
5/21/04	1.33	1.42	1.52	2.87	2.13	1.47	3.36	1.22	1.57	2.80
5/27/04	1.16	2.10	1.36	1.59	1.91	1.82	2.04	1.37	1.57	1.77
6/2/04	1.18	1.44	1.15	1.46	1.33	NA	1.65	1.17	1.32	1.27
6/8/04	1.29	3.04	1.86	3.75	2.22	2.81	3.29	1.39	2.15	2.78
6/14/04	1.09	1.48	1.29	1.88	2.09	1.80	2.42	0.98	1.62	2.09
6/20/04	1.36	1.95	1.37	1.71	1.77	1.70	2.13	1.18	1.81	1.49
6/26/04	1.10	NA	1.46	1.35	2.01	1.55	1.83	1.11	1.30	1.47
7/2/04	2.08	NA	2.44	2.85	1.46	NA	2.76	1.63	2.00	2.86
7/8/04	1.66	1.82	1.25	1.38	2.15	NA	1.67	1.46	1.51	1.41
7/14/04	2.53	1.93	1.53	1.56	1.89	2.53	2.00	2.95	1.69	1.65
7/20/04	3.13	6.20	3.51	3.75	4.85	4.99	5.12	2.44	4.55	5.17
7/26/04	2.66	2.47	1.87	1.85	2.32	NA	2.28	2.39	2.03	1.79
8/1/04	2.21	3.17	2.00	2.30	3.01	NA	2.26	2.05	2.68	2.93
8/7/04	1.81	3.00	1.73	1.63	2.51	2.09	1.96	NA	2.19	1.97
8/13/04	1.63	2.21	1.62	1.40	1.88	1.50	1.71	1.49	1.45	1.44
8/19/04	1.00	2.67	NA	4.28	3.51	NA	3.60	1.08	1.55	3.50
8/25/04	1.68	2.85	NA	1.70	1.49	2.19	2.25	1.31	1.25	1.35
8/31/04	1.50	2.31	1.67	1.66	2.16	1.75	2.35	NA	1.68	2.13
9/6/04	1.11	2.34	2.17	2.31	1.77	3.12	3.21	0.97	NA	2.63
9/12/04	2.54	3.28	2.05	2.63	2.75	2.98	3.03	1.94	NA	2.77
9/18/04	1.99	1.38	1.49	1.35	2.09	NA	1.66	1.32	1.54	1.14
9/24/04	1.24	3.52	2.04	2.97	3.39	NA	3.62	0.94	1.79	3.51
9/30/04	1.48	1.71	0.94	1.72	2.22	1.05	1.71	1.30	NA	2.26
10/6/04	1.64	1.66	NA	1.55	2.07	1.75	1.80	1.71	1.53	1.76
10/12/04	1.75	1.78	1.00	1.72	1.62	1.22	1.95	1.54	NA	1.63
10/18/04	NA	1.21	1.16	1.65	1.50	0.95	NA	0.88	1.37	1.61
10/24/04	NA	1.33	1.24	1.40	2.66	1.25	2.16	1.21	NA	1.85
10/30/04	0.88	1.65	0.97	1.53	1.48	NA	2.30	NA	1.41	1.88

11/5/04	1.19	1.37	1.26	1.24	NA	1.41	2.04	1.13	NA	1.49
11/11/04	1.13	1.33	1.26	1.68	2.07	NA	2.41	0.87	NA	1.48
11/17/04	1.33	1.96	1.70	1.91	1.79	1.67	2.93	1.11	2.01	2.35
11/23/04	0.99	1.43	1.18	1.78	1.56	1.67	2.32	0.99	1.45	1.47
11/29/04	1.04	1.91	0.95	1.31	1.48	1.59	2.16	0.98	NA	1.51
12/5/04	1.07	1.41	1.22	1.66	2.14	1.11	2.45	NA	NA	1.64
12/11/04	1.25	1.33	0.91	0.99	1.22	1.35	1.65	1.19	1.49	0.84
12/17/04	1.10	1.39	1.32	1.96	2.20	1.25	NA	NA	1.71	2.05
12/23/04	1.05	1.24	1.31	1.41	1.31	1.06	NA	1.05	1.36	1.35
12/29/04	1.33	2.48	2.35	1.93	2.61	2.12	2.90	1.21	2.82	2.43
1/4/05	1.20	1.46	1.20	1.07	1.26	1.22	1.43	1.04	NA	1.04
1/10/05	1.20	1.44	1.08	1.38	1.79	NA	NA	0.85	1.42	1.61
1/16/05	NA	1.47	0.91	1.08	1.32	NA	1.80	1.18	1.72	1.35
1/22/05	1.11	1.13	1.15	1.55	1.32	1.16	2.06	0.81	1.33	1.35
1/28/05	1.17	1.64	1.13	NA	1.73	1.65	NA	1.15	1.70	1.49
2/3/05	1.24	NA	1.72	NA	NA	2.03	3.55	1.13	2.29	2.82
2/9/05	1.02	1.01	NA	1.17	NA	1.26	1.95	NA	1.42	1.44
2/15/05	1.01	1.32	NA	1.37	1.38	1.59	1.98	NA	NA	1.24
2/21/05	1.23	1.50	NA	NA	1.62	1.59	1.94	NA	NA	1.47
2/27/05	1.36	1.29	1.29	NA	NA	1.38	2.40	NA	NA	1.64

Table 2b. Concentrations for PM$_{2.5}$ levoglucosan in units of ng/m^3 from the 1-in-6 day 24 hour midnight to midnight archived Teflon filter samples analyzed at each of the ten sites where NA = not available and ND = not detected. Date shown as month/day/year.

Date	And	AP	BW	Cinc	ESL	HL	Mech	ML	NB	WP
3/4/04	2.75	21.82	NA	27.90	NA	22.54	42.93	4.30	8.69	71.37
3/10/04	6.38	15.12	6.93	8.50	19.79	32.02	78.31	5.86	3.59	126.39
3/16/04	10.06	5.72	10.35	3.45	NA	9.57	20.64	14.23	1.23	29.21
3/22/04	43.87	4.82	17.99	2.07	31.85	9.36	28.78	26.47	36.91	45.67
3/28/04	4.70	9.11	8.41	43.86	5.12	24.12	74.59	1.85	7.94	86.86
4/3/04	19.20	25.21	12.06	3.84	67.45	12.65	23.53	15.33	NA	24.10
4/9/04	4.46	16.54	12.32	5.38	81.17	11.84	44.84	9.38	13.44	68.28
4/15/04	21.12	6.37	40.27	7.29	13.73	NA	50.96	34.53	11.68	0.37
4/21/04	1.22	6.46	ND	2.40	1.94	NA	20.92	1.13	0.86	34.27
4/27/04	9.09	9.21	1.06	1.19	9.42	4.55	10.15	30.44	0.50	39.49
5/3/04	24.25	7.31	7.15	2.57	14.52	2.63	16.84	8.94	0.83	33.78
5/9/04	10.94	17.96	4.68	12.13	27.62	34.14	22.42	14.68	9.20	39.87
5/15/04	108.45	3.39	ND	ND	13.36	4.14	3.65	4.13	0.85	12.72
5/21/04	6.76	3.16	2.29	6.86	7.59	7.08	15.59	0.66	0.30	27.62
5/27/04	5.65	22.52	3.09	ND	5.46	12.27	10.61	2.35	4.90	11.67
6/2/04	2.95	3.21	1.64	ND	3.83	NA	8.66	ND	ND	18.27
6/8/04	3.69	13.13	6.85	5.27	19.01	7.16	31.45	8.87	1.16	27.87
6/14/04	2.48	4.88	0.24	0.21	9.62	10.34	9.68	6.71	ND	14.66
6/20/04	30.61	73.97	14.34	4.45	7.94	14.81	26.85	6.40	12.37	29.28

6/26/04	15.83	NA	5.04	0.85	58.87	8.79	32.45	48.95	0.59	61.81
7/2/04	11.06	NA	10.25	15.05	ND	NA	26.11	7.03	2.56	30.85
7/8/04	23.93	2.39	ND	ND	26.18	NA	21.55	10.91	0.53	16.46
7/14/04	6.59	2.04	ND	ND	ND	12.84	7.49	36.64	0.32	6.19
7/20/04	9.02	49.27	17.76	16.43	34.81	36.64	53.80	11.08	17.43	63.74
7/26/04	26.61	4.81	9.34	4.11	5.82	NA	14.58	17.80	3.19	22.78
8/1/04	15.80	26.97	7.27	8.00	14.39	NA	54.85	32.35	12.45	117.69
8/7/04	20.32	92.78	10.63	8.91	59.85	36.34	39.16	NA	5.18	69.84
8/13/04	24.66	20.26	5.27	6.41	29.07	17.53	48.63	27.08	0.83	40.50
8/19/04	2.77	9.42	NA	50.60	26.17	NA	24.38	12.75	0.11	26.70
8/25/04	14.32	9.80	NA	ND	ND	6.54	5.99	3.71	ND	8.13
8/31/04	25.45	24.46	5.75	ND	58.83	6.96	21.24	NA	4.53	82.67
9/6/04	2.17	16.82	18.13	11.06	14.38	27.16	41.65	3.38	NA	40.77
9/12/04	35.77	64.71	17.82	26.20	57.67	26.62	48.48	22.32	NA	126.24
9/18/04	31.46	4.76	3.74	ND	28.34	NA	3.52	14.64	6.41	19.33
9/24/04	14.44	24.70	3.54	8.96	41.85	NA	30.80	8.18	1.81	76.36
9/30/04	16.68	37.05	1.49	1.21	22.81	1.69	15.15	5.19	NA	163.04
10/6/04	13.14	14.71	NA	9.89	29.98	3.84	32.12	3.83	1.13	130.07
10/12/04	69.46	19.87	3.72	1.82	17.48	16.62	13.90	14.36	NA	32.21
10/18/04	NA	10.14	11.85	7.09	17.79	24.82	NA	3.45	22.46	141.08
10/24/04	NA	16.07	9.30	1.10	75.20	9.54	48.51	20.02	NA	206.69
10/30/04	8.29	5.86	ND	0.39	10.50	NA	9.38	NA	0.31	13.40
11/5/04	64.78	20.63	7.23	1.49	NA	18.56	23.96	37.83	NA	39.45
11/11/04	87.41	16.05	14.36	21.71	96.11	NA	63.92	18.33	NA	66.87
11/17/04	21.49	52.61	36.01	75.53	49.14	48.13	114.81	30.84	28.39	145.46
11/23/04	23.18	35.40	16.20	73.62	18.07	61.19	101.90	68.40	19.38	95.10
11/29/04	43.19	102.36	12.99	39.96	37.16	79.88	105.21	42.91	NA	172.44
12/5/04	25.79	23.90	28.05	10.94	86.53	15.23	120.92	NA	NA	111.26
12/11/04	73.42	3.75	0.85	0.26	5.25	10.12	9.86	35.11	3.09	24.32
12/17/04	60.65	9.39	23.52	63.90	222.11	25.28	NA	NA	22.43	215.88
12/23/04	25.07	33.68	6.98	4.35	29.20	19.64	NA	28.13	16.52	98.87
12/29/04	59.22	87.28	63.05	9.06	85.41	74.36	73.74	47.01	99.81	145.32
1/4/05	53.88	21.29	15.64	1.28	36.13	6.99	19.43	42.82	NA	25.79
1/10/05	19.32	30.68	10.83	24.04	50.59	NA	NA	28.16	11.53	77.87
1/16/05	NA	80.91	15.10	55.48	40.62	NA	57.73	106.16	39.57	86.26
1/22/05	46.42	10.89	21.36	10.42	19.31	4.83	74.58	21.24	5.94	85.81
1/28/05	34.40	44.29	27.11	NA	97.27	28.86	NA	44.51	42.26	120.71
2/3/05	36.97	NA	20.27	NA	NA	46.22	108.47	32.84	69.30	171.96
2/9/05	16.42	8.54	NA	14.68	NA	5.68	30.90	NA	3.16	40.58
2/15/05	13.23	24.97	NA	4.51	42.90	11.49	29.72	NA	NA	55.89
2/21/05	19.58	28.19	NA	NA	21.99	29.32	41.78	NA	NA	61.34
2/27/05	21.97	8.62	25.42	NA	NA	16.36	91.57	NA	NA	137.34

Table 2c. Concentrations for PM$_{2.5}$ potassium in units of µg/m^3 from the 1-in-6 day 24 hour midnight to midnight archived Teflon filter samples analyzed at each of the ten sites where NA = not available and ND = not detected. Date shown as month/day/year.

Date	And	AP	BW	Cinc	ESL	HL	Mech	ML	NB	WP
3/4/04	0.073	0.102	NA	0.115	NA	0.062	0.026	0.024	0.073	0.046
3/10/04	0.024	0.087	0.098	0.104	0.092	0.041	0.120	0.007	0.052	0.073
3/16/04	0.080	0.063	0.181	0.048	NA	0.010	0.164	0.023	0.022	0.018
3/22/04	0.039	0.020	0.042	0.028	0.087	0.036	0.023	0.021	0.047	0.030
3/28/04	0.014	0.035	0.039	0.079	0.054	0.056	0.053	ND	0.064	0.062
4/3/04	0.051	0.029	0.044	0.053	0.081	0.004	0.053	0.011	NA	0.071
4/9/04	0.037	0.058	0.053	0.082	0.072	0.031	0.063	0.018	0.030	0.031
4/15/04	0.116	0.032	0.067	0.061	0.094	NA	0.089	0.044	0.083	0.081
4/21/04	0.017	0.050	0.046	0.045	0.155	NA	0.071	0.040	0.018	0.041
4/27/04	0.027	0.029	0.064	0.039	0.073	0.012	0.009	0.020	0.013	0.048
5/3/04	0.035	0.033	0.127	0.035	0.094	0.067	0.030	0.012	0.011	0.069
5/9/04	0.060	0.106	0.064	0.103	0.133	0.055	0.036	0.049	0.120	0.062
5/15/04	0.114	0.024	0.043	0.012	0.059	0.008	0.001	0.005	0.032	0.007
5/21/04	0.025	0.033	0.056	0.098	0.112	0.006	0.062	0.009	0.044	0.046
5/27/04	0.016	0.064	0.059	0.059	0.083	0.024	0.067	0.003	0.032	0.064
6/2/04	0.063	0.020	0.044	0.041	0.046	NA	0.034	0.001	0.014	0.042
6/8/04	0.019	0.227	0.146	0.521	0.207	0.138	0.352	0.010	0.194	0.182
6/14/04	0.029	0.037	0.032	0.111	0.071	0.020	0.081	ND	0.074	0.048
6/20/04	0.052	0.054	0.055	0.069	0.045	0.016	0.030	0.003	0.113	0.059
6/26/04	0.060	NA	0.038	0.037	0.549	0.017	0.025	0.015	0.016	0.153
7/2/04	0.180	NA	0.174	0.419	0.066	NA	0.046	0.021	0.024	0.221
7/8/04	0.097	0.061	0.039	0.128	0.091	NA	0.009	0.009	0.010	0.062
7/14/04	0.040	0.017	0.048	0.058	0.037	0.068	0.094	0.037	0.018	0.076
7/20/04	0.160	0.139	0.094	0.136	0.123	0.073	0.074	0.019	0.122	0.166
7/26/04	0.094	0.042	0.051	0.055	0.097	NA	0.014	0.028	0.026	0.034
8/1/04	0.063	0.058	0.077	0.081	0.121	NA	0.039	0.028	0.093	0.269
8/7/04	0.047	0.058	0.039	0.042	0.113	0.002	0.038	NA	0.090	0.081
8/13/04	0.045	0.024	0.053	0.037	0.053	0.009	0.099	0.005	0.029	0.086
8/19/04	0.009	0.024	NA	0.364	0.123	NA	0.075	ND	0.085	0.152
8/25/04	0.061	0.065	NA	0.107	0.058	0.069	0.015	0.014	0.103	0.036
8/31/04	0.029	0.030	0.039	0.068	0.071	0.048	0.025	NA	0.051	0.033
9/6/04	0.009	0.063	0.053	0.075	0.045	0.104	0.077	0.004	NA	0.059
9/12/04	0.131	0.106	0.055	0.101	0.116	0.060	0.047	0.038	NA	0.073
9/18/04	0.092	0.018	0.101	0.039	0.082	NA	0.020	0.008	0.060	0.028
9/24/04	0.015	0.136	0.088	0.180	0.160	NA	0.045	ND	0.059	0.127
9/30/04	0.012	0.051	0.010	0.059	0.052	0.014	0.053	0.006	NA	0.100
10/6/04	0.046	0.051	NA	0.048	0.072	0.023	0.024	0.040	0.024	0.139
10/12/04	0.158	0.084	0.039	0.055	0.070	0.013	0.014	0.032	NA	0.033
10/18/04	NA	0.049	0.459	0.058	0.037	ND	NA	ND	0.040	0.051
10/24/04	NA	0.011	0.035	0.033	0.068	0.007	0.099	ND	NA	0.118
10/30/04	0.003	0.029	0.022	0.047	0.036	NA	0.162	NA	0.007	0.299

11/5/04	0.043	0.054	0.100	0.043	NA	0.043	0.096	0.020	NA	0.173
11/11/04	0.027	0.025	0.059	0.111	0.115	NA	0.047	0.002	NA	0.112
11/17/04	0.045	0.117	0.079	0.116	0.040	0.049	0.094	0.020	0.092	0.186
11/23/04	0.010	0.066	0.055	0.090	0.035	0.070	0.051	0.010	0.043	0.123
11/29/04	0.045	0.058	0.034	0.055	0.048	0.020	0.041	0.014	NA	0.152
12/5/04	0.021	0.112	0.063	0.051	0.055	ND	0.047	NA	NA	0.089
12/11/04	0.038	0.071	0.021	0.028	0.017	0.040	0.051	0.011	0.040	0.011
12/17/04	0.027	0.057	0.053	0.146	0.108	0.008	NA	NA	0.048	0.115
12/23/04	0.030	0.011	0.069	0.123	0.043	ND	NA	0.019	0.033	0.094
12/29/04	0.060	0.152	0.099	0.084	0.093	0.057	0.057	0.046	0.176	0.113
1/4/05	0.041	0.062	0.053	0.043	0.052	0.011	0.026	0.025	NA	0.022
1/10/05	0.044	0.067	0.050	0.118	0.054	NA	NA	0.020	0.021	0.042
1/16/05	NA	0.035	0.032	0.044	0.031	NA	0.042	0.044	0.042	0.059
1/22/05	0.028	0.030	0.058	0.110	0.035	0.005	0.089	0.012	0.024	0.049
1/28/05	0.061	0.066	0.046	NA	0.077	0.029	NA	0.052	0.175	0.066
2/3/05	0.061	NA	0.114	NA	NA	0.091	0.086	0.009	0.125	0.144
2/9/05	0.041	0.018	NA	0.070	NA	0.023	0.033	NA	0.011	0.024
2/15/05	0.038	0.057	NA	0.051	0.028	0.035	0.047	NA	NA	0.143
2/21/05	0.050	0.036	NA	NA	0.049	0.031	0.017	NA	NA	0.107
2/27/05	0.099	0.014	0.058	NA	NA	0.022	0.046	NA	NA	0.066

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

3.1.1. Overview

For clarity all the time series will be presented as two figures, each one containing data for 5 sites. One figure will contain the data for AP, Cinc, HL, Mech, and WP, the five more eastern sites, and the second figure will contain the data for And, BW, ESL, ML, and NB. Also throughout the text when referring to summer vs. winter, summer is meant to focus on the data from May through September and winter from November through February.

Figure 3 shows the time series for WSOC for all 10 sites. The WSOC concentration was generally greater than 1 µg C/m^3 and was elevated in the summer. It also appears that the WSOC had a large regional component since the concentrations appear to rise and fall together. There are of course some exceptions to this. These exceptions generally occurred for the two sites in MN, which also often times had the lowest WSOC concentrations. At times the two MN sites themselves had similar air transport patterns, but differed from the other 8 sites. An example of this occurred on June 8, 2004. This is illustrated in Figure 4, which shows the 72 hour back trajectory analysis ending on June 8 from using the NOAA ARL (National Oceanic and Atmospheric Administration Air Resources Laboratory) HYSPLIT trajectory model [*Draxler and Rolph*, 2003; *Rolph*, 2003] at all sites.

The time series for the levoglucosan concentrations at all 10 sites are shown in Figure 5. The first thing to notice is the increase in levoglucosan concentration at all sites starting around November. 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. As seen in Table 3, the levoglucosan becomes somewhat more correlated with both potassium and WSOC across several sites in the winter than summer.

During the summer, the levoglucosan is more likely to originate from wildfires or prescribed burning. Based on the NOAA Satellite Fire Detections viewer (http://map.ngdc.noaa.gov/website/firedetects/viewer.htm) there were wildfires burning in Alaska from June through September 2004 and some smaller ones in central Canada from the end of September through October 2004 that periodically impacted the sites included in this study.
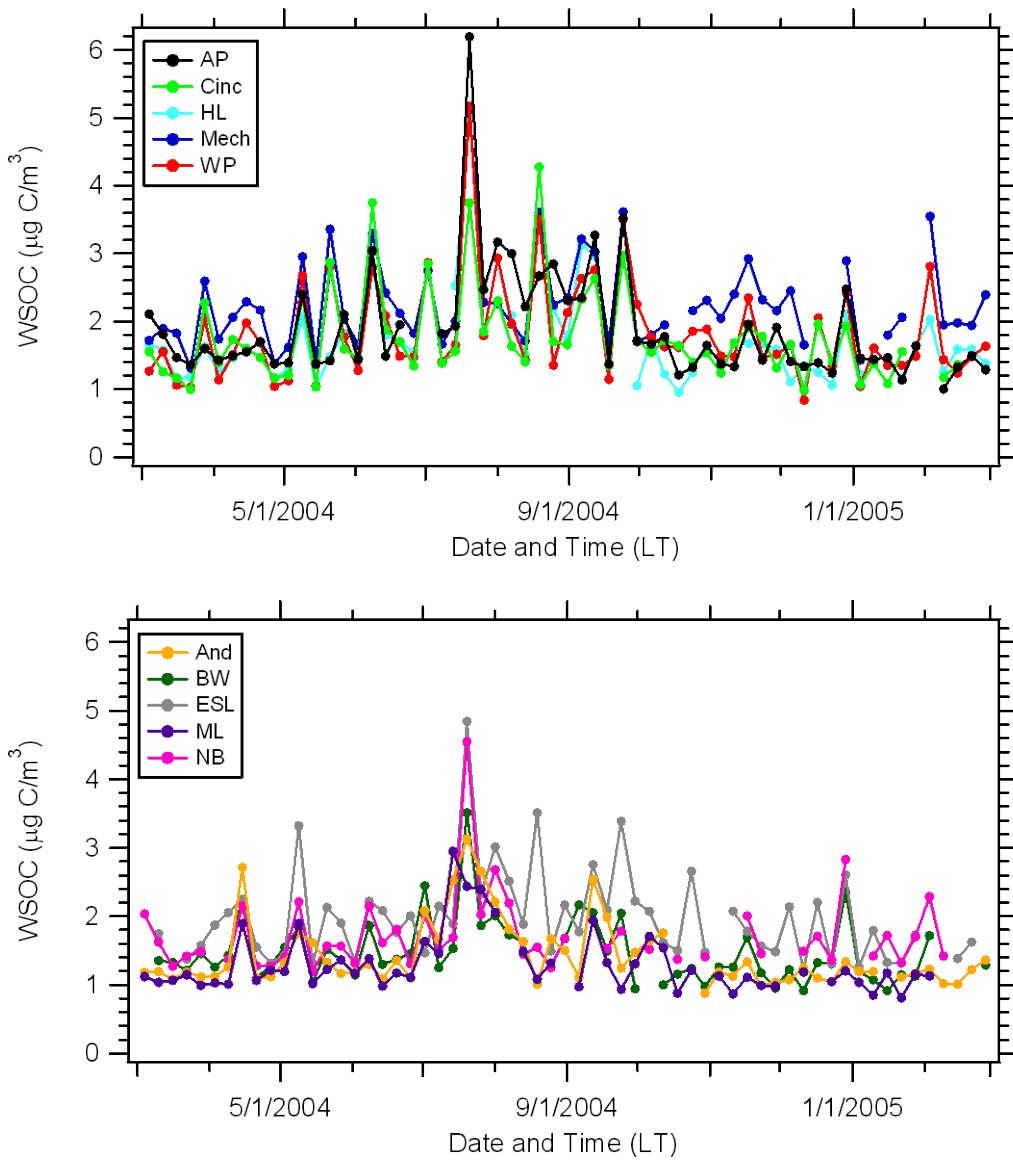
Figure 3. Time series for PM$_{2.5}$ WSOC for all 10 sites. For clarity the data have been graphed as 5 sites per figure.

Focusing first on the period from June through September, in Figure 5 periodic peaks in the levoglucosan concentration can be seen. However, it can also be seen that these peaks in the levoglucosan are not always observed at every site when they happen.
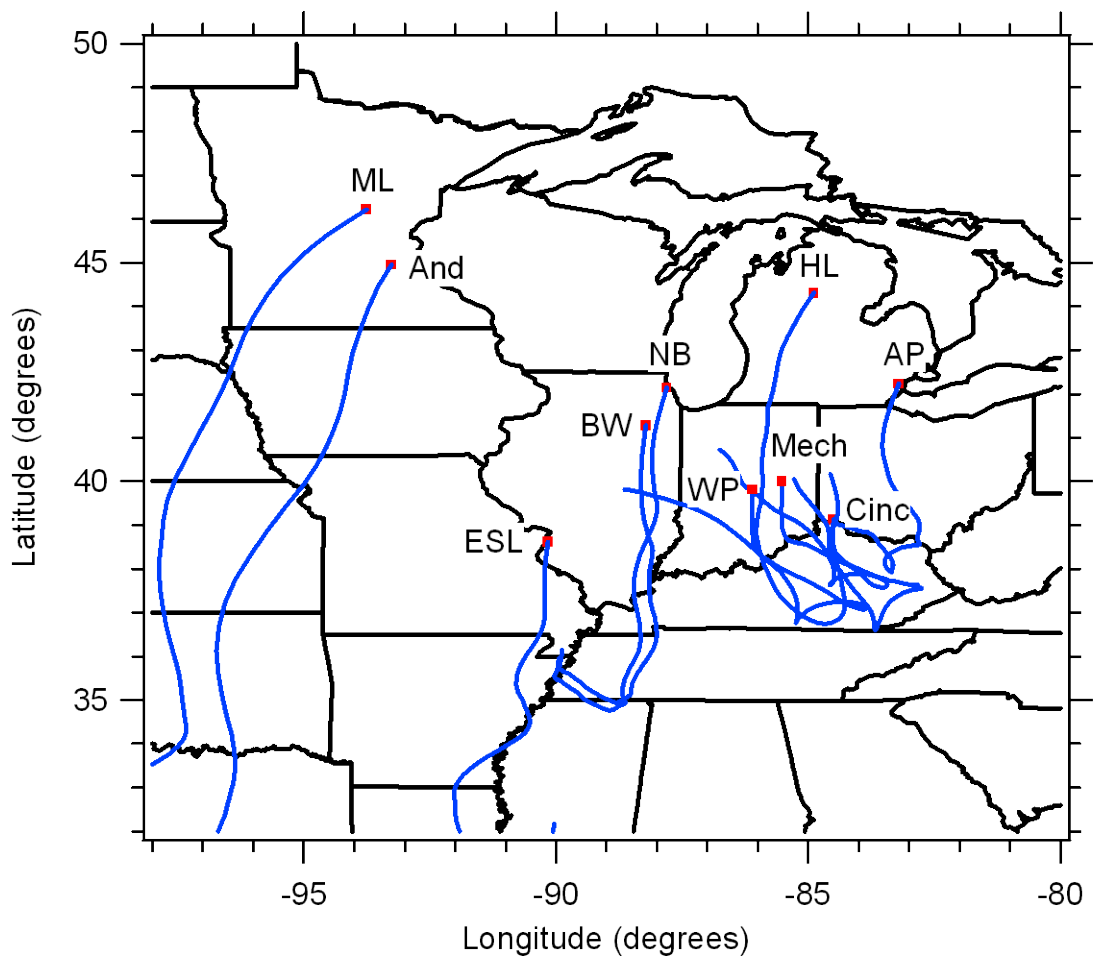
Figure 4. Characteristic 72 hour air mass back trajectories ending on June 8, 2004 for each of the sites. All back trajectories are based on the NOAA ARL HYSPLIT trajectory model.

From the WSOC data (Figure 3) and back trajectory analysis we know that generally all the sites are influenced by similar air masses. Since the emissions from these fires are being transported long distances, in order for the site to see evidence from the burning not only does the (horizontal) location of the transport for the air mass need to be right, but the air mass also needs to come from aloft. An example of this occurred on June 26, 2004. The back trajectories for ESL, HL, and WP were all similar on this day, yet the
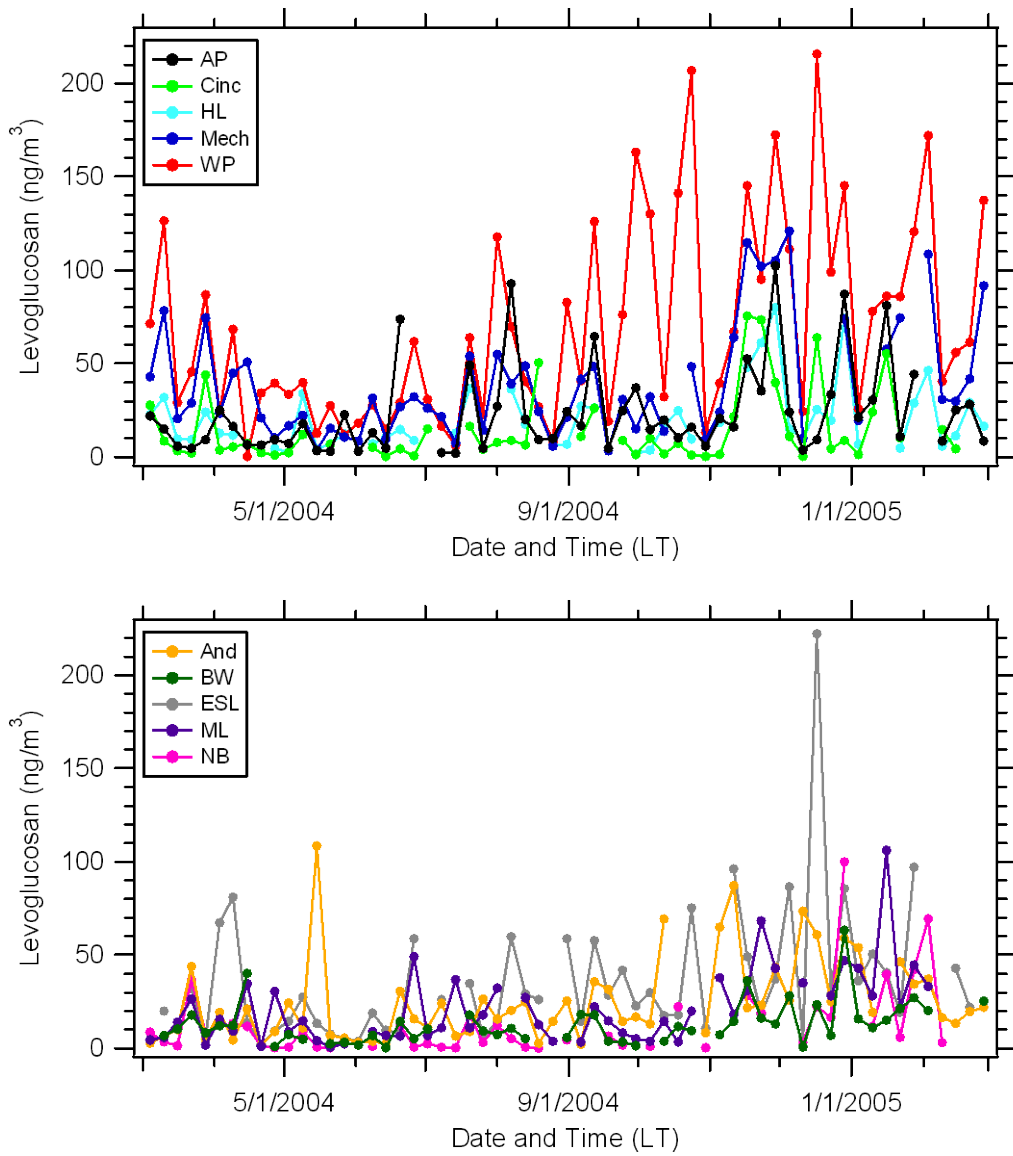
Figure 5. Time series for PM$_{2.5}$ levoglucosan for all 10 sites. For clarity the data have been graphed as 5 sites per figure.

levoglucosan only increases at ESL and WP. It turns out that only the air masses

transported to ESL and WP come from above 2 km (see Figure 6).

Table 3. Correlation coefficients for the relationship between levoglucosan, WSOC, and potassium at all of the sites in summer and winter. Summer includes data from May through September and winter includes data from November through February. The levoglucosan vs. WSOC correlation is on a carbon mass basis (i.e., the units of levoglucosan have been converted from $\mu g/m^3$ to $\mu g\ C/m^3$) and its fit has been forced through zero.

| Site	Summer Levoglucosan vs. WSOC	Summer Potassium vs. WSOC	Summer Potassium vs. Levoglucosan	Winter Levoglucosan vs. WSOC	Winter Potassium vs. WSOC	Winter Potassium vs. Levoglucosan
And	0	0.49	0.13	0.03	0.49	0.03
AP	0.22	0.40	0.06	0.60	0.61	0.17
BW	0.37	0.26	0.04	0.50	0.63	0.20
Cinc	0.37	0.58	0.19	0.16	0.48	0.16
ESL	0.10	0.03	0.21	0.31	0.62	0.65
HL	0.39	0.37	0.01	0.31	0.64	0.25
Mech	0.22	0.11	0.04	0.44	0.31	0.09
ML	0.19	0.56	0.20	0.19	0.31	0.27
NB	0.43	0.24	0.24	0.89	0.63	0.71
WP	0.11	0.34	0.13	0.51	0.30	0.20
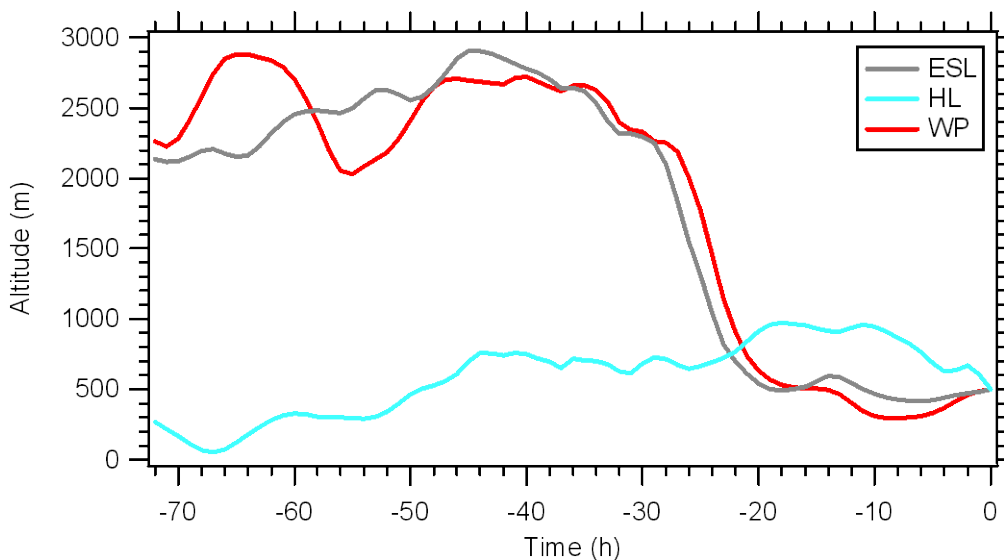
Figure 6. The altitude profiles from the 72 hour air mass back trajectory analysis ending on June 26, 2004 for ESL, HL, and WP. The back trajectories were calculated using the NOAA ARL HYSPLIT trajectory model.

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For the period from the end of the September through October, with the exception of WP, this same pattern is observed where only the sites with the right conditions for long-range transport observe an increase in levoglucosan. The increases in levoglucosan are not as large during this time as for the other period except at WP, which has considerably higher concentrations of levoglucosan than the other sites. The higher levoglucosan at WP during this time may be due to a local source of burning, such as clearing of agriculture fields.

Potassium is considered to be a good inorganic marker for biomass burning. However, unlike levoglucosan as can be seen in Figure 7 there is no seasonal pattern observed at any of the sites for potassium, suggesting for this data set potassium is not as useful of a biomass burning marker. There are times during the summer when the potassium appears to increase at almost all the sites. But if these potassium increases are compared to the WSOC data in Figure 3, it can be seen that these potassium increases also happen when the WSOC increases at almost every site. However, no subsequent increase in levoglucosan is observed at these times. Therefore, it is suspected that the peaks in the potassium concentration are not likely related to biomass burning, but rather regional pollution events. In addition, as can be seen in Table 3, potassium and levoglucosan are not correlated in the summer at any site. It is possible this could be because levoglucosan is destroyed during aerosol aging in long-range transport events. In the winter at times potassium can be somewhat correlated with levoglucosan and generally there is a bit more of a correlation between potassium and WSOC during this time as well. This is likely due to the increase in local biomass burning in the winter and decrease of secondary organic aerosol formation.
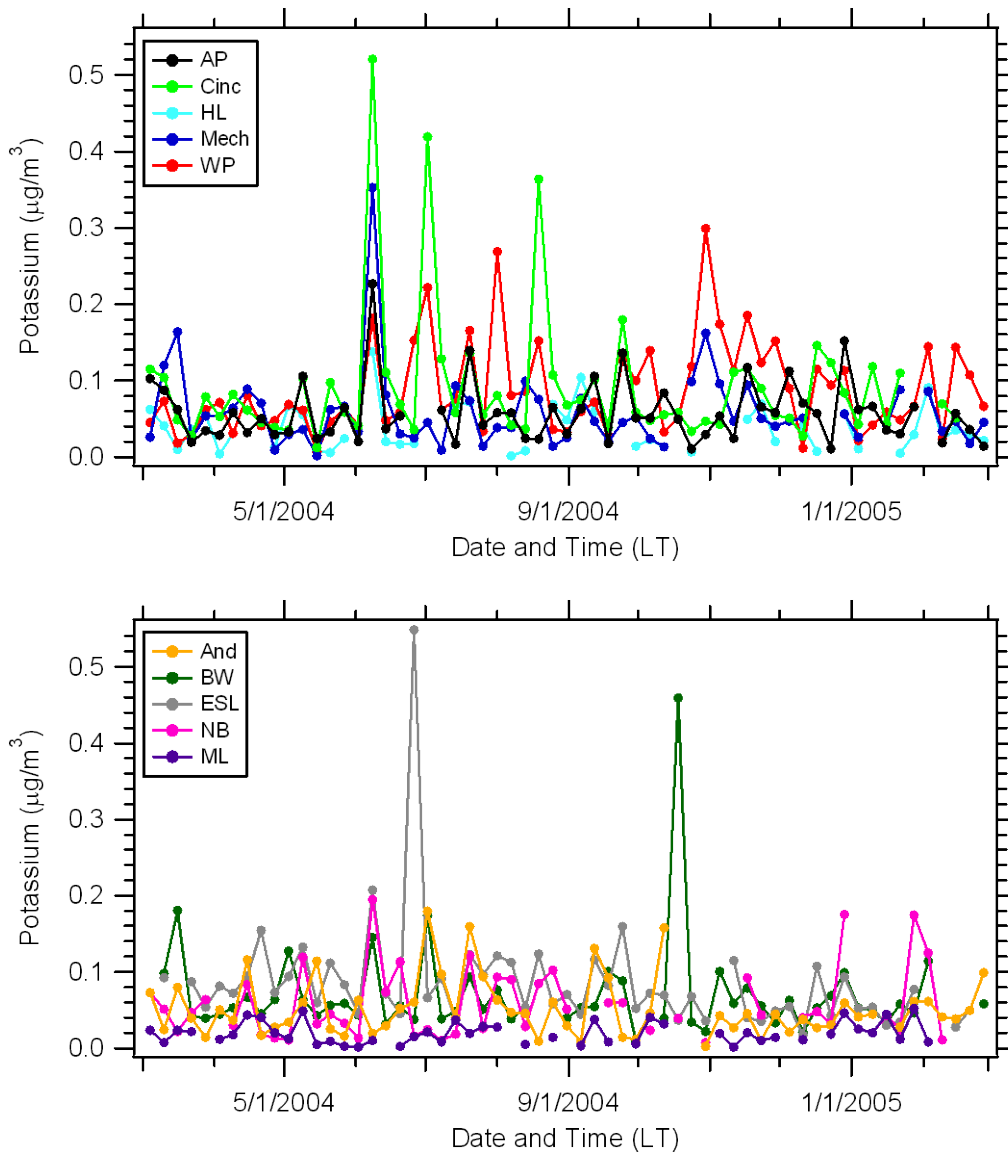
Figure 7. Time series for PM$_{2.5}$ potassium for all 10 sites. For clarity the data have been graphed as 5 sites per figure.

3.1.2. Urban vs. Rural Sites

In this data set there are 3 urban/rural pairs which can be compared. These pairs include: WP and Mech, AP and HL, and And and ML. For all of these pairs the

potassium is higher at the urban site than the rural site. This is likely due to the fact that in addition to being an inorganic marker for biomass burning, potassium can come from incinerators and fly ash, which are sources more likely to be found in urban areas.

As previously discussed the levoglucosan concentration in summer is more dependent on long-range transport and therefore is independent of whether the site is rural or urban. However, during the winter the levoglucosan is generally slightly higher at the urban sites than the rural sites for all three pairs. Based on population differences between an urban and rural site, this would be expected.

For WSOC the concentrations are quite similar during the entire year for both the urban and rural site at the pairs of AP/HL and And/ML. However, in winter for the pair of WP and Mech, the concentrations are higher at the rural site. This might be due to the fact that the WP and Mech pair is the only set where the rural site is downwind of the urban site. This is important for WSOC because the fraction of the organic aerosol that is water-soluble is the more processed or aged fraction. Therefore if the rural site is downwind of the urban site it would be sampling air masses containing processed urban emissions.

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

The contribution of $PM_{2.5}$ OC due to primary biomass burning particle emissions 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

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

For the levoglucosan/OC ratio of the sample, the levoglucosan value used comes from our measurement made off of the Teflon filters. However, as previously mentioned OC was not measured off of these same filters because the OC measurement can not be made off of a Teflon filter. It turns out, however, that all but 3 of the sampling sites (BW, ESL, and HL) are co-located STN (Speciation Trends Network) sites. The STN network routinely collects a quartz filter sample to determine the $PM_{2.5}$ OC concentration. The OC is analyzed from the quartz filter samples using thermal-optical transmittance (TOT). Figure 8 shows the time series for the available STN OC data for our sites. As with the WSOC, the OC appears to have a large regional component, again with the two sites in MN (And and ML) being the exception at times.

The ratio of WSOC/OC can be calculated by combining our WSOC data with the STN OC data and is shown in Figure 9. Interestingly, the WSOC/OC ratio is fairly constant all year long. For almost all of the sites, the WSOC/OC ratio is approximately 0.5 µg C/µg C. Only during the summer at the rural site of Mech is the average ratio generally higher, being approximately 0.75 µg C/µg C. Therefore, if OC data are not available for a site (i.e., BW, ESL, and HL), a WSOC/OC ratio of 0.5 µg C/µg C will be assumed in the calculation for determining the contribution of organic carbon due to primary biomass burning emissions.

For the levoglucosan/OC ratio from a source profile, as previously mentioned, the sources of biomass burning are different in the summer and winter and therefore two different sets of source profiles are needed. For the winter data, the source profiles come
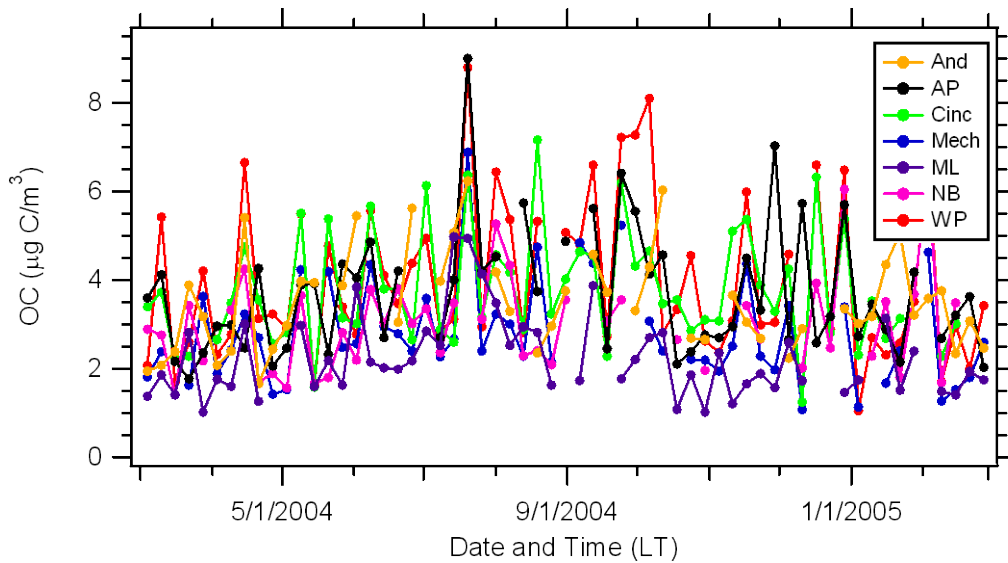
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Figure 8. Time series for STN PM$_{2.5}$ OC for the 7 FRM sites co-located with STN sites.
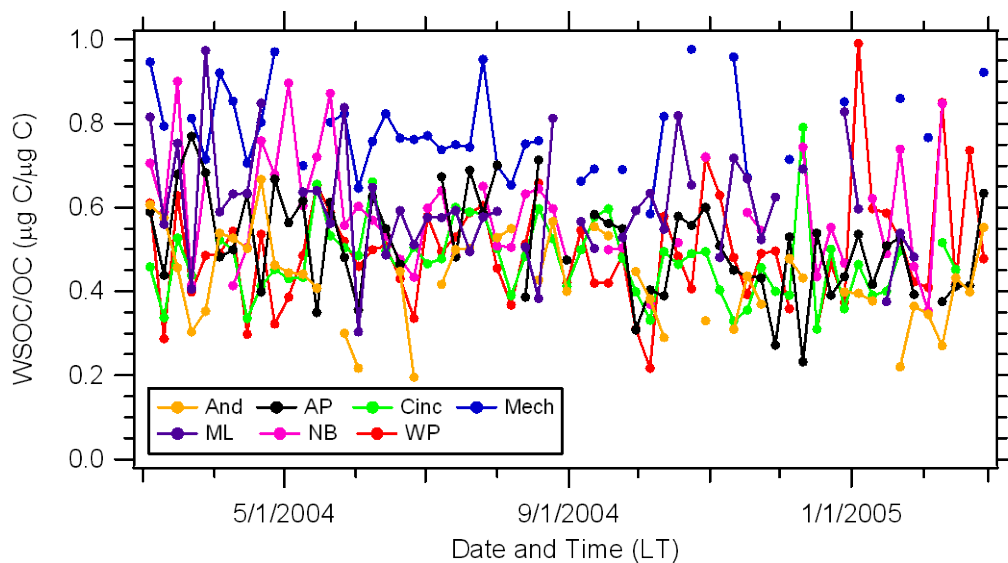

Figure 9. Time series for the WSOC/OC ratio for the 7 FRM sites co-located with STN sites. The WSOC was determined from the FRM Teflon filters and the OC was determined from the STN quartz filters.

from the work of *Fine et al.* [2004]. In this work, the emissions of fireplace combustion

for 10 different woods from the Western and Midwestern U.S. were examined. The

average levoglucosan/OC ratio determined, 0.071 µg C/µg C, will be used.

For the summer data, the source profiles come from the work of *Sullivan et al.*

[2008]. *Sullivan et al.* [2008] 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 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, 3.34 and 3.73 min, in the chromatogram has been observed based

on the fuel component being burned.   (Note, the retention times have been updated for

using a PA-1 column, the *Sullivan et al.* [2008] reference was using a PA-10 column.)

The lines in Figure 10 represent the best fits to the response ratios observed in the source

samples. The source profile data appear to create bounds that can then be used to

determine the fuel component involved in the burn. As can be seen in Figure 10, the

ambient data appear to fall on these lines, allowing for the most appropriate source

profile for each sample to be chosen. For the majority of the data the average

levoglucosan/OC ratio for the combustion of leaves (0.023 µg C/µg C) was used.

The time series for the contribution of $PM_{2.5}$ OC due to biomass burning for all of

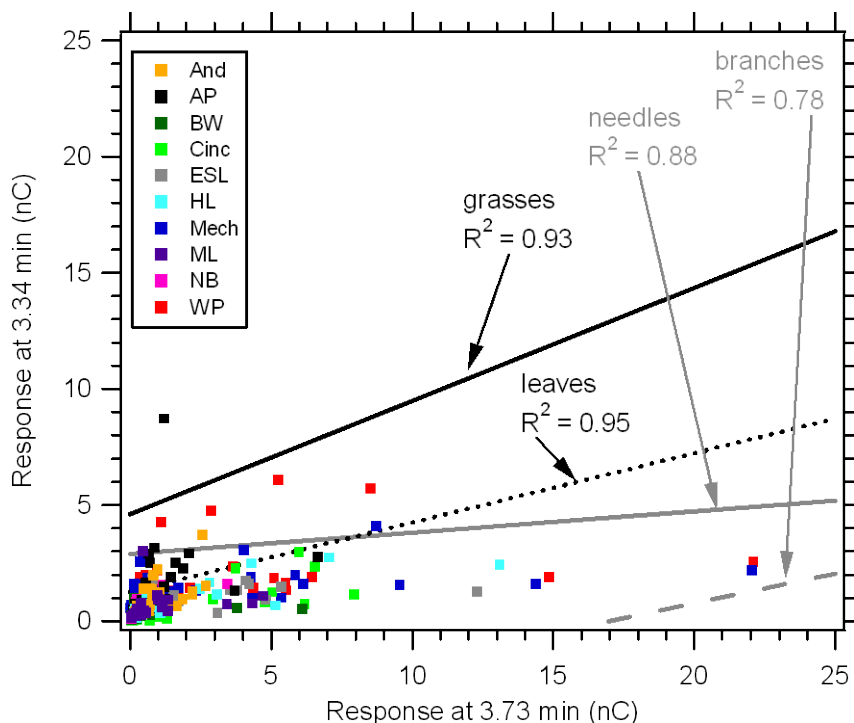the sites is shown in Figure 11. These data are available in Table 4 and the concentration

Figure 10. Correlation between the peak response at 3.34 min and 3.73 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 ten sites.

of OC due to biomass burning is in Table 5. 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 not quantified. This would be more of a factor in summer since during this time there is more potential for the aging of transported emissions from wildfires and prescribed fires and there is greater photochemical activity.

Overall, the contribution from biomass burning is highest in Mech and WP. On average the contribution from biomass burning at these two sites is about 15%, with peaks often up to 30 to 35% and a high of 90% on October 24, 2004 at WP. For And,
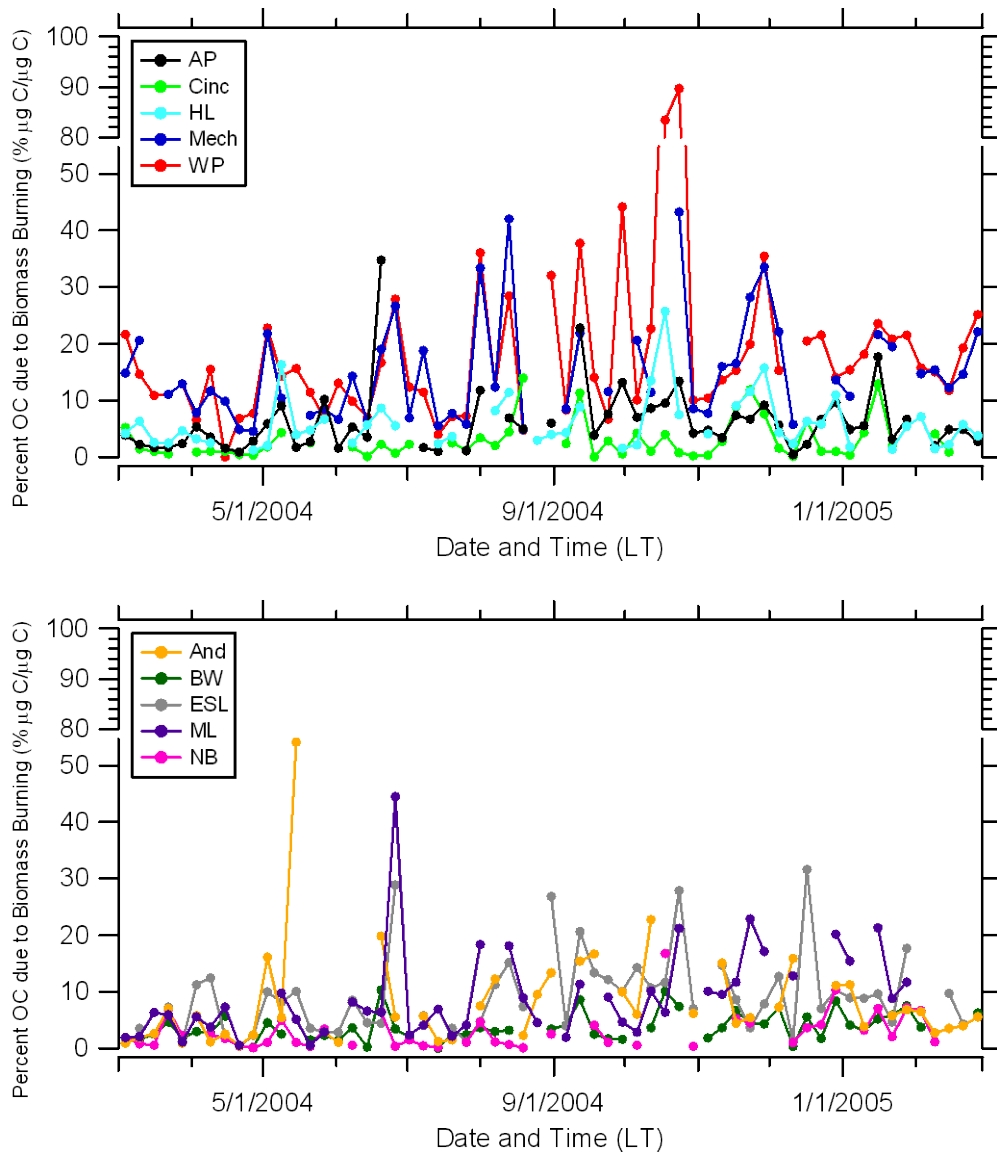
Figure 11. Time series for the percentage of PM$_{2.5}$ OC due to primary biomass burning particle emissions for all 10 sites. For clarity the data have been graphed as 5 sites per figure.

AP, ESL, HL, and ML the contribution from biomass burning is generally less than 10%.

Not surprisingly considering the generally low concentrations of levoglucosan at BW,

NB, and Cinc, the biomass burning contribution is quite low at these sites being generally

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Table 4. Percentage of PM$_{2.5}$ OC due to biomass burning primary particle emissions from the 1-in-6 day 24 hour midnight to midnight archived Teflon filter samples analyzed at each of the ten sites where NA = not available. Date shown as month/day/year.

Date	And	AP	BW	Cinc	ESL	HL	Mech	ML	NB	WP
3/4/04	0.9	4	NA	5	NA	4	15	2	2	22
3/10/04	2	2	2	1	4	6	21	2	0.8	15
3/16/04	3	2	2	1	NA	3	NA	6	0.5	11
3/22/04	7	2	5	0.6	7	2	11	6	7	11
3/28/04	0.9	2	2	NA	1	5	13	1	2	13
4/3/04	6	5	3	0.9	11	3	8	6	NA	7
4/9/04	1	3	3	1	12	3	12	4	3	15
4/15/04	2	2	6	1	2	NA	10	7	2	0.1
4/21/04	0.5	1	NA	0.4	0.4	NA	5	0.6	0.3	7
4/27/04	2	3	0.3	0.3	2	1	4	NA	0.2	8
5/3/04	16	6	5	2	10	2	22	NA	1	23
5/9/04	5	9	3	4	8	16	10	10	5	14
5/15/04	54	2	NA	NA	10	4	NA	5	1	16
5/21/04	NA	3	1	3	4	5	7	0.6	0.3	11
5/27/04	3	10	2	NA	3	7	8	3	3	7
6/2/04	1	2	1	NA	3	NA	7	NA	NA	13
6/8/04	NA	5	4	2	8	3	14	8	0.6	10
6/14/04	NA	4	0.2	0.1	5	6	7	7	NA	7
6/20/04	20	35	10	2	4	9	19	6	6	17
6/26/04	6	NA	3	0.6	29	6	27	45	0.4	28
7/2/04	NA	NA	2	2	NA	NA	7	2	2	12
7/8/04	6	2	NA	NA	6	NA	19	4	0.4	11
7/14/04	1	1	NA	NA	NA	2	6	7	0.2	4
7/20/04	1	NA	2	3	4	4	8	2	NA	7
7/26/04	NA	1	2	1	1	NA	6	4	1	7
8/1/04	7	12	4	3	5	NA	33	18	5	36
8/7/04	12	NA	3	2	11	8	12	NA	1	12
8/13/04	NA	7	3	4	15	12	42	18	0.7	28
8/19/04	2	5	NA	14	7	NA	5	9	0.1	5
8/25/04	10	NA	NA	NA	NA	3	NA	5	NA	NA
8/31/04	13	6	3	NA	27	4	NA	NA	3	32
9/6/04	NA	NA	4	2	4	4	8	2	NA	8
9/12/04	15	23	9	11	21	9	22	11	NA	38
9/18/04	17	4	2	NA	13	NA	NA	NA	4	14
9/24/04	NA	8	2	3	12	NA	12	9	1	6
9/30/04	10	13	2	0.6	10	2	NA	5	NA	44
10/6/04	6	7	NA	4	14	2	21	3	0.5	10
10/12/04	23	9	4	1	11	13	11	10	NA	23
10/18/04	NA	10	10	4	12	26	NA	6	17	83
10/24/04	NA	13	7	0.8	28	8	43	21	NA	90
10/30/04	6	4	NA	0.2	7	NA	8	NA	0.3	10

Date	And	AP	BW	Cinc	ESL	HL	Mech	ML	NB	WP
11/5/04	NA	5	2	0.3	NA	4	8	10	NA	10
11/11/04	15	3	4	3	15	NA	16	10	NA	14
11/17/04	4	7	7	9	9	9	17	12	5	15
11/23/04	5	7	4	12	4	12	28	23	5	20
11/29/04	NA	9	4	8	8	16	34	17	NA	36
12/5/04	7	6	7	2	13	4	22	NA	NA	15
12/11/04	16	0.4	0.3	0.1	1	2	6	13	1	NA
12/17/04	NA	2	6	6	32	6	NA	NA	4	21
12/23/04	NA	7	2	1	7	6	NA	NA	4	22
12/29/04	11	10	8	1	10	11	14	20	10	14
1/4/05	11	5	4	0.4	9	2	11	15	NA	15
1/10/05	4	6	3	4	9	NA	NA	NA	3	18
1/16/05	NA	18	5	13	10	NA	22	21	7	24
1/22/05	6	3	6	2	5	1	20	9	2	21
1/28/05	7	7	8	NA	18	5	NA	12	7	22
2/3/05	6	NA	4	NA	NA	7	15	NA	7	16
2/9/05	3	2	NA	4	NA	1	15	NA	1	15
2/15/05	4	5	NA	0.9	10	2	12	NA	NA	12
2/21/05	4	5	NA	NA	4	6	15	NA	NA	19
2/27/05	6	3	6	NA	NA	4	22	NA	NA	25

Table 5. Concentration of $PM_{2.5}$ OC due to biomass burning primary particle emissions in units of µg C/m^3 from the 1-in-6 day 24 hour midnight to midnight archived Teflon filter samples analyzed at each of the ten sites where NA = not available. Date shown as month/day/year.

Date	And	AP	BW	Cinc	ESL	HL	Mech	ML	NB	WP
3/4/04	0.02	0.14	NA	0.18	NA	0.14	0.27	0.03	0.05	0.45
3/10/04	0.04	0.09	0.04	0.05	0.12	0.20	0.49	0.04	0.02	0.79
3/16/04	0.06	0.04	0.07	0.02	NA	0.06	NA	0.09	0.01	0.18
3/22/04	0.28	0.03	0.11	0.01	0.20	0.06	0.18	0.17	0.23	0.29
3/28/04	0.03	0.06	0.05	NA	0.03	0.15	0.47	0.01	0.05	0.55
4/3/04	0.12	0.16	0.08	0.02	0.42	0.08	0.15	0.10	NA	0.15
4/9/04	0.03	0.10	0.08	0.03	0.51	0.07	0.28	0.06	0.08	0.43
4/15/04	0.13	0.04	0.25	0.05	0.09	NA	0.32	0.22	0.07	0.01
4/21/04	0.01	0.04	NA	0.02	0.01	NA	0.13	0.01	0.01	0.22
4/27/04	0.06	0.06	0.01	0.01	0.06	0.03	0.06	NA	0.01	0.25
5/3/04	0.48	0.14	0.14	0.05	0.29	0.05	0.33	NA	0.02	0.67
5/9/04	0.22	0.35	0.09	0.024	0.55	0.67	0.44	0.29	0.18	0.79
5/15/04	2.14	0.07	NA	NA	0.26	0.08	NA	0.08	0.02	0.25
5/21/04	NA	0.06	0.05	0.14	0.15	0.14	0.31	0.01	0.01	0.55
5/27/04	0.11	0.44	0.06	NA	0.11	0.24	0.21	0.05	0.10	0.23
6/2/04	0.06	0.06	0.03	NA	0.08	NA	0.17	NA	NA	0.36
6/8/04	NA	0.26	0.14	0.10	0.38	0.14	0.62	0.18	0.02	0.55
6/14/04	NA	0.10	0.01	0.01	0.19	0.20	0.19	0.13	NA	0.29

6/20/04	0.60	1.46	0.28	0.09	0.16	0.29	0.53	0.13	0.24	0.58
6/26/04	0.31	NA	0.10	0.02	1.16	0.17	0.64	0.97	0.01	1.22
7/2/04	NA	NA	0.10	0.14	NA	NA	0.25	0.07	0.05	0.61
7/8/04	0.23	0.05	NA	NA	0.25	NA	0.43	0.10	0.01	0.33
7/14/04	0.06	0.04	NA	NA	NA	0.12	0.15	0.35	0.01	0.12
7/20/04	0.09	NA	0.17	0.16	0.50	0.36	0.53	0.11	NA	0.63
7/26/04	NA	0.05	0.09	0.04	0.05	NA	0.14	0.17	0.03	0.22
8/1/04	0.31	0.53	0.14	0.16	0.28	NA	1.08	0.64	0.25	2.32
8/7/04	0.40	NA	0.10	0.08	0.57	0.34	0.37	NA	0.05	0.66
8/13/04	NA	0.40	0.10	0.13	0.57	0.35	0.96	0.53	0.02	0.80
8/19/04	0.05	0.19	NA	1.00	0.52	NA	0.23	0.25	0.01	0.25
8/25/04	0.28	NA	NA	NA	NA	0.13	NA	0.07	NA	NA
8/31/04	0.50	0.29	0.11	NA	1.16	0.14	NA	NA	0.09	1.63
9/6/04	NA	NA	0.18	0.11	0.21	0.27	0.41	0.03	NA	0.40
9/12/04	0.71	1.28	0.35	0.52	1.14	0.53	0.96	0.44	NA	2.49
9/18/04	0.62	0.09	0.07	NA	0.56	NA	NA	NA	0.13	0.38
9/24/04	NA	0.49	0.07	0.18	0.83	NA	0.61	0.16	0.04	0.48
9/30/04	0.33	0.73	0.03	0.02	0.45	0.03	NA	0.10	NA	3.22
10/6/04	0.26	0.29	NA	0.20	0.59	0.08	0.63	0.08	0.02	0.82
10/12/04	1.37	0.39	0.07	0.04	0.35	0.33	0.27	0.28	NA	0.64
10/18/04	NA	0.20	0.23	0.14	0.35	0.49	NA	0.07	0.44	2.79
10/24/04	NA	0.32	0.18	0.02	1.49	0.19	0.96	0.40	NA	4.08
10/30/04	0.16	0.12	NA	0.01	0.21	NA	0.19	NA	0.01	0.26
11/5/04	NA	0.13	0.05	0.01	NA	0.12	0.15	0.24	NA	0.25
11/11/04	0.55	0.10	0.09	0.14	0.60	NA	0.40	0.12	NA	0.42
11/17/04	0.13	0.33	0.23	0.47	0.31	0.30	0.72	0.19	0.18	0.91
11/23/04	0.15	0.22	0.10	0.46	0.11	0.38	0.64	0.43	0.12	0.60
11/29/04	NA	0.64	0.08	0.25	0.23	0.50	0.66	0.27	NA	1.08
12/5/04	0.16	0.15	0.18	0.07	0.54	0.10	0.76	NA	NA	0.70
12/11/04	0.46	0.02	0.01	0.01	0.03	0.06	0.06	0.22	0.02	NA
12/17/04	NA	0.06	0.15	0.40	1.40	0.16	NA	NA	0.14	1.36
12/23/04	NA	0.21	0.04	0.03	0.18	0.12	NA	NA	0.10	0.62
12/29/04	0.37	0.55	0.40	0.06	0.54	0.47	0.46	0.30	0.63	0.91
1/4/05	0.34	0.13	0.10	0.01	0.23	0.04	0.12	0.27	NA	0.16
1/10/05	0.12	0.19	0.07	0.15	0.32	NA	NA	NA	0.07	0.49
1/16/05	NA	0.51	0.09	0.35	0.26	NA	0.36	0.67	0.25	0.54
1/22/05	0.29	0.07	0.13	0.07	0.12	0.03	0.47	0.13	0.04	0.54
1/28/05	0.22	0.28	0.17	NA	0.61	0.18	NA	0.28	0.27	0.76
2/3/05	0.23	NA	0.13	NA	NA	0.29	0.68	NA	0.44	1.08
2/9/05	0.10	0.05	NA	0.09	NA	0.04	0.19	NA	0.02	0.25
2/15/05	0.08	0.16	NA	0.03	0.27	0.07	0.19	NA	NA	0.35
2/21/05	0.12	0.18	NA	NA	0.14	0.18	0.26	NA	NA	0.39
2/27/05	0.14	0.05	0.16	NA	NA	0.10	0.58	NA	NA	0.86

below 5%. Interestingly, considering there are higher concentrations of levoglucosan in the winter, on average there is not a higher contribution from biomass burning at any of the sites in winter vs. the summer. Although in Mech, ML, and WP there is a noticeably higher biomass burning contribution compared to the other sites after November. Also, when comparing the three urban/rural pairs, it is only for the pair in MN that the rural site has a larger contribution from biomass burning in the winter compared to the urban site (ML vs. And). At the other two pairs the contribution is quite similar at both the urban and rural site during winter.

4. Summary

Archived 1-in-6 day FRM Teflon filters collected at 10 sites in the Upper Midwest from March 2004 though February 2005 were analyzed for levoglucosan, water-soluble potassium, and WSOC. The main goal of this work was to better understand the impact of biomass burning on fine particle concentrations in this region.

A direct alternative method, HPAEC-PAD, for measuring levoglucosan was used. This technique offers numerous advantages over traditional methods because the filter samples can be extracted directly in DI Water and levoglucosan (and other carbohydrates) can then be determined directly from the liquid extract. Most importantly, this method also has enough sensitivity to be able to determine levoglucosan from daily 47 mm filter samples collected with a low flowrate (i.e., 16.7 LPM).

It was observed that WSOC appears to contain a substantial regional component. The levoglucosan concentrations were higher at each of the 10 sites during the winter than summer, consistent with an increase in biomass burning due to residential wood

burning. During the summer, peaks in the levoglucosan were observed due to long-range transport of emissions from wildfires burning in Alaska and central Canada. However, these levoglucosan peaks were not observed at all sites regardless of the regional nature of air masses in the Upper Midwest. It appeared this was largely due to whether the air masses carrying the fire emissions came from aloft or not. Potassium really exhibited no clear pattern during the entire year suggesting in this case potassium was not a useful marker for biomass burning.

The contribution to OC from primary particle emissions from biomass burning was calculated for all of the samples. On average the contribution of biomass burning to $PM_{2.5}$ OC was not higher in the winter than the summer at any of the sites. The contribution from biomass burning was highest at Mech and WP being on average 15%. The contribution was generally less than 10% at And, AP, ESL, HL, and ML. At BW, NB, and Cinc the contribution from biomass burning was lowest, generally being less than 5%. Additional biomass burning contributions through secondary organic aerosol formation were not accounted for and could be significant, especially during summer when photochemical activity is greater and long-range transport from distant fires allows more time for aging.

throughout the project. We would like to acknowledge the state representatives from IL,

IN, MI, MN, and OH for providing the archived filter samples.

Appendix A

The contribution of OC from spores can be determined using the mannitol and OC concentrations. This is based on the work of *Bauer et al.* [2008], who found there was a relationship between the concentration of mannitol, the number of spores, and the concentration of OC. These conversion factors are 1.7 pg mannitol/spore and 13 pg OC/spore. Similar to the calculations performed for determining the contribution of OC due to biomass burning, for the three sites (BW, ESL, and HL) with no OC data available, the WSOC data will be used along with an assumed WSOC/OC ratio of 0.5 µg C/µg C.

Figure A1 shows the time series for the contribution of OC due to spores for all 10 sites. Since spores are not active during winter and spring generally the concentrations for mannitol are below the detection limit during this time. Therefore only data from May through November is shown. The contribution from spores appears to be less than 1% at all of the sites. The contribution of OC due to spores is highest at ESL, at times being as high as 2 to 3 %. When comparing the three urban/rural pairs, it is only for the pair in MN that the rural site of ML has a larger contribution compared to the urban site of And. At the other two pairs the contribution is quite similar at both the urban and rural site.
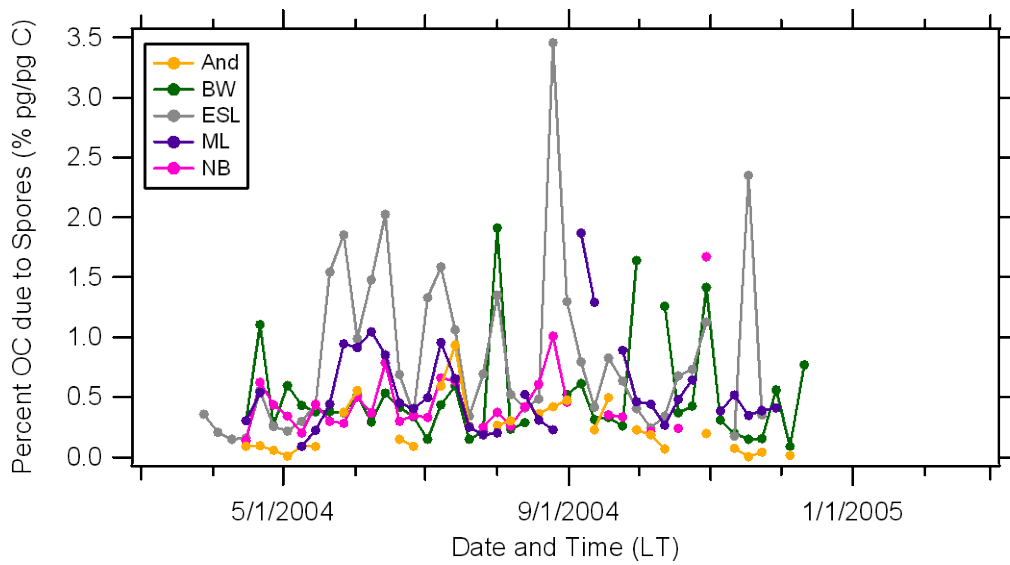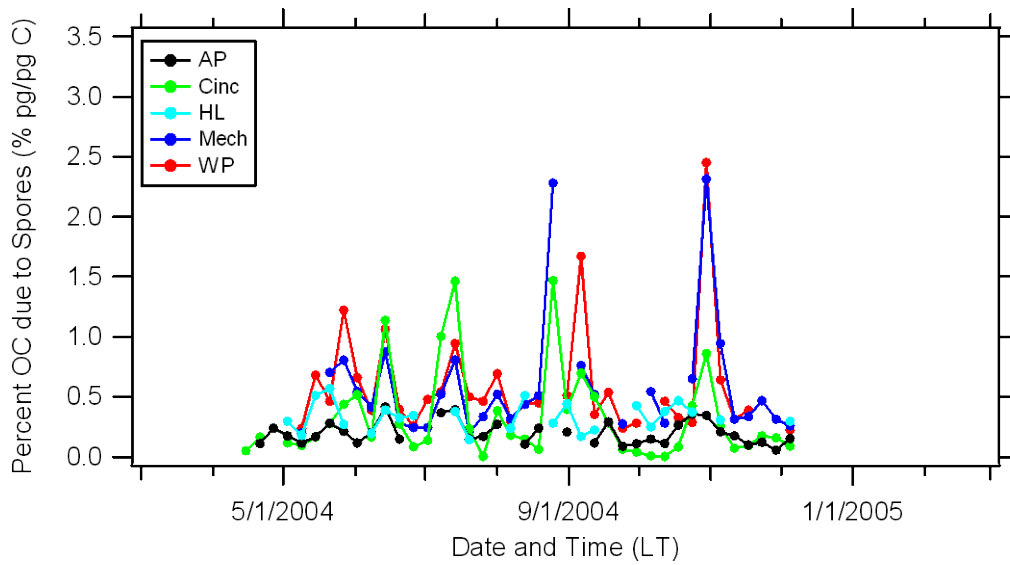
Figure A1. Time series for the percentage of $PM_{2.5}$ OC due to spores for all 10 sites. For clarity the data have been graphed as 5 sites per figure.

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