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Biomass burning impact on $PM_{2.5}$ over the southeastern US during 2007: integrating chemically speciated FRM filter measurements, MODIS fire counts and PMF analysis

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Abstract. Archived Federal Reference Method (FRM) Teflon filters used by state regulatory agencies for measuring $PM_{2.5}$ mass were acquired from 15 sites throughout the southeastern US and analyzed for water-soluble organic carbon (WSOC), water-soluble ions and carbohydrates to investigate biomass burning contributions to fine aerosol mass. Based on over 900 filters that spanned all of 2007, levoglucosan and K^+ were studied in conjunction with MODIS Aqua fire count data to compare their performances as biomass burning tracers. Levoglucosan concentrations exhibited a distinct seasonal variation with large enhancement in winter and spring and a minimum in summer, and were well correlated with fire counts, except in winter when residential wood burning contributions were significant. In contrast, K^+ concentrations had no apparent seasonal trend and poor correlation with fire counts. Levoglucosan and K^+ only correlated well in winter ($r^2 = 0.59$) when biomass burning emissions were highest, whereas in other seasons they were not correlated due to the presence of other K^+ sources. Levoglucosan also exhibited larger spatial variability than K^+. Both species were higher in urban than rural sites (mean 44% higher for levoglucosan and 86% for K^+). Positive Matrix Factorization (PMF) was applied to analyze $PM_{2.5}$ sources and four factors were resolved: biomass burning, refractory material, secondary light absorbing WSOC and secondary sulfate/WSOC. The biomass burning source contributed 13% to $PM_{2.5}$ mass annually, 27% in winter, and less than 2% in summer, consistent with other souce apportionment studies based on levoglucosan, but lower in summer compared to studies based on K^+.

1 Introduction

Biomass burning is a major source of ambient $PM_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5 μm) and has significant impacts on human health (Lighty et al., 2000), regional to global air quality (Lelieveld et al., 2001) and climate (Penner et al., 1992; Hobbs et al., 1997). Numerous studies have attempted to assess the impact of biomass burning on local and regional $PM_{2.5}$ concentrations. Typically, either source-oriented or receptor-oriented methods are used to quantify biomass burning contributions. Source-oriented approaches use chemical transport models (CTMs) to simulate the emissions from biomass burning sources, but are limited by large uncertainties in fire emission inputs (Zeng et al., 2008; Tian et al., 2009). Receptor-oriented approaches quantify source contribution through measurements of specific marker species for biomass burning (e.g. Schauer et al., 1996; Rogge et al., 1998; Schauer and Cass, 2000; Zheng et al., 2002) and have been used more widely.

A number of chemical species have been used as particle-phase biomass burning emission tracers. Water-soluble potassium (K^+) has been used extensively as an inorganic tracer to apportion biomass burning contributions to ambient aerosol (Ramadan et al., 2000; Kim et al., 2003a, b; Ma et al., 2003; Liu et al., 2005; Lee et al., 2008). K^+ is not an ideal tracer as it has other sources, such as sea salt and soil dust (Wang et al., 2005; Duvall et al., 2008). Attempts have been made to eliminate these sources by calculating non-sea-salt non-dust K^+ (Cachier et al., 1991; Puxbaum et al., 2007; Pio et al., 2008), but this requires knowledge of the source characteristics and an assumption that they are invariant among different locations and seasons. Organic compounds are the largest component produced from fires and there are specific

compounds found to be exclusively emitted from biomass burning. The most commonly used organic tracer is levoglucosan, a sugar anhydride produced during the combustion of cellulose (Simoneit et al., 1999; Puxbaum et al., 2007; Zheng et al., 2007; Sullivan et al., 2008).

PM$_{2.5}$ concentrations are high in the southeastern US (Goldstein et al., 2009) and the impact of biomass burning emissions in this region has been extensively studied (Tanner et al., 2004; Liu et al., 2005; Zheng et al., 2006, 2007; Lee et al., 2008; Zeng et al., 2008; Tian et al., 2009; Yan et al., 2009). Zeng et al. (2008) suggested that prescribed fire emissions can result in a daily increase of PM$_{2.5}$ mass up to 25 µg m^{-3}, leading to PM$_{2.5}$ nonattainment in regions affected by the fires. Tian et al. (2009) attributed 55% and 80% of PM$_{2.5}$ to prescribed burning in January and March 2002, respectively. Receptor model studies using levoglucosan as a biomass-burning tracer suggested that wood burning is the dominant contributor (9%–51%) to OC and one of the major sources of PM$_{2.5}$ at several urban and rural sites in the southeast during September 2003 and January 2004 (Zheng et al., 2006, 2007). Using both PMF and CMB receptor models and K$^+$ as a tracer, Lee et al. (2008) attributed 5%–20% of the PM$_{2.5}$ mass to biomass burning emissions at four sites in Georgia and Alabama from January 2000 to December 2002.

These previous studies indicated that biomass burning is a major PM$_{2.5}$ source with contributions that vary with seasons; however, they are based on data for only a few months at a limited number of sites and are further restricted by uncertainties in biomass burning emissions and tracer concentrations. In this study, an extensive data set of PM$_{2.5}$ mass concentrations and chemical speciation was generated from archived FRM filters acquired from state regulatory agencies for the year of 2007. This study compares K$^+$ and levoglucosan as biomass-burning tracers and employs a PMF analysis to quantify average mass contributions from biomass burning and other sources over the southeastern US throughout 2007.

2 Methodology

2.1 FRM filter sampling

State agencies use an EPA Federal Reference Method (FRM) to determine ambient PM$_{2.5}$ mass at sites throughout the country to assess compliance with National Ambient Air Quality Standards (NAAQS). Once mass has been determined gravimetrically, the filters are stored and are eventually discarded. For this study, archived FRM filters that had been in storage (in the dark at a $T < -20\,°C$) for roughly a year were acquired from state regulatory agencies in Georgia (GA Department of Natural Resources), South Carolina (SC Department of Health and Environmental Control) and Alabama (AL Department of Environmental Management and the Jefferson Co. Department of Health). The FRM method

Table 1. Locations and types of the FRM sampling sites in this study.

No.	State	City	Site name	Latitude	Longitude	Type
1	GA	Decatur	South Dekalb*	33.6881	−84.2902	Urban
2	GA	Rome	Rome*	34.2611	−85.3230	Urban
3	GA	Augusta	AUG-BRS*	33.4339	−82.0224	Urban
4	GA	Macon	Macon*	32.7773	−83.6412	Urban
5	GA	Yorkville	Yorkville	33.9285	−85.0453	Rural
6	GA	Sandersville	Sandersville	32.9747	−82.8089	Rural
7	GA	Columbus	COL-CRS*	32.4309	−84.9318	Urban
8	GA	Athens	ATNS-UGA*	33.9179	−83.3446	Urban
9	AL	Birmingham	N'BHM*	33.5530	−86.8149	Urban
10	AL	Wylam	Wylam	33.4997	−86.9241	Urban
11	AL	Providence	Providence	33.4596	−87.3055	Rural
12	AL	Ashland	Ashland	33.2849	−85.8036	Rural
13	AL	Crossville	Crossville	34.2886	−85.9699	Rural
14	SC	Long Creek	Long Creek	34.8053	−83.2377	Rural
15	SC	Trenton	Trenton	33.7400	−81.8536	Rural

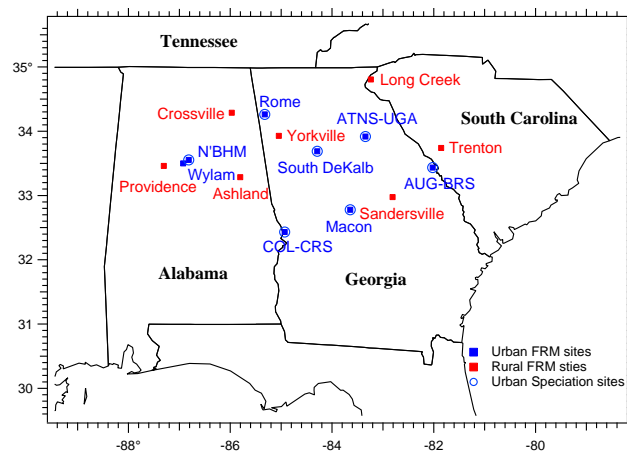* Sampling stations with co-located EPA Speciation sites.

Fig. 1. Map of the EPA FRM and co-located Speciation sampling sites used in this study. Site names and locations are given in Table 1.

for collecting ambient fine particles onto Whatman 47 mm Teflon filter substrates involved 24-hour integrated sampling at a nominal flow rate of 16.7 L/min with PM$_{2.5}$ sharp cut cyclone size selector or PM$_{2.5}$ WINS impactor and with no gas-denuders (Patashnick et al., 2001). Fifteen sampling sites throughout the southeastern US were chosen within the EPA FRM monitoring network, on the basis of geographic location, site type (i.e. urban and rural) and source influences. Among these fifteen sites, eight were urban and seven were rural. Table 1 lists the sites, and their locations are shown in Fig. 1. A subset of all field samples corresponding to a one-in-six-day sampling schedule produced 60 filters for analysis per site and a total of 900 filters. In addition to these filters, a series of field blanks (36 filters) and replicated filters (43 filters) were included for quality control.

2.2 Chemical analyses

This suite of filters was extracted in water and a number of chemical components and physical properties were quantified. Each archived FRM Teflon filter was placed in a precleaned 30 mL Nalgene amber HDPE bottle and extracted with 30 mL of 18-MΩ Milli-Q water via 30-minute sonication. The liquid extract was then filtered using a 0.45 µm PTFE syringe filter and transferred to a separate pre-cleaned 30 mL Nalgene amber bottle. Various chemical analyses were performed on aliquots from these bottles, which were stored in the refrigerator (~4 °C) for at most one week until all analyses were completed.

For each species quantified, overall uncertainty was determined based on a sum of squares that included measurement uncertainties (e.g. liquid extraction volumes, etc.), variability in calibrations performed throughout the analyses of all 900 filters, variability in field blanks and water blanks, and precision based on variability of a standard placed at intervals of every tenth sample throughout the sample queues.

Water-soluble organic carbon (WSOC) in the extract was quantified using a Sievers Model 800 Turbo Total Organic Carbon analyzer (GE Water Systems, Boulder, CO; for more details see Sullivan et al., 2004). The instrument was calibrated using a series of sucrose standards ($N = 5$, linear regression $r^2 = 0.9998$; variability in slope based on three separate calibrations throughout the analysis period was ~3%). The method limit of detection (LOD) of 0.33 µg Carbon m^{-3} (µg C m^{-3}) for WSOC was estimated by three times the standard deviation of field blanks, translated to ambient air concentration assuming, in all cases, a flow rate of 16.7 L/min and 24 h sampling period. Overall measurement uncertainty was 9%.

High-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) was utilized to quantify various carbohydrate compounds, including levoglucosan. This technique involved a Dionex DX-500 series ion chromatograph coupled with Dionex ED 50 electrochemical detector with a gold working electrode operating in integrating amperometric mode, and a Dionex CarboPac PA-1 anion-exchange column with gradient elution of 200 mM NaOH at a flow rate of 0.5 mL min^{-1}. The elution profile was as follows: 0–8 min, isocratic elution with 10 mM NaOH; 8–25 min, linear gradient elution from 10 mM to 60 mM NaOH; 25–38 min, column cleaning step with 180 mM NaOH; and 38–56 min, column re-equilibration step with 10 mM NaOH. Detailed descriptions of eluent preparation, peak detection and calibrations of HPAEC-PAD have been presented elsewhere (Engling et al., 2006; Sullivan et al., 2008). Calibrations were based on serial dilutions from a stock solution made by dissolving individual compounds in solid form (purchased from Sigma-Aldrich) with Milli-Q water. The LOD for the various carbohydrates was estimated at 6 ng/m^3 and the overall measurement uncertainty for levoglucosan was 21%. Previous studies have found that
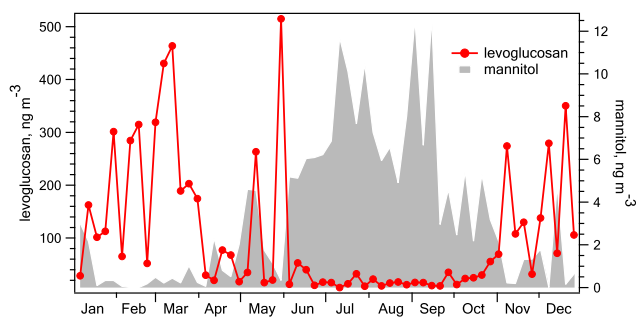

Fig. 2. Mean concentrations of levoglucosan and mannitol for all the sites in 2007.

the peaks of levoglucosan and arabitol, a sugar alcohol from fungal spores, cannot be fully separated by a CarboPac PA-1 column (Caseiro et al., 2007; Sullivan et al., 2008), as a result the integrated peak area of levoglucosan was corrected for this interference by arabitol. Ambient mannitol and arabitol concentrations correlate well and a ratio of 1.5 between the two has been obtained in PM$_{10}$ samples (Bauer et al., 2008). Since mannitol can be quantitatively measured with the CarboPac PA-1 column, the arabitol concentration was determined by dividing mannitol by 1.5. The peak area of arabitol was then calculated and subtracted from the levoglucosan peak area. This correction adds uncertainty to the measured levoglucosan concentration, as using a uniform conversion factor from mannitol to arabitol assumes a same mannitol/arabotol ratio for PM$_{2.5}$ samples and does not necessarily reflect the varied ratio as a function of physical environments (i.e. temperature), aerosol sources, etc. This uncertainty is larger in summer (can be on order of 25%) when levoglucosan concentrations are typically low than in winter when levoglucosan is most abundant (on order of 3%) (Fig. 2).

To validate the HPAEC-PAD method, levoglucosan concentrations were determined via independent GC-MS measurements (Zheng et al., 2006) from a series of quartz fiber filters ($N = 33$) collected from May 2004 to Apr 2005. A portion of the same filters were extracted in water and levoglucosan was measured by HPAEC-PAD following the method described above. The two datasets showed good agreement, with a linear regression r^2 of 0.92, and a zero intercept regression slope of 1.09 ± 0.04 (± one STD). No significant underestimation by the HPAEC-PAD method due to arabitol correction was found. On average levoglucosan concentrations determined by HPAEC-PAD for the summertime filters were 14% lower than those determined by GC-MS.

Water-soluble anions (chloride, nitrate, sulfate and oxalate) and cations (sodium, ammonium, potassium, magnesium and calcium) were quantified on a dual channel Dionex DX-500 Ion Chromatograph with suppression and conductivity detection, employing a Dionex AS11-HC anion column and Dionex CS12A cation column. Calibrations were based on NIST traceable liquid standards. Measurement

uncertainties were 40 % for Na$^+$, 28 % for NH$_4^+$, 63 % for Mg^{2+}, 17 % for K$^+$, 7 % for SO$_4^{2-}$ and 36 % for oxalate. Ca^{2+} uncertainty was 755 %, which was subsequently found to be due to a contaminated DI water supply. Thus, Ca^{2+} results are not reported. Instead, Mg^{2+} is used as a mineral dust indicator in the following analysis. LODs for the ions were in the range of 0.01 (K$^+$) to 0.1 (SO$_4^{2-}$) µg/m^3.

The UV-Vis light absorption spectra for the liquid extracts were determined with a 1-m path-length Liquid Waveguide Capillary Cell (LWCC-2100, World Precision Instrument, Sarasota, FL) to investigate the link between brown carbon and biomass burning. Hecobian et al. (2010) provides a detailed description of the method and results investigating brown carbon sources, based in part on the FRM filters used in this work. Briefly, the method involved injecting 1 mL of FRM-filter extract through the LWCC via a syringe pump (Klohn, LTD; Las Vegas, NV). The absorption spectra between wavelengths of nominally 200 and 800 nm was saved 30 s after the sample entered the LWCC. After each measurement, the LWCC was flushed thoroughly with 1 mL of 0.6 N HCl and 3 mL of Milli-Q DI water, and the baseline was re-zeroed with reference to 18-MΩ Milli-Q water. The absorption was determined using the ratio of transmitted to incident light intensity following Beer's Law, such that the absorption is linear with the absorbers concentration and mass absorptivity, and LWCC path length (∼1 m). We used the product of all three since in our samples mass absorptivities were unknown. In this study, the average absorption between wavelengths 360 and 370 nm (Abs$_{365}$, in units of m^{-1}, see (Eqs. 1 and 2) in Hecobian et al., 2010) was used as a measure of brown carbon.

PM$_{2.5}$ mass concentrations were determined gravimetrically by each of the three state regulatory agencies following their protocols. It is important to note that FRM Teflon filters are not designed for PM$_{2.5}$ composition measurements. Although Teflon filters are known to be relatively inert to gas absorption, the un-denuded sampling method may contribute to positive artifacts. Furthermore, this sampling method and the year-long storage of the Teflon filters may also lead to loss of semi-volatile components (Watson et al., 2009). Effort has been made to estimate these semi-volatile components retained on FRM Teflon filters (Frank, 2006). In this paper, known semi-volatile species such as nitrate are not discussed, and the reported WSOC and other components (including FRM PM$_{2.5}$ mass) should be viewed as a measure of the more non-volatile species associated with ambient PM$_{2.5}$.

To assess the quality of the FRM filter data, the results were compared to a number of components, i.e. PM$_{2.5}$ mass, NH$_4^+$, K$^+$, and SO$_4^{2-}$, from seven co-located EPA Speciation sites (South Dekalb, Rome, Macon, AUG-BRS, COL-CRS, ATNS-UGA and N′BHM; see Table 1), where the chemical analyses were done through Research Triangle Institute on quartz fiber filters and were completely independent of the FRM data. The results are shown in Fig. 3. All compo-
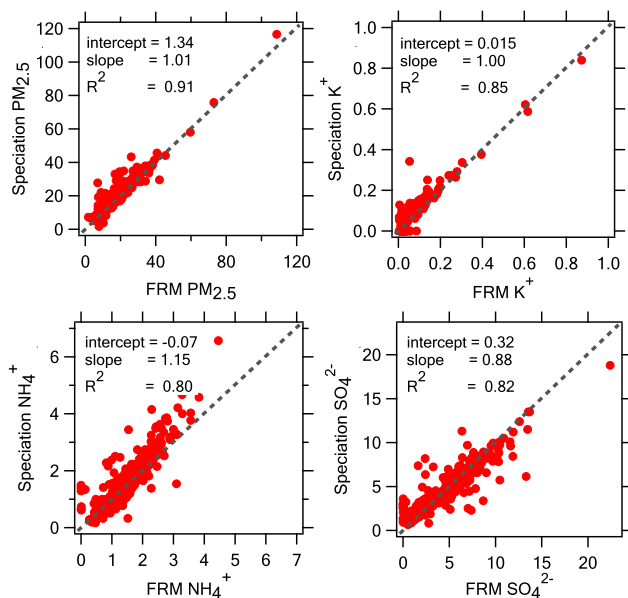

Fig. 3. Intercomparison of PM$_{2.5}$ mass, K$^+$, NH$_4^+$, SO$_4^{2-}$ concentrations (in µg/m^3) between seven co-located EPA FRM and Speciation sites. FRM K$^+$, NH$_4^+$ and SO$_4^{2-}$ are from the methods used in the analysis of all sites presented in this study. In all cases $N = 420$.

nents show good agreement between the two types of filters, with linear regression slopes from 0.88 to 1.15. It is noteworthy that the Speciation NH$_4^+$ concentrations were on average 15 % higher than the FRM NH$_4^+$ concentrations (a slope of 1.15), reflecting possible loss of semi-volatile NH$_4^+$ associated with NO$_3^-$ from the FRM filters.

2.3 MODIS fire counts

Fire counts detected by remote sensing have been used to examine seasonal biomass burning emissions (Eva and Lambin, 1998; Duncan et al., 2003; Zeng et al., 2008). In this work, MODIS fire count data from the NASA Aqua satellite (Giglio et al., 2003) were used as a measure of outdoor biomass burning over the southeast in 2007. The data set had a horizontal resolution of 1 km × 1 km, and a time resolution of 1 day. The sum of fire counts in each month was used to investigate monthly and seasonal variations. Fire counts for seven states were used, including the three states in which our sampling sites were located and four other surrounding states to ensure that all possible biomass burning source regions were considered. An analysis of fires over continental United States indicated no evidence for long-range transport of smoke to the sites during 2007; however, episodic influence from longer-range transport of smoke cannot be ruled out.

Table 2. Annual and seasonal mean concentrations ($\pm$ STD) of measured PM$_{2.5}$ components from FRM filters. Winter (J, F, D), Spring (M, A, M), Summer (J, J, A) and Fall (S, O, N).

Component		Annual	Winter	Spring	Summer	Fall
PM$_{2.5}$	μg m^{-3}	15.56$\pm$8.67	11.68$\pm$6.25	17.33$\pm$11.19	19.17$\pm$7.87	13.61$\pm$5.74
WSOC	μg C m^{-3}	2.07$\pm$1.53	1.45$\pm$1.01	2.47$\pm$2.22	2.58$\pm$1.21	1.70$\pm$0.83
NH$_4^+$	μg m^{-3}	1.40$\pm$0.71	1.06$\pm$0.61	1.39$\pm$0.63	1.78$\pm$0.79	1.36$\pm$0.63
K$^+$	ng m^{-3}	53.7$\pm$104.1	45.0$\pm$32.1	55.6$\pm$51.8	70.8$\pm$194.8	42.9$\pm$46.2
SO$_4^{2-}$	μg m^{-3}	4.43$\pm$2.99	2.60$\pm$1.90	4.24$\pm$2.40	6.41$\pm$3.68	4.38$\pm$2.46
Oxalate	ng m^{-3}	136.0$\pm$91.3	82.6$\pm$57.2	172.4$\pm$110.5	173.2$\pm$85.6	108.3$\pm$59.5
Levoglucosan	ng m^{-3}	107.5$\pm$221.9	169.9$\pm$180.3	180.3$\pm$339.2	18.7$\pm$44.7	55.7$\pm$134.7
Xylose	ng m^{-3}	1.23$\pm$2.44	1.71$\pm$2.12	1.99$\pm$3.84	0.52$\pm$0.78	0.68$\pm$1.31

2.4 Positive Matrix Factorization (PMF) source apportionment

A PMF analysis on the chemical and physical data was used to quantify contributions from biomass burning and other sources to the FRM PM$_{2.5}$ mass concentrations. Detailed information on EPA-PMF (v3.0) can be found on US EPA website (http://www.epa.gov/heasd/products/pmf/pmf.html). Two datasets, (i.e. a concentration/physical property dataset and an uncertainty dataset) are required for PMF input. PMF is able to identify underlying covariance among chemical or physical parameters. While most previous PMF source apportionment studies use concentrations of chemical species as objects for analysis, in this work, along with chemical species (WSOC, Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, SO$_4^{2-}$, oxalate, xylose, and levoglucosan), the UV-Vis light absorption data at 365 nm (Abs$_{365}$) from the FRM filter water-extract were also incorporated, as light absorption is an important aerosol property dependent on source and composition of the aerosols (Andreae and Gelencser, 2006). Data from the 15 sampling sites on each sampling date were merged to form the concentration dataset. Considering potentially different source types for urban and rural sites, PMF analysis was also performed separately using two datasets from urban and rural sites, and the results, i.e. source composition profiles and contributions, showed little difference from those discussed in Sect. 3.3. Missing values for each component were replaced with the mean concentration of this component, and values below the LOD were replaced with half of the detection limit of the corresponding component (Polissar et al., 1998), ensuring that all values were positive. The uncertainty for each component was determined based on the methods discussed in Sect. 2.2. For missing data points and values below the LOD, the uncertainties were assigned as 4 and 5/6 times the concentration values, respectively (Polissar et al., 1998). Numerous PMF runs were performed with 3–7 factors and various combinations of the concentration and absorption data set. Based on Q values (the objective function to be minimized) and physical interpretation of the solution, four factors appeared to be the optimal solution. The

model output files include factor profiles, relative factor contributions and residuals (unexplained fractions).

In order to quantify the contribution to PM$_{2.5}$ mass from each factor-related source, multivariate linear regression (MLR) analysis was performed to scale relative factor contributions to the measured total PM$_{2.5}$ mass. Light absorption data were not included in the regression analysis since it is not a mass concentration measurement.

3 Results and discussion

3.1 Spatiotemporal variations of levoglucosan and water-soluble potassium (K$^+$)

The 12 months of 2007 were separated into four seasons as: January, February and December (winter); March, April and May (spring); June, July and August (summer); September, October and November (fall). Table 2 presents the annual and seasonal mean concentrations of levoglucosan and K$^+$, together with those of PM$_{2.5}$ mass, water-soluble organic carbon (WSOC), ammonium (NH$_4^+$), sulfate (SO$_4^{2-}$), oxalate and xylose. Figure 4 shows the seasonal mean concentrations of levoglucosan and K$^+$ at each site.

3.1.1 Levoglucosan

In general, levoglucosan concentrations obtained in this study were comparable with those in previous studies in the same region (Zheng et al., 2007; Ding et al., 2008), but were considerably higher than those at other locations in the US, such as Pittsburgh, PA (annual mean at ~21 ng/m^3) (Robinson et al., 2006), suggesting much larger impact from biomass burning in the southeast. The annual mean concentration of levoglucosan for all sampling sites was 107.5 ng/m^3 (Table 2). Clear seasonal variations of levoglucosan concentrations were observed, with significantly higher concentrations in spring and winter and minimum levels in summer. Mean concentrations for spring and winter were 180 ng/m^3 and 170 ng/m^3, respectively; whereas the mean summer concentration was only 19 ng/m^3, which
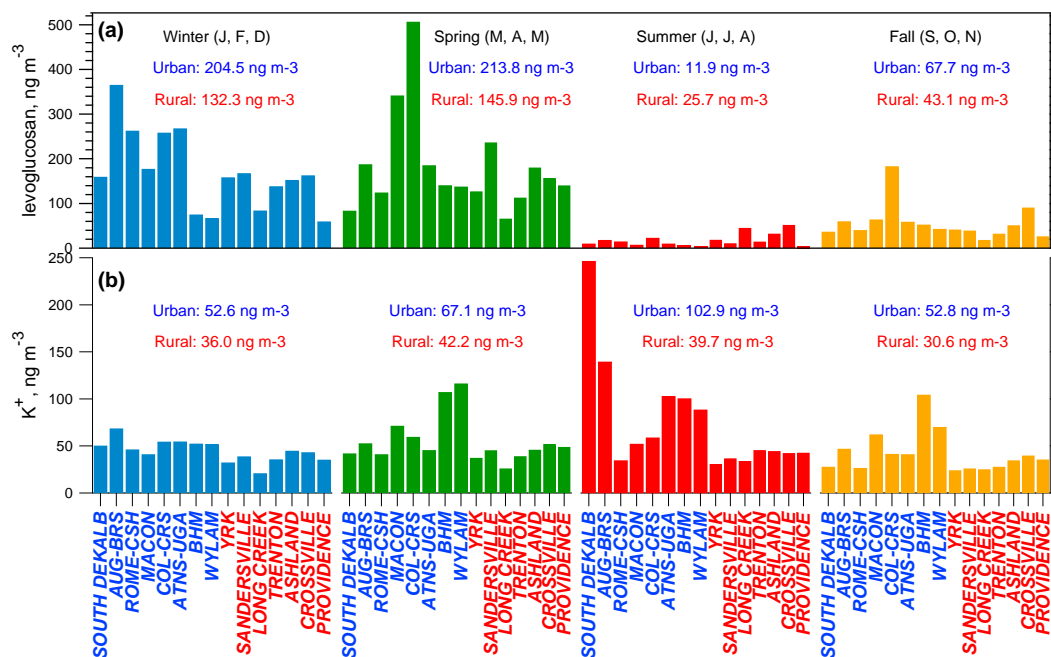
Fig. 4. Seasonal (Winter, Spring, Summer, Fall) variations of levoglucosan **(a)** and K$^+$ **(b)** concentrations at each site. Site names in blue and red are urban and rural sites, respectively. The mean concentrations of levoglucosan and K$^+$ by urban/rural segregation for each season are given in the plots.

is within the range of levels (5 to 52 ng/m^3) reported by Puxbaum et al. (2007) at six background stations in Europe. Significantly enhanced levoglucan concentrations at several sites were detected for several days in spring. For instance, 2950 ng/m^3 of levoglcusoan was recorded at the Macon site on 12 May, almost 2 orders of magnitude higher than the level observed six days before (31 ng/m^3). Similarly, on 30 May, levoglucosan concentrations at COL-CRS, N'BHM, Wylam, Ashland and Providence all exceeded 1000 ng/m^3, much higher than those at other sites on the same day (3.93 ng/m^3–346 ng/m^3). Such unusual levoglucosan concentrations at these sites were due to significant but sporadic impacts from unique wildfire events in spring of 2007. Extensive wildfires started in the Okefenokee Swamp in southern Georgia/northern Florida in April and spread across Georgia and adjacent states during the following two months (Yan et al., 2010[1]).

Figure 4a also shows the spatial distributions of levoglucosan for different seasons. In general, there were significant site-to-site variations, suggesting varied impacts from biomass burning emissions among the sampling sites. Winter and spring showed the largest variations in terms of absolute concentrations. In spring, variability was largely due to the sporadic impacts from wildfire events at different sites. In

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[1]Yan, B., Hu, Y. T., Zhang, X., Tian, D., Balachandran, S., Kim, H. K., Weber, R. J., Zheng, M., and Russell, A. G.: Detailed chemical characterization and aging of wildfire aerosols in the southeastern US, manuscript in preparation, 2010.
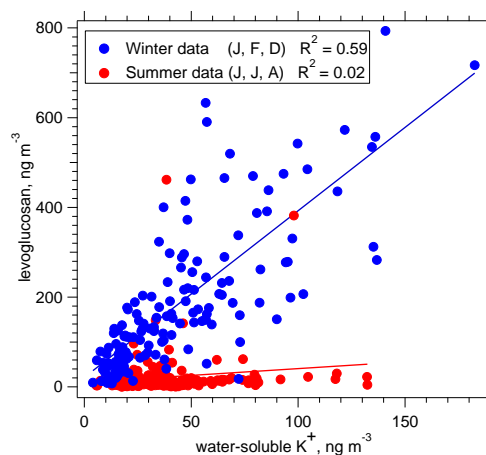

Fig. 5. Relationship between levoglucosan and water-soluble K$^+$ concentrations in winter (January, February and December) and summer (June, July and August). Data on 5 July 2007 were not plotted and excluded from the regression calculation due to abnormally elevated levels of K$^+$ associated with fourth of July fireworks.

winter, biomass burning was likely mainly in the form of residential wood burning (discussed in more detail below), thus spatial variability at these time periods likely reflect population densities and frequency of burning in different regions. Levoglucosan concentrations in urban sites were generally higher than those in rural sites, except during summer when
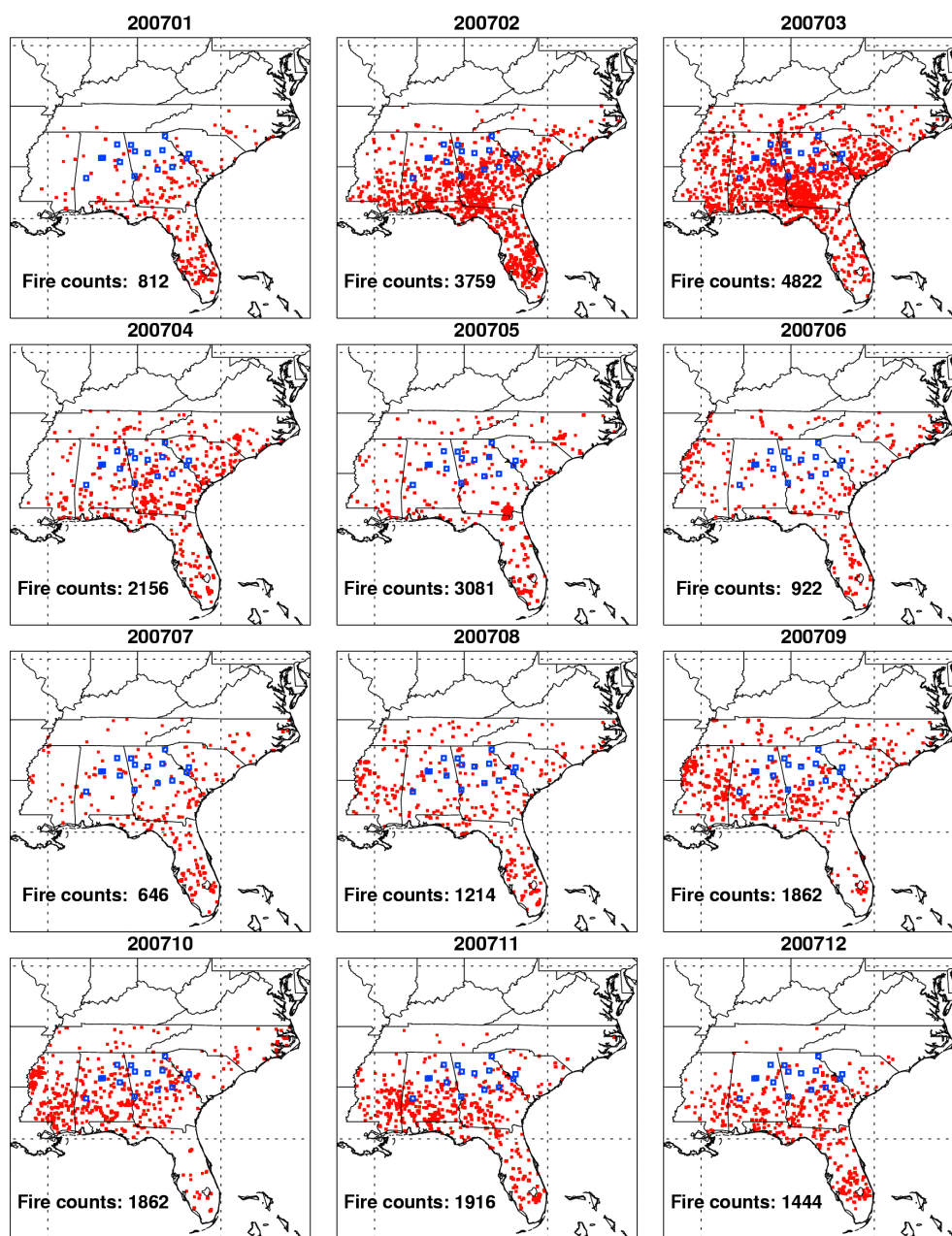
Fig. 6. Monthly MODIS Aqua fire counts (red points) in 2007 over seven states in the southeastern US. FRM sampling sites are shown as blue square symbols.

rural sites tended to have slightly higher levoglucosan concentrations, implying that residential wood burning in urban areas is an important source of levoglucosan when other forms of biomass burning, such as wildfires, are absent. High spatial variability was observed for levoglucosan during all seasons, as indicated by the large relative standard deviations (RSD, standard deviations of concentrations in each season divided by the corresponding seasonal mean concentration) (51%–79%).

3.1.2 Water-soluble Potassium (K$^+$)

Compared to levoglucosan, K$^+$ concentrations exhibited different spatiotemporal variability. First, K$^+$ had an opposite seasonal pattern to levoglucosan with much less seasonal variability (from 45 ng/m^3 in winter to 71 ng/m^3 in summer, Table 2). Smaller site-to-site concentration differences suggested by the lower RSD values (25%–75%) for all four seasons indicate more uniform K$^+$ concentrations compared to levoglucosan. The significantly higher levels of K$^+$ at South
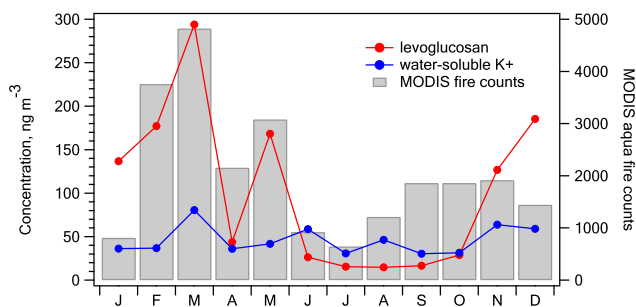
Fig. 7. Monthly mean levoglucosan and water-soluble potassium concentrations from all sites compared with monthly mean MODIS Aqua fire counts from seven states in the southeastern US.

Fig. 8. Correlations of monthly mean concentrations of levoglucosan and K$^+$ versus fire counts. The red solid line is the fit of levoglucosan-fire counts correlation ($r^2 = 0.54$). The red dashed line is the fit without January and December ($r^2 = 0.86$).

Dekalb and AUG-BRS sites during summer (Fig. 4b) were due to K$^+$ spikes detected at these two sites on 5 July, likely reflecting pyrotechnique (fireworks) emissions. Excluding these data, RSD value in summer (75%) would be much smaller, and K$^+$ concentrations would be even more uniform (The 5 July sampling day was excluded from all further analysis). Similar to levoglucosan, K$^+$ tended to have slightly higher concentrations at urban sites (Fig. 4b).

A comparison of 24-h averaged levoglucosan and K$^+$ shows different degrees of correlation in winter and summer (Fig. 5). In winter, when biomass burning was expected to be more prevalent, levoglucosan and K$^+$ were reasonably correlated ($r^2 = 0.59$), suggesting their common emission sources. In summer, however, there was almost no correlation between levoglucosan and K$^+$ ($r^2 = 0.02$), reflecting distinctly different behaviours of these two tracers when biomass-burning emissions are expected to be significantly lower. Higher relative uncertainty in summertime levoglucosan concentrations due to the scaling of arabitol to mannitol (Sect. 2.2) may have also contributed to the poor correlation.

3.2 Relationships between K$^+$, levoglucosan and MODIS fire counts

MODIS fire count data can be used as a measure of wildfire and prescribed burning events, two of the major forms of biomass burning over the southeast (Zeng et al., 2008). Other forms of biomass burning such as residential wood burning cannot be detected by remote sensing and thus are not reflected in the fire counts. Since our sampling dates are evenly distributed in each month, the monthly fire counts over the region encompassing our sampling sites should reflect the outdoor biomass burning impacts on the measured PM$_{2.5}$ mass and composition.

In 2007 there was a distinct seasonal variation of fire counts, with maximum in spring (counts ranging from 2156 to 4822) and minimum in summer (646–1214) (Fig. 6), indicating extensive outdoor biomass burning events in spring, and fewer such events in summer. The highly concentrated
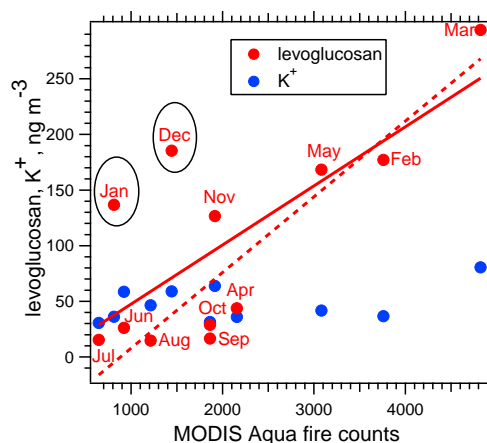
fire points in May along Georgia-Florida boarder (Fig. 6) were identified as the Okefenokee Swamp fires discussed above.

The relationships between monthly fire counts and monthly mean concentrations of levoglucosan and K$^+$ are shown in Figs. 7 and 8. Monthly fire counts tracked levoglucosan concentrations well. For example, fire counts dropped from a March peak of 4822 by a factor of 8 to 646 in July, corresponding to levoglucosan concentrations changing from 294 ng/m^3 to 15 ng/m^3, a factor of 9 decrease. The exceptions in January and December (Fig. 7) when levoglucosan appeared to deviate from fire counts were likely due to residential wood burning as a source of levoglucosan being prevalent in these two months, yet could not be detected as fire counts by satellite (Tian et al., 2009). Levoglucosan and K$^+$ concentrations are also shown as a function of fire counts in Fig. 8. For the levoglucosan and fire counts correlation, r^2 was 0.54; excluding January and December, r^2 was 0.86. K$^+$ concentrations showed poor correlation with fire counts throughout the year ($r^2 = 0.16$, and 0 excluding January and December in Fig. 8). Since residential burning is minimal in summer, while fire count data also showed a large decrease in outdoor burning during summer, biomass burning emissions in summer was expected to be significantly lower than the cooler seasons. Levoglucosan had a similar trend as fire counts, whereas K$^+$ did not. The scatters at the lower concentrations in summer months may be due to some fraction of levoglucosan being lost through oxidation (Hennigan et al., 2010), as well as the larger measurement uncertainty of levoglucosan in summer (Sect. 2.2). The difference in levoglucosan concentrations in January and December when fire counts were low (Fig. 8) suggests residential wood burning throughout the southeastern US, on average, contributed roughly 135 ng/m^3 to 145 ng/m^3 of levoglucosan
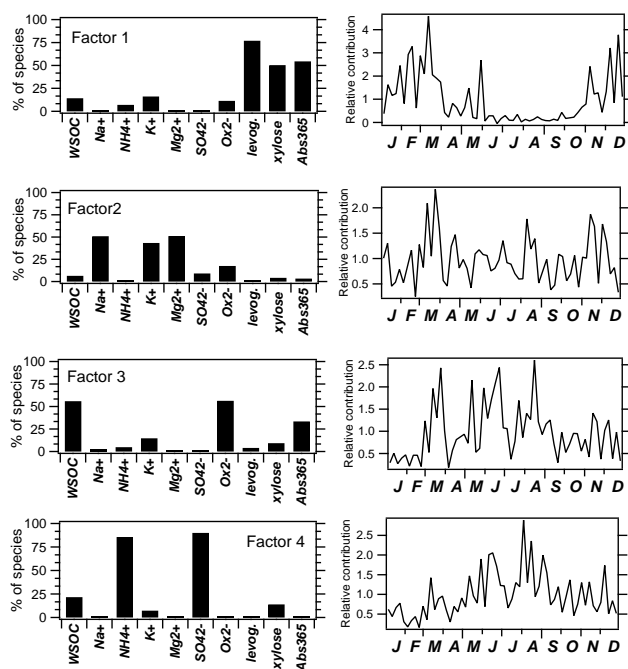
Fig. 9. Composition profiles (% of total of each species) for the four factors resolved by PMF based on data from the whole year (2007) at all sites (left panel), and the time series of relative contribution of each factor (right panel).

during these two months. This corresponds to approximately 2.6 µg/m^3 of PM$_{2.5}$ mass (based on an average emission factor determined in Sect. 3.3.3).

The distinct seasonal trends of levoglucosan and K$^+$, with only the former tracking fire counts well, appear to be evidence that levoglucosan is a better tracer of biomass burning (including wildfire and prescribed burning) than K$^+$. Although poor correlation between levoglucosan and K$^+$ may also be due to highly variable emissions, which as shown in laboratory studies depend on burning conditions and types of material burned (Sullivan et al., 2008), this alone cannot explain the distinct temporal trends of K$^+$ and levoglucosan. The lack of correlation between fire counts and K$^+$ clearly points to additional significant sources of K$^+$ other than biomass burning, such as soil dust, sea salt, vegetation and meat cooking (Lawson and Winchester, 1979; Morales et al., 1996; Schauer et al., 1999), which at time can limit its use as a unique indicator of biomass burning emissions.

A receptor modelling study was conducted to comprehensively understand the sources of PM$_{2.5}$ in the southeast and was also used to further assess the performances of these two biomass burning tracers.

3.3 Source apportionment of PM$_{2.5}$ using PMF

3.3.1 Source profiles and relative contributions

Composition profiles for the 4 factors resolved by PMF are shown in Fig. 9 (left panel). Values in the composition profiles represent average fractions (in percent) of those species distributed amongst the four factors. Relative contributions of the four factors obtained from the PMF output were averaged among all sampling sites for each sampling date, shown on the right panel, to illustrate their temporal variation throughout the year.

Factor 1 is characterized by high levels of levoglucosan (i.e. 77% of levoglucosan is in factor 1), xylose (50%), and UV-Vis light absorption (Abs$_{365}$) (55%). Also associated with this factor are K$^+$ (16%), WSOC (14%), oxalate (11%), and NH$_4^+$ (7%). Factor 1 composition profile is consistent with biomass burning emissions. Levoglucosan is the dominant component and almost exclusively associated with this factor, consistent with it being a unique biomass burning tracer (Simoneit et al., 1999; Schkolnik and Rudich, 2006). Xylose is also a carbohydrate emitted in biomass burning (Simoneit, 2002). Consistent with the discussions in Sects. 3.1–3.2, PMF analysis indicates that K$^+$ is not a unique biomass-burning tracer, while it is more associated with other factors, mostly factor 2 (43%), as shown below. Biomass burning emissions also produce significant levels of brown carbon (Andreae and Gelencser, 2006; Hecobian et al., 2010), which explains the presence of light absorption (Abs$_{365}$) in this factor. Oxalate has also been found in biomass burning smoke (Kundu et al., 2009). The appreciable amount of WSOC associated with this factor is consistent with previous studies suggesting biomass burning and secondary organic aerosol (SOA) formation are the two major sources of WSOC (Fuzzi et al., 2006; Sullivan et al., 2006; Weber et al., 2007; Saarikoski et al., 2008). The seasonal pattern of factor 1 shows that averaged over the southeast, biomass burning is most prevalent in the cold months compared to its little impact in summer, with wild-fire events in the springtime in South Georgia.

Factor 2 is characterized by refractory material: Na$^+$ (51%), K$^+$ (43%), and Mg^{2+} (51%), indicating PM$_{2.5}$ from mineral dust (e.g. Lee et al., 1999). These refractory materials are likely related to coarse-mode particles, windy conditions and possibly long-range transport. The factor 2 time series has no clear seasonal pattern.

Factors 3 and 4 are thought to be linked to secondary aerosol formation. Factor 3 has the highest percentages of WSOC (56%) and oxalate (56%), along with light absorbing species (e.g. brown carbon) (34%), and K$^+$ (15%). Factor 4 is distinguished by NH$_4^+$ (86%) and SO$_4^{2-}$ (90%), as well as a considerable amount of WSOC (22%), but little oxalate and little light absorbing species. In this factor, the molar ratio of NH$_4^+$ to SO$_4^{2-}$ is 1.6, indicating that for much of the southeast sulfate is not fully neutralized, as noted in other

Table 3. Seasonal and annual source contributions of each PMF factor to $PM_{2.5}$ mass (% of $PM_{2.5}$ mass). Winter (J, F, D), Spring (M, A, M), Summer (J, J, A) and Fall (S, O, N).

	Winter	Spring	Summer	Fall	Annual
Biomass Burning (F1)	27	15	2	7	13
Refractory (F2)	7	6	6	6	6
Secondary Light Abs WSOC (F3)	16	27	31	26	25
Secondary Sulfate/WSOC (F4)	30	32	46	44	38
Residual	20	20	16	16	18

studies (Lee et al., 2008) (any NH_4^+ associated with nitrate is not considered). Both factors are correlated with temperature ($r^2 = 0.62$ for F3 and $r^2 = 0.81$ for F4), and the high levels of WSOC in both factors and the abundant sulfate in factor 4 are attributed to secondary aerosol formation processes that are known to be prevalent during summer (Lim and Turpin, 2002; Kondo et al., 2007; Weber et al., 2007; Miyazaki et al., 2009). The differences between factors 3 and 4 and the linking of WSOC, oxalate and light absorbing organics (brown carbon) suggest insights into secondary organic aerosol formation, which is investigated further elsewhere (Hecobian et al., 2010; Zhang et al., 2010[2]).

3.3.2 Contributions of factors to yearly $PM_{2.5}$ mass, levoglucosan, K^+ and WSOC

Using multivariate linear regression (MLR), the four factors isolated by PMF, along with the residual, can be used to estimate source contributions (percent of total mass and concentrations in μg/m^3) to overall $PM_{2.5}$ mass and various $PM_{2.5}$ components. Results are summarized in Table 3 and Figs. 10 and 11.

Annually, the four factors resolved by PMF explained 82% of the total $PM_{2.5}$ mass (Fig. 10). The largest contribution (38%) was from factor 4 (secondary sulfate/WSOC), followed by 25% from factor 3 (secondary light absorbing WSOC), and 13% from factor 1 (biomass burning). The 18% of the total $PM_{2.5}$ mass from residual likely reflects contributions from sources related to unmeasured species contributing to $PM_{2.5}$ mass, such as elemental carbon (EC) and water-insoluble organic species, which can be associated with primary emissions from both biomass burning and fossil fuel combustion. At the seven co-located EPA Speciation sites (see Sect. 2.2, all located at urban areas), measurements were made of organic and elemental carbon by Thermal Optical Reflectance (TOR) and Transmittance (TOT) and several elements by Energy Dispersive X-Ray Fluorescence (EDXRF). Incorporating OC, EC, Ca, Cu and Fe data along with the FRM chemical species/light absorption data that were measured at these seven sites, a PMF analysis on this dataset

[2]Zhang, X., Weber, R. J., Edgerton E., Zheng, M., and Frank, N. H.: WSOC spatial distribution over the southeastern US in 2007, manuscript in preparation, 2010.
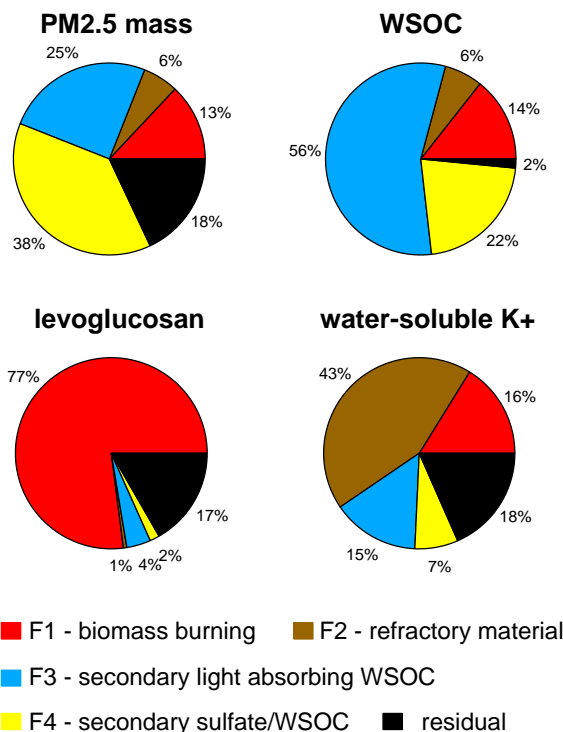

Fig. 10. PMF results showing annually averaged source contributions to $PM_{2.5}$ mass, WSOC, levoglucosan, and water-soluble K^+.
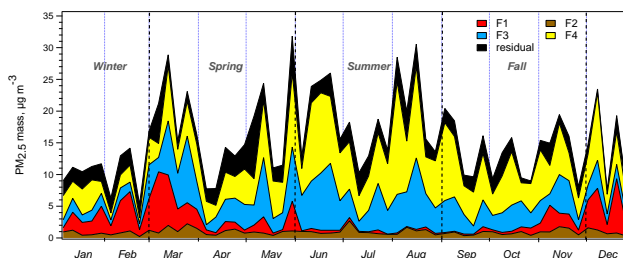

Fig. 11. Time series of $PM_{2.5}$ composition by four factors resolved by PMF and masses predicted by multivariant linear regression (MLR).

resolved 5 factors. A mobile source emission factor characterized by abundant EC (70%) and Cu (57%) was identified, contributing 8% of the $PM_{2.5}$ mass on an annual basis. Meanwhile, the residual fraction dropped from 18% to 7%. The other 4 factors were very similar to the PMF analysis based on just the FRM data shown in Figs. 9, 10 and 11 (details are provided in the supplementary material, Figs. S1 and S2).

Relative contributions of various sources (factors) to WSOC, levoglucosan, and K^+ are also shown in Fig. 10. On an annual basis, most of the WSOC is associated with secondary light absorbing WSOC source (56%), followed by secondary sulfate/WSOC (22%) and biomass burning (14%). For levoglucosan, the dominant source is the

biomass-burning factor (77%). In contrast, K$^+$ has several sources, with refractory material (43%) being the largest, and each of the other three sources contributing from 7 to 16%.

Table 3 shows the separated fractional contributions of the factors to PM$_{2.5}$ mass by season. Although biomass burning only contributed 13% on an annual basis, it accounted for 27% of the PM$_{2.5}$ during winter and only 2% in summer, consistent with the PMF results that included Speciation data, in which case biomass burning contributed 29% and 1% in winter and summer, respectively (Table S1). Factors involving secondary aerosol formation processes (F3 and F4) show the opposite trend, contributing 46% in winter and 77% in summer. This rather large relative increase in summertime secondary sources corresponds to an average WSOC increase of roughly 1 µg C/m^3 from winter to summer (Table 2).

Figure 11 is similar to the time series plot for each factor (Fig. 9, right panel), but in this case the contributions in terms of estimated mass of each factor (source) throughout the year are given. While refractory material (F2) contributions remained consistently low (<7%), secondary sulfate/WSOC was the largest PM$_{2.5}$ contributor throughout the year (30%–46%), partially due to the relatively large and uniform distribution of sulfate in this region (Kim et al., 2003a, b; Liu et al., 2005). Biomass-burning sources (F1) dominated in winter and on average made little contribution to PM$_{2.5}$ mass in summer. The secondary light absorbing WSOC factor (F3) also shows enhancement in summer, but was higher relative to the other secondary factor (F4) in March during a period of unusually warm weather. The source of this factor will be addressed in detail in Zhang et al. (2010[2]).

3.3.3 Comparisons to other studies

Studies using a variety of techniques have investigated contributions of biomass burning to air quality in the southeast. These results are compared to the PMF analysis using the FRM filter data presented here. First, PM$_{2.5}$ mass to levoglucosan ratios from emission studies have been found to vary from 9.7 ± 2.4 g/g for hardwoods to 24.4 ± 4.3 g/g for softwoods (Fine et al., 2002), and 11.5 g/g for a prescribed burning episode in Georgia during April 2004 (Lee et al., 2005). From PMF factor 1 – the biomass burning factor, the annual PM$_{2.5}$ mass to levoglucosan ratio was 18.3 ± 5.4 (± STD) g/g, roughly midway between hard and softwood emissions, but higher than emissions from prescribed burning. Emission studies have also characterized ratios of K$^+$ to levoglucosan, with median ratios in the range of (0.03–0.16) (Fine et al., 2001, 2002, 2004a, b; Lee et al., 2005), depending on the type of material burnt. For factor 1 the K$^+$/levoglucosan ratio was 0.10, similar to the emission profiles. In contrast, for the FRM dataset the ratio is 0.50 in terms of annual mean and 0.26 for winter. These values are not in the range found in the studies mentioned above, likely due to other sources for K$^+$.

Our PMF-predicted annual mean contribution of 13% from biomass burning is comparable with previous PMF results using K$^+$ alone as the tracer. For example, Kim et al. (2003a, b) estimated 14% in Atlanta, and Liu et al. (2005) estimated 13% for the southeastern US. However, different seasonal patterns were found in our study and those PMF studies using K$^+$. Our PMF results suggest significant biomass burning contribution in winter (27%), and a small impact (2%) in summer, consistent with a Chemical Mass Balance analysis based on Molecular Markers (CMB-MM) using levoglucosan as the biomass-burning tracer (0.4% in summer) (Zheng et al., 2007). In contrast, previous PMF studies using K$^+$ predicted similar biomass-burning contributions for all the seasons (e.g. Kim et al., 2003a; Liu et al., 2005). The discrepancy depends on the choice of biomass burning tracer used. During periods of significant biomass burning emissions, typically the colder months, levoglucosan and K$^+$ tend to be correlated (Fig. 5) and the predicted biomass burning impacts are similar, using either levoglucosan or K$^+$ as the tracer. During these periods the biomass-burning source for K$^+$ appears to dominate over other sources. However, due to the relatively higher contributions of non-biomass burning K$^+$ sources observed in summer, it is expected that a source apportionment analysis using K$^+$ alone as a tracer would overestimate biomass burning emission during those periods.

Alternatively, levoglucosan may be substantially depleted in the summer due to photochemical oxidation reactions, leading to a large underestimation of summertime biomass-burning contribution (Hennigan et al., 2010; Hoffmann et al., 2010). This, however, is not consistent with the low fire counts in summer. Considering such uncertainties and that the results from previous studies might overestimate biomass burning contribution in summer (>10%) due to non-biomass burning K$^+$ sources (e.g. Kim et al., 2003a; Liu et al., 2005), we conclude that biomass burning contribution in summer is likely in the range of 2%–10%. In winter, levoglucosan is relatively stable and likely provides a reasonable estimate of biomass burning contributions to PM$_{2.5}$ levels. Based on a number of studies, including this work, typical winter contribution of biomass burning to PM$_{2.5}$ in the southeast (on a mass basis) is estimated to be near 25%, which in December and January appears to be mostly from residential wood-burning.

4 Conclusions

We investigate the biomass burning impact on PM$_{2.5}$ in the southeastern US in 2007 through analysis of chemical and physical properties of over 900 24-h integrated FRM Teflon filters collected by state regulatory agencies.

Two commonly used biomass burning tracers, i.e. levoglucosan and K$^+$, were compared in conjunction with MODIS Aqua fire counts. Levoglucosan concentrations showed large seasonal variations and correlated well with fire counts,

except in winter (January and December) when residential wood burning not detected by satellites led to increased levoglucosan. During these months, residential burning was estimated to contribute 2.6 µg/m^3, on average, to the ambient PM$_{2.5}$ mass throughout the region. K$^+$ concentrations exhibited no apparent seasonal trends and poor correlation with fire counts. Levoglucosan and K$^+$ correlated well ($r^2 = 0.59$) in winter, suggesting their common origin from biomass burning when its emissons were relatively high. In other seasons, K$^+$ poorly correlated with levoglucosan apparently due to additional K$^+$ sources other than biomass burning. Both levoglucosan and K$^+$ concentrations were higher at urban sites than at rural sites, with levoglucosan showing larger spatial variations than K$^+$. Comparison of K$^+$ and levoglucosan measurements in conjunction with fire count data suggests that K$^+$ was not a good tracer for biomass burning emissions due to multiple sources in addition to biomass burning, whereas levoglucosan was a reasonable indicator of biomass burning emissions, including emissions from wildfires and prescribed burnings, as well as emissions from wood combustion for residential heating. Although chamber study results show that levoglucosan reacts with the hydroxyl radical at atmospherically relevant concentrations (Hennigan et al., 2010), the good correlation between fire counts and levoglucosan concentrations suggest that this was not a large effect. This may be due to little biomass burning occurring in summer when this effect would be most important due to enhanced photochemistry, whereas in winter and spring when biomass burning emissions were higher and from local sources (e.g., residential or prescribed burning along with the occasional wildfire), relatively fresh emissions and slow photochemistry minimize this effect.

Positive Matrix Factorization (PMF) was applied to analyze PM$_{2.5}$ sources from the FRM data. Four factors were resolved, including a biomass burning factor characterized by high levels of levoglucosan and light absorbing compounds (brown carbon), a refractory component characterized by K$^+$, Na$^+$ and Mg^{2+}, and two secondary aerosol components, one charaterized by high WSOC, organic acids (oxalate) and light absorbing compounds, and the other by high SO$_4^{2-}$, NH$_4^+$, and WSOC. Secondary sulfate/WSOC component was the largest source of PM$_{2.5}$ in all seasons and combined, the two secondary sources dominated in all seasons. The biomass burning source contributed 13% to the PM$_{2.5}$ mass annually, 27% in winter, and only approximately 2% in summer. The refractory component contributed the least and was consistent throughout the year. Overall, the results show that K$^+$ is a poor biomass burning tracer especially in summer and can lead to large over-prediction of biomass burning contributions by source apportionment analyses. Extensive photochemical degradation of levoglucosan may lead to under-prediction of biomass buring in summer; however, in this study there was reasonable consistency between levoglucosan concentrations and summertime outdoor burning quantified by remotely sensed fire count data.

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