Characterization and Source Apportionment of Water-Soluble Organic Matter in Atmospheric Fine Particles (PM$_{2.5}$) with High-Resolution Aerosol Mass Spectrometry and GC−MS

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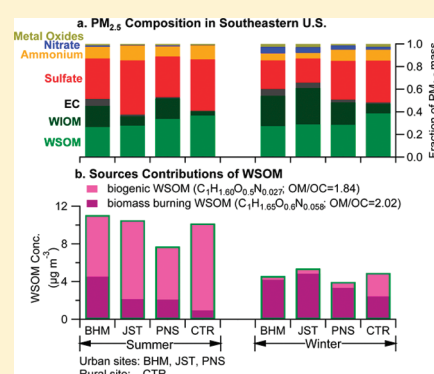[§]College of Environmental Sciences and Engineering, Peking University, Beijing 100871, People's Republic of China
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Ⓢ *Supporting Information*

ABSTRACT: Water-soluble organic matter (WSOM) in fine particles (PM$_{2.5}$) collected at one rural and three urban sites from the Southeastern Aerosol Research and Characterization network were characterized with a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR−ToF−AMS). These samples were also analyzed for a suite of molecular markers by Gas Chromatography−Mass Spectrometry (GC-MS) to assist in the interpretation of WSOM sources. The HR−ToF−AMS measurements allow a direct determination of the organic mass-to-carbon ratios (average $\pm1\sigma$ = 1.93 $\pm$ 0.12) and hence the quantification of WSOM on the same filters used to close the aerosol mass budget. WSOM constitutes a major fraction of total PM$_{2.5}$ mass (26−42%) and organic mass (50−90%) at all sites. The concentrations of WSOM are substantially higher in summer, mainly due to enhanced production of biogenic secondary organic aerosol (SOA). WSOM is composed mainly of oxygenated species with average oxygen-to-carbon (O/C) ratio of 0.56 ($\pm$0.08). Positive matrix factorization (PMF) of the high resolution mass spectra of WSOM identifies a less oxidized component (denoted as *l*OOA, O/C = 0.50) associated with biogenic SOA and a more oxidized component (denoted as *m*OOA, O/C = 0.60) associated with WSOM contributed by wood combustion. On average, *l*OOA accounts for 75 ($\pm$13) % of WSOM in summer while *m*OOA accounts for 78 ($\pm$21) % in winter, suggesting that WSOM in the southeastern U.S. is primarily contributed by SOA production from biogenic species in summer and by wood burning emissions in winter. This work also demonstrates the utility of HR−ToF−AMS for investigating the bulk chemical composition of WSOM as well as for evaluating its source contributions.

a. PM$_{2.5}$ Composition in Southeastern U.S.

b. Sources Contributions of WSOM
biogenic WSOM (C$_1$H$_{1.60}$O$_{0.5}$N$_{0.027}$; OM/OC=1.84)
biomass burning WSOM (C$_1$H$_{1.65}$O$_{0.6}$N$_{0.058}$; OM/OC=2.02)
Urban sites: BHM, JST, PNS
Rural site: CTR

1. INTRODUCTION

Water-soluble organic matter (WSOM) has often been found to be an important component of atmospheric fine particles and is likely a determinant of their impacts on visibility, human health, and climate.[1,2] Airborne particulate organic matter (aka, organic aerosol, OA) can be divided into primary OA (POA) emitted directly to the atmosphere (e.g., from combustion sources) and secondary OA (SOA) formed in the atmosphere from reactions of volatile organic compounds (VOCs). Recent studies indicate that SOA formed from both anthropogenic and biogenic VOCs (e.g., refs 1,3−5) and POA emitted from biomass burning (e.g., refs 5−7) may be the major contributors to WSOM in fine particles.

WSOM absorbs water at ambient humidity, affecting the water content in aerosols and thus their optical and cloud nucleating properties.[8,9] WSOM may also influence the microphysical and radiative properties of clouds [2,9] as some compounds are surface-active [10] and light absorbing.[11] While characterizing the composition of WSOM is important for understanding aerosol's climatic and health effects, it is challenging since WSOM may contain numerous polar compounds with a wide range of physical chemical properties.[1] Analysis of individual compounds typically explains <20% of the WSOM mass (e.g., refs 9,12−14). Bulk characterization approaches, such as functional group analysis using nuclear magnetic resonance (NMR),[12,15,16] infrared (IR) spectroscopy,[17] and chemical class analyses,[7,15] have been proven effective at accounting for the majority of the WSOM mass in atmospheric particles. These studies also reveal that WSOM is typically dominated by compounds with oxygenated and nitrogenated functional groups (e.g., carbonyl, carboxylate, hydroxyl, and amino). However, knowledge of the chemical properties and sources of WSOM is still limited.

In recent years, Aerodyne Aerosol Mass Spectrometers (AMSs) have been applied widely for characterizing OA in both ambient and laboratory studies (ref 18 and references therein). Via thermal vaporization and 70 ev electron impact (EI) ionization, the AMS quantifies the total mass of OM in particles and at the same time provides average ensemble mass spectra that bear information on aerosol composition. The HR—AMS, i.e., AMS built with a high-resolution time-of-flight mass spectrometer, is further able to determine the elemental ratios and the oxidation states of OM.[19−21] In addition to studies of ambient aerosol particles, HR—AMS has also been successfully adapted to characterize OM in aqueous samples. For instance, a recent study of ours highlighted the utility of HR—AMS for elucidating the chemical composition and formation mechanisms of WSOM from aqueous-phase reactions of phenolic VOCs.[22]

In this work, we combine high-resolution aerosol mass spectrometry with Gas Chromatography—Mass Spectrometry (GC—MS) and Ion Chromatography (IC) to characterize the composition and sources of WSOM in $PM_{2.5}$ collected from the southeastern United States (SE U.S.). Herein we report: (1) the mass concentrations, bulk compositions, and average empirical formulas of WSOM; (2) the variations of WSOM characteristics between urban and rural locations and between winter and summer seasons; (3) the deconvolution and quantification of distinct WSOM factors using Positive matrix factorization (PMF) of the high resolution spectra of HR—AMS; and (4) the investigation of the sources of WSOM based on PMF and tracer—based source apportionment approaches.

2. EXPERIMENTAL METHODS

2.1. Sample Collection and Extraction. The 24-h integrated $PM_{2.5}$ samples were collected on quartz filters using high volume samplers in 2004 and 2005 at three urban sites, i.e., North Birmingham, Alabama (BHM), Jefferson Street, Atlanta, Georgia (JST), and Pensacola, Florida (PNS), and one rural site— Centreville, Alabama (CTR) as part of the Southeastern Aerosol Research and Characterization (SEARCH) air quality monitoring network.[23] In this work, a total of 24 quartz filter samples (6 at each site) collected in summer (20 June, 20 July, and 19 August) and winter (8 December, 29 December, and 21 February) were analyzed. For each filter sample, one round punch (diameter: 1 in.) for average ambient concentrations of OC > 5 $\mu g\ m^{-3}$ or two punches for OC < 5 $\mu g\ m^{-3}$ was sonicated in 15 mL deionized—distilled (DD) water for 60 min. The solution was then filtered with 0.45 μm Acrodisc syringe filters. WSOM in this work is thus operationally defined as any organic material that can pass through the filter. A total number of 8 field blank samples (2 at each site; 1 from winter and 1 from summer) were also extracted and analyzed in the same way as the ambient samples. All of the data reported in this work were blank-corrected using the results from corresponding blank filters.

2.2. HR—AMS Analysis. Detailed procedures for HR—AMS analysis of liquid samples are given in Sun et al.[22] Briefly, aliquots of aerosol extracts were aerosolized using a constant output atomizer (TSI, Model 3076), dried by a diffusion dryer, and then analyzed by the HR—AMS. Between every two samples, DD-water was aerosolized and analyzed in the same way as an analytical blank. The HR—AMS was operated under both the high sensitive V-mode and the high mass resolution W-mode (~6000). Mass spectra up to m/z 600 were acquired for both modes.

The HR—AMS data were analyzed using the AMS data analysis software Squirrel v1.46[24] and Pika v1.06 written in Igor Pro (Wavemetrics, Lake Oswego, OR).[20] Elemental analysis was performed on the high-resolution mass spectra (HRMS) up to m/z 150 to determine the O/C, H/C, N/C, and organic mass-to-carbon (OM/OC) ratios of WSOM. The organic CO^+, H_2O^+, HO^+, and O^+ signals were scaled to the measured CO_2^+ signal: $CO^+ = 0.7 \times CO_2^+$ and $H_2O^+ = CO_2^+$ ($HO^+ = 0.25 \times H_2O^+$ and $O^+ = 0.04 \times H_2O^+$) based on evaluations of the H_2O^+ and CO^+ signals in the samples (see Section 1 in the Supporting Information, SI). Note that elemental analysis using the ratios suggested by Aiken et al.[19] for ambient OA (i.e., $CO^+ = CO_2^+$ and $H_2O^+ = 0.225 \times CO_2^+$) would report 22%, 14%, 2%, and 10% lower O/C, H/C, N/C, and OM/OC, respectively, for the WSOM of this work.

2.3. Chemical Analyses. Ionic species (e.g., SO_4^{2-}, NO_3^-, Cl^-, $HCOO^-$, CH_3COO^-, $C_2O_4^{2-}$, NH_4^+, K^+, Na^+, Mg^{2+}, and Ca^{2+}) were analyzed by two Ion Chromatographs (Metrohm AG, Switzerland) equipped with a Metrosep A Supp 5−250 anion column and a Metrosep C 4−150 cation column, respectively. The total organic carbon (TOC) contents in the extracts were analyzed by a Sievers 900 TOC Analyzer (GE Analytical Instruments, Boulder, CO). The recoveries for the IC and TOC analyses (i.e., the amounts of added (spiked) analyte recovered during analyses) are generally within 95−110% and the relative standard errors for replicate analyses are always within 3%.

The same filters were also analyzed with GC—MS for molecular markers, e.g., alkanes, branch-alkanes, levoglucosan— a tracer for biomass burning OA (BBOA), and biogenic SOA tracers—2-methyltetrols and cis-pinonic acid (Table S1 of the SI). Briefly, filter samples were spiked with deuterated internal standards and extracted twice with hexane and three times with 2:1 mixture of benzene and 2-propanol. The extracts were then filtered and concentrated. Organic acids were converted to their methyl analogue by adding diazomethane before GC—MS analysis. Details on GC—MS analysis and QA/QC measures including recovery tests, field and laboratory blank analysis, and method detection limits can be found elsewhere.[23,25]

In addition, OC and elemental carbon (EC) were analyzed using the thermo-optical transmittance method.[25] Trace gases and meteorology data were downloaded from the SEARCH public data archive (ftp://mail.atmospheric-research.com).

2.4. Determination of WSOM and WIOM Concentrations. The mass concentrations of WSOM and water-insoluble OM (WIOM) and the average OM/OC ratio of organic matter (= WSOM + WIOM) in $PM_{2.5}$ are estimated accordingly:

$$WSOM = WSOC \times OM/OC_{WSOM} \tag{1}$$

$$WIOM = (OC - WSOC) \times 1.3 \tag{2}$$

$$OM/OC_{OM} = (WSOM + WIOM)/OC \tag{3}$$

where WSOC is the carbon content determined in the filter extract, OM/OC_{WSOM} is the OM/OC ratio of WSOM determined by the HR—AMS, OC is from filter measurements using thermo-optical transmittance method, 1.3 is the estimated OM/OC of WIOM, and OM/OC_{OM} denotes the average OM/OC ratio of organic matter in $PM_{2.5}$. Note that 1.3 is estimated based on the OM/OC ratios of POA (~1.2−1.4) determined from high resolution mass spectrometry[19,26] and those (~1.1 − 1.5)
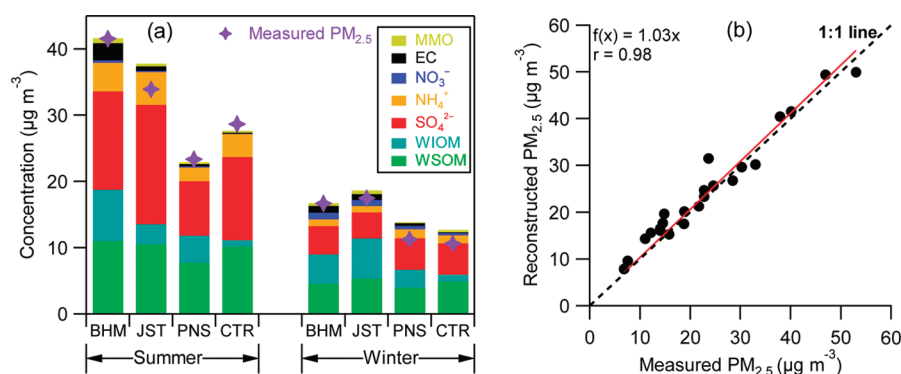
Figure 1. (a) Average chemical composition of $PM_{2.5}$ at three urban sites (BHM, JST, and PNS) and one rural site (CTR) and (b) comparison of the reconstructed $PM_{2.5}$ mass concentrations to the measured concentrations by a Tapered Element Oscillating Microbalance (TEOM). Reconstructed $PM_{2.5}$ mass = MMO + EC + NO_3^- + NH_4^+ + $SO4^{2-}$ + WIOM + WSOM. The data for MMO (i.e., major metal oxides) were obtained from the SEARCH Public Data Archive (ftp://mail.atmospheric-research.com).

calculated from the molecular formulas of less water-soluble OA compounds measured in ambient air.[1,27]

2.5. Source Contribution Analysis. To investigate the sources of WSOM, we performed PMF analysis [28] on the HRMS of WSOM using the PMF Evaluation Toolkit (PET) v2.02.[29] Although limited by the number of samples, the variances among samples are significant, allowing us to obtain physically meaningful PMF results. After thorough evaluations of the solutions, including comparing the mass spectra of the factors from different solutions vs previously reported reference spectra and the time series of the factors vs external tracers, the 2-factor solution with the rotational forcing parameter (fpeak) = 0 was chosen. The 3-factor and 4-factor solutions (Figure S2 of the SI) show some unrealistic split and possibly artifacts due to limited number of samples thus variance.

We also applied the EC-tracer method [30] to estimate the concentrations of primary OC (POC) and secondary OC (SOC):

$$POC = (OC/EC)_{pri} \times EC + POC_{NC} \qquad (4)$$

$$SOC = OC - POC \qquad (5)$$

where $(OC/EC)_{pri}$ is the OC/EC ratio of combustion POC and POC_{NC} denotes the noncombustion POC. Due to limited number of samples, we used the values of $(OC/EC)_{pri}$ and POC_{NC} determined from the York regression technique based on the annual hourly OC and EC data at the same sites in 2002 by Saylor et al.[31] The $(OC/EC)_{pri}$ and POC_{NC} values along with details on how the values are determined are given in Table S2 of the SI. In addition, to characterize the impact of biomass burning on WSOC and SOC, we identified samples with significant BB impact based on elevated levoglucosan concentrations (>160 ng m^{-3}) and the AMS spectral signature for BBOA — ratio of m/z 60 to organic signal (>0.3%).

3. RESULTS AND DISCUSSION

3.1. Mass Concentrations and Variation Patterns of WSOM and WIOM. Figure 1a presents the average chemical composition of $PM_{2.5}$ acquired at one rural (CTR) and three urban (BHM, JST, and PNS) sites. Organic species (WSOM + WIOM) account for 40−55% of the $PM_{2.5}$ mass at all sites (Table 1). Good chemical mass closure is achieved; the reconstructed $PM_{2.5}$ mass concentrations agree well with the

Table 1. Summary of the Average ($\pm 1\sigma$) Concentrations and Mass Fractions of WSOM and WIOM in $PM_{2.5}$ Collected from the Southeastern U.S.

	urban		rural	
	Summer	Winter	Summer	Winter
concentrations (μg m^{-3})				
WSOM[a]	9.8 ± 3.1	4.6 ± 0.9	10 ± 2.5	4.9 ± 0.8
WIOM[b]	5.0 ± 3.9	4.4 ± 2.5	1.0 ± 0.4	1.1 ± 0.2
OM[c]	15 ± 5.9	9.1 ± 3.2	11 ± 2.4	6.0 ± 1.0
mass ratios				
WSOM/OM	0.70 ± 0.15	0.54 ± 0.11	0.90 ± 0.04	0.82 ± 0.004
WIOM/OM	0.30 ± 0.15	0.46 ± 0.11	0.10 ± 0.04	0.18 ± 0.004
OM/$PM_{2.5}$	0.43 ± 0.09	0.55 ± 0.13	0.40 ± 0.04	0.51 ± 0.17

[a] WSOM = WSOC $\times$ OM/OC$_{WSOM}$ [b] WIOM = 1.3 $\times$ (OC − WSOC) [c] OM = WSOM + WIOM

concentrations measured gravimetrically ($r = 0.98$, slope =1.03; Figure 1b), demonstrating that the WSOM and WIOM are quantified well in this work. Overall, WSOM constitutes a larger fraction of the organic mass in summer and at the rural site (Table 1). The mass concentrations of WSOM are similar among sites but are substantially higher in summer than in winter (9.9 ± 2.8 vs 4.7 ± 0.8 μg m^{-3}). Comparatively, WIOM concentrations are similar between seasons but they are on average more than 4 times higher in urban (4.7 ± 3.2 μg m^{-3}) than in rural atmospheres (1.1 ± 0.3 μg m^{-3}).

The higher WSOM concentrations in summer are likely due to active SOA formation associated with higher O_3, solar radiation, and biogenic VOC emissions during the warm season. Indeed, WSOM correlates well with both sulfate ($r = 0.82$; Figure 2c)— an important secondary inorganic species produced mainly on regional scale and 2-methyltetrols ($r = 0.94$; Figure S3 of the SI)— the tracer species for biogenic SOA.[32] In addition, the carbon contents of WSOM (i.e., WSOC) correlate with the secondary organic carbon (SOC) concentrations estimated based on the EC-tracer method (see Section 2.5). The agreement between WSOC and SOC is especially good in absence of biomass burning (BB; $r = 0.97$; slope = 0.92; Figure 2a). One reason
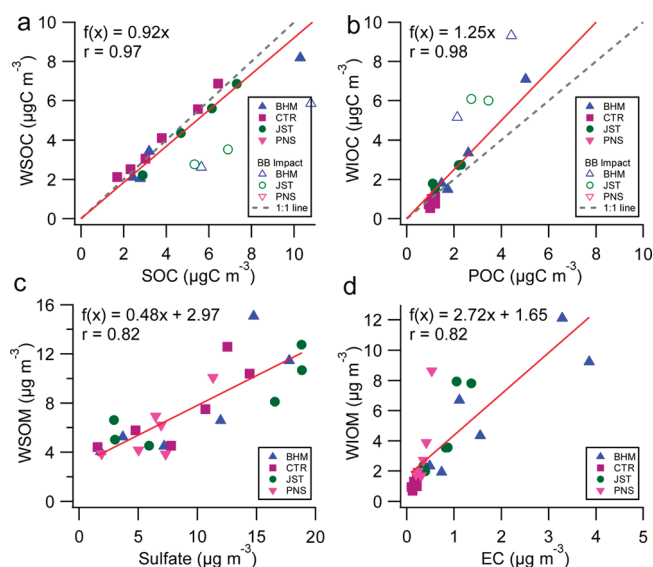
Figure 2. Scatter plots that compare (a) WSOC vs SOC, (b) WIOC vs POC, (c) WSOM vs Sulfate, and (d) WIOM vs EC. Note that the linear regressions shown in (a) and (b) do not include samples influenced by biomass burning, which are shown in open symbols.

for the deviations of the BB-impacted samples is that we used $(OC/EC)_{pri}$ representative of fossil fuel combustions $(1.05-2.41)$ for SOC calculation although the $(OC/EC)_{pri}$ of BBOA are likely much higher. For example, the OC/EC ratio observed in prescribed burning in the SE U.S. is ~15.[33] Another reason for the deviation is elevated contributions of BBOA to WSOC in the BB-impacted samples (see discussion in Section 3.3).

In contrast, WIOM appears to be strongly associated with primary combustion emissions, showing tight correlation with EC ($r = 0.82$; Figure 2d), CO ($r = 0.75$), and NO_x ($r = 0.68$; Figure S3 of the SI) but poor correlations with sulfate ($r = 0.07$) and methyltetrols ($r = 0.15$). The carbon contents of WIOM (i.e., WIOC) also correlate well with the concentrations of primary organic carbon (POC) estimated using the EC-tracer method (Figure 2b). In addition, the fraction of WIOM in the BB-impacted samples is $32 \pm 7\%$ of OM, ~2 times higher compared to the other samples (WIOM/OM = $16 \pm 10\%$).

Overall, there are strong indications that WSOM is mainly associated with secondary aerosol species while WIOM with primary combustion emissions. Similar results were observed in Tokyo,[3] where WIOM was found to correlate well with HOA (a surrogate for combustion POA) and WSOM with oxygenated OA (a surrogate for SOA[34]). Furthermore, the paired samples t test shows that the differences of WIOM and EC between urban and rural sites are significant ($p < 0.05$), corroborating the association of WIOM with local emissions. Both WSOM and sulfate, however, are not significantly different among sites ($p > 0.05$, mostly >0.1), indicating the regional characteristic of WSOM.

3.2. Bulk Chemical Composition and Elemental Ratios of WSOM. Figure 3 summarizes the average HRMS and the elemental ratios of WSOM at each site as well as the comparisons of them between summer and winter. The HRMS of WSOM are overall similar among all sites, showing the characteristics of ambient OOA.[35,36] The average ($\pm 1\sigma$) O/C ratios of WSOM are 0.52 ± 0.03 in summer and 0.59 ± 0.11 in winter, in the range of the O/C ratios of semivolatile OOA (0.35 ± 0.14) and low-volatility OOA (0.73 ± 0.14) observed in a number of

different atmospheric environments.[36,37] The N/C ratios of WSOM vary between 0.03 and 0.06, systematically higher than the average value (~0.01) of ambient OA.[19,38,39] The major nitrogen-containing ions in the HRMS of WSOM include CH_4N^+, $C_2H_6N^+$, $C_3H_8N^+$, and $CHNO^+$ (Figure 3), suggesting the dominance of reduced nitrogen functional groups including amines, amino acids, and amides (Sun and Zhang, in preparation). The hydrophilic properties of these N-containing functional groups[1] may explain their enrichment in the water-soluble fraction of particles.

The average empirical formulas of WSOM on a one-carbon basis during summer and winter are $C_{1.0}H_{1.6}O_{0.5}N_{0.04}$ and $C_{1.0}H_{1.6}O_{0.6}N_{0.05}$, corresponding to OM/OC ratios of 1.88 (± 0.04) and 1.98 (± 0.15), respectively. Similar OM/OC ratios ($1.8-2.0$) were determined for the water-soluble constituents of ambient OA using ^1H NMR spectroscopy[5] and an elemental analyzer.[17] The OM/OC ratios for total OM (WSOM + WIOM) are estimated at 1.64 (± 0.11) (urban) and 1.77 (± 0.08) (rural), consistent with the values suggested by Turpin and Lim.[27]

WSOM in the winter samples appear to be influenced by BB, displaying elevated MS peaks at m/z 60 ($C_2H_4O_2^+$) and 73 ($C_3H_5O_2^+$)—the AMS spectral markers for BBOA.[26,40] In contrast, the HRMS of WSOM in the summer samples suggest the presence of biogenic SOA, consistently showing higher signals at m/z 43 (mostly $C_2H_3O^+$) with an overall pattern similar to ambient and chamber produced biogenic SOA.[41]

3.3. Determination of the Sources of WSOM. PMF analysis was performed on the HRMS of WSOM to examine the source contributions of WSOM in fine particles. Two components were identified, including a less oxidized and a more oxidized WSOM component denoted as lOOA and mOOA, respectively. The O/C ratios of lOOA (= 0.50) and mOOA (= 0.60) are similar to the average ratios of ambient OOAs observed at various locations.[36,37] As shown in Figure 4, these two components are significantly different in mass spectral patterns and season variation trends due to distinct source attributions.

The mass spectrum of lOOA closely resembles those of biogenic SOAs formed from biogenic VOC precursors in chamber experiments ($r = 0.97-0.99$, Figures 4a and S4 of the SI)[41,42] and ambient OA with significant biogenic influences.[38,43] All these spectra are characterized by prominent peaks at m/z 43 (mainly $C_2H_3O^+$), 44 (mainly CO_2^+ with some $C_2H_4O^+$), and 29 (mainly CHO^+ with some $C_2H_5^+$). In addition, lOOA correlates well with secondary species, including biogenic SOA tracers ($r = 0.94$), O_3 ($r = 0.71$), and sulfate ($r = 0.81$; Figure 4d). Together, these observations suggest that lOOA is associated with SOA formed from the oxidation of biogenic VOCs. Further support for this association is that the mass concentration of lOOA is substantially higher in summer ($7.4 \pm 2.7 \mu g m^{-3}$) than in winter ($1.0 \pm 1.0 \mu g m^{-3}$) (Figure 4b), reflecting the intensive emissions of biogenic VOCs in summer in the SE U.S.[4,44] The contributions of lOOA to WSOM in summer are $70 \pm 11\%$ and $90 \pm 8\%$ at urban and rural sites, respectively, consistent with previous reports that over 50% of the WSOC is biogenic during summer in the SE U.S.[4,45]

Chhabra et al.[42] observed a distinct peak at m/z 75 ($C_3H_7O_2^+$) in the HR-AMS spectra of SOA formed from photo-oxidation of isoprene under high-NO_x conditions and related it to the fragmentation of 2-methyltetrols via the cleavage of the C—C bond.[46] While $C_3H_7O_2^+$ is only a small peak in the HR-AMS spectra of the WSOM (<0.2% of the total signal; Figure 3), it correlates tightly with 2-methyltetrols ($r = 0.98$) and is almost completely apportioned to the lOOA component—the
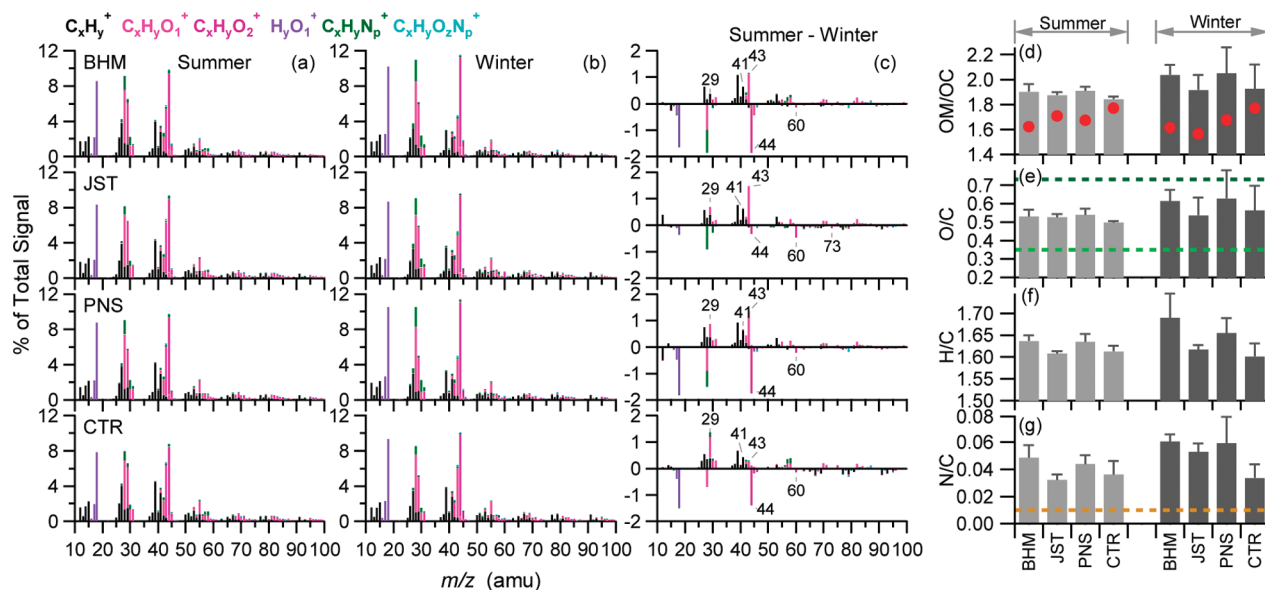
Figure 3. Average HRMS of WSOM colored by the contributions of six ion categories at different sites in (a) summer and (b) winter. (c) The spectral differences of WSOM between summer and winter. (d)−(g) The average OM/OC, O/C, H/C, and N/C ratios of WSOM at each site in summer and winter. The red dots in (d) indicate the average OM/OC ratios of total OM (= WSOM + WIOM) for this work. The dashed lines in (e) show the average O/C ratios of ambient LV-OOA (0.73) and SV-OOA (0.35) components from other studies.[36,37] The dash line in (g) indicates the typical N/C ratio determined for ambient OA.
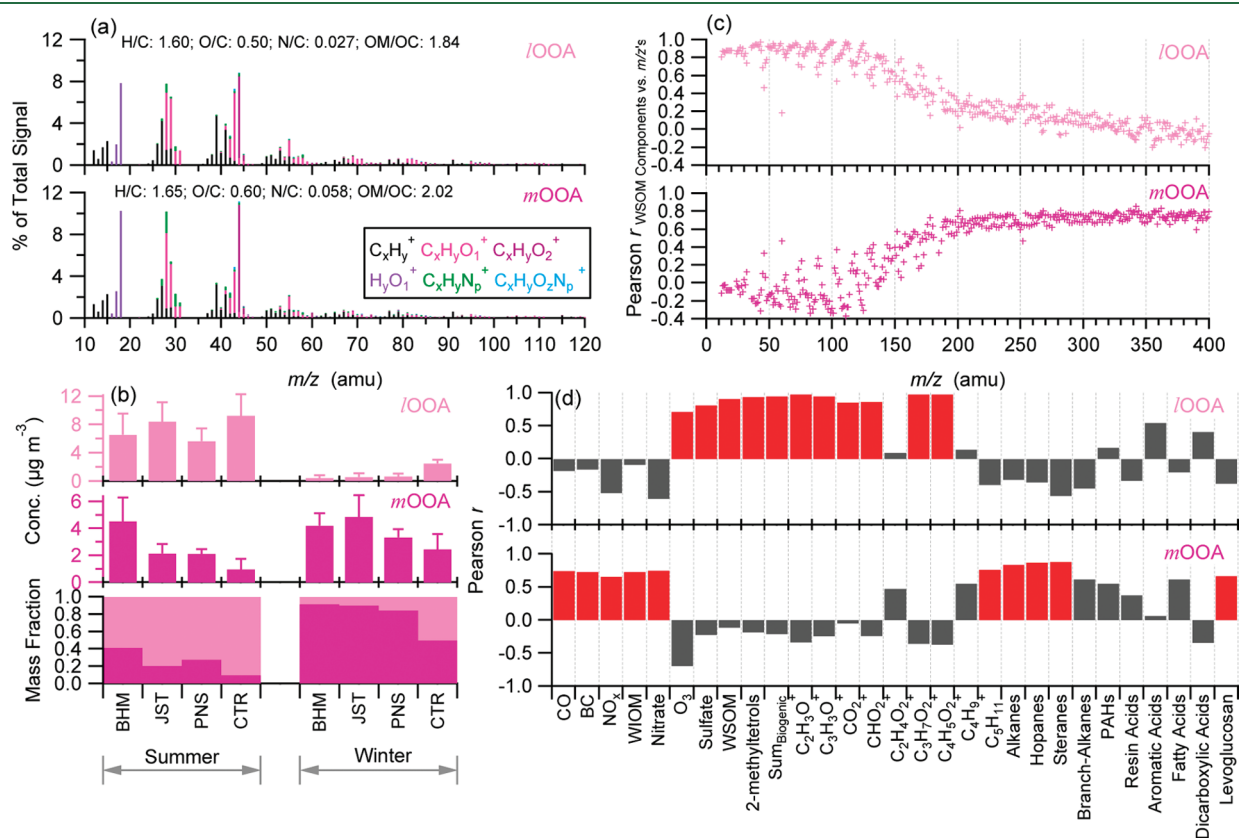

Figure 4. (a) The HRMS of the less-oxidized (*l*OOA) and the more oxidized (*m*OOA) WSOM components. The spectra are colored by the contributions of six ion categories with calculated elemental ratios shown in the legend. (b) The average mass concentrations and fractions of *l*OOA and *m*OOA at urban and rural sites in summer and winter. (c) Covariance plot of *l*OOA and *m*OOA vs individual *m/z*. (d) Covariance plot of *l*OOA and *m*OOA vs tracer species with the red bars highlighting $r > 0.65$ (scatter plots are shown in Figure S5 of the SI). Note: Sum$_{biogenic}$ = 2-methyltetrols + *cis*-pinonic acid.

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Pearson's r between $C_3H_7O_2^+$ and lOOA is 0.97 (Figure 4d). These results indicate that $C_3H_7O_2^+$ may possibly be used as an AMS spectral tracer for isoprene-derived biogenic SOA. The mass ratio of $C_3H_7O_2^+$ to lOOA is 0.16%, a value that might be useful for estimating isoprene-derived biogenic SOA based on HR–AMS data.

The more oxidized WSOM component (i.e., mOOA) shows an overall similar spectra pattern to those of ambient OOA,[29,35] yet with elevated m/z 60 (~0.5% of total signal) compared to the level (<0.3% of total signal) in absence of significant BB impact.[36] As shown in Figure 4d, mOOA correlates well with most of the primary emission tracer species (e.g., CO, BC, NO$_x$, and WIOM, $r = 0.66-0.74$) and poorly correlates with species representative of secondary aerosols such as sulfate ($r = -0.22$) and 2-methyltetrols ($r = -0.19$). In addition, mOOA correlates well ($r = 0.67-0.88$, Figure 4d) with levoglucosan—a GC–MS molecular marker for biomass burning emissions and alkanes, hopanes, and steranes, all of which were found significantly elevated in samples from prescribed forest fire.[33] Specifically, the winter samples show an average levoglucosan-to-mOOA ratio of 92 ($\pm$41) ng m^{-3} μgC^{-1}, very close to the 99 ng m^{-3} μgC^{-1} (levoglucosan/WSOC) observed from an open forest fire in the SE U.S.[25,33] These results together indicate that mOOA might be primarily contributed by the water-soluble species in BBOA, especially during wintertime. Indeed, the mOOA concentrations are significantly higher in winter than in summer (3.7 vs 2.4 μg m^{-3}), likely due to the ubiquitous prescribed burning[47,48] and residential wood burning for heating. The observation that mOOA accounts for $88 \pm 10\%$ and $48 \pm 16\%$ of the WSOM mass in winter at urban and rural sites, respectively, are similar to the findings from a previous source apportionment study, which reported that wood combustion is the primary contributor to OC in winter in the SE U.S.[49]

Recent studies reported that aged BBOA may comprise a significant fraction of SOA and WSOC.[6,33] Chamber experiments also show that photochemical processing can lead to a quick aging of wood smoke to OOA.[50] Compared to the BBOA component resolved from PMF analysis of ambient AMS data,[51] the water-soluble fraction of BBOA (i.e., mOOA identified in this study) is more oxidized with higher O/C and OM/OC ratios, possibly due to the significant contribution of mono-, dicarboxylic acids to BBOA.[6,12] However, mOOA may also be contributed by highly aged, regional OOA, which is likely the case for the summertime aerosols. In addition, as shown in Figure 4c, while lOOA correlates with most of the m/z's less than 100 amu, mOOA correlates much better with large m/z's (>200 amu). This is an indication that the BB-impacted WSOM likely comprises a significant amount of high molecular weight humic-like substances (e.g., polycarboxylic acids).[6]

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Additional information including three tables and five figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Saxena, P.; Hildemann, L. M. Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds. *J. Atmos. Chem.* **1996**, *24* (1), 57–109.

(2) Ervens, B.; Feingold, G.; Kreidenweis, S. M. Influence of water-soluble organic carbon on cloud drop number concentration. *J. Geophys. Res.* **2005**, *110*, D18211.

(3) Kondo, Y.; Miyazaki, Y.; Takegawa, N.; Miyakawa, T.; Weber, R.; Jimenez, J.; Zhang, Q.; Worsnop, D. R. Oxygenated and water-soluble organic aerosols in Tokyo. *J. Geophys. Res.* **2007**, *112*, D01203, doi:10.1029/2006JD007056.

(4) Weber, R. J.; Sullivan, A. P.; Peltier, R. E.; Russell, A.; Yan, B.; Zheng, M.; de Gouw, J.; Warneke, C.; Brock, C.; Holloway, J. S.; Atlas, E. L.; Edgerton, E. A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States. *J. Geophys. Res.* **2007**, *112*, D13302.

(5) Decesari, S.; Mircea, M.; Cavalli, F.; Fuzzi, S.; Moretti, F.; Tagliavini, E.; Facchini, M. C. Source Attribution of Water-Soluble Organic Aerosol by Nuclear Magnetic Resonance Spectroscopy. *Environ. Sci. Technol.* **2007**, *41* (7), 2479–2484.

(6) Mayol-Bracero, O. L.; Guyon, P.; Graham, B.; Roberts, G.; Andreae, M. O.; Decesari, S.; Facchini, M. C.; Fuzzi, S.; Artaxo, P. Water-soluble organic compounds in biomass burning aerosols over Amazonia—2. Apportionment of the chemical composition and importance of the polyacidic fraction. *J. Geophys. Res.-Atmos.* **2002**, *107* (D20), 8091.

(7) Sullivan, A. P.; Weber, R. J. Chemical characterization of the ambient organic aerosol soluble in water: 2. Isolation of acid, neutral, and basic fractions by modified size-exclusion chromatography. *J. Geophys. Res.* **2006**, *111* (D5), D05315.

(8) Saxena, P.; Hildemann, L. M.; McMurry, P. H.; Seinfeld, J. H. Organics alter hygroscopic behavior of atmospheric particles. *J. Geophys. Res.* **1995**, *100* (D9), 18755–18770.

(9) Facchini, M. C.; Mircea, M.; Fuzzi, S.; Charlson, R. J. Cloud albedo enhancement by surface-active organic solutes in growing droplets. *Nature* **1999**, *401* (6750), 257–259.

(10) Facchini, M. C.; Decesari, S.; Mircea, M.; Fuzzi, S.; Loglio, G. Surface tension of atmospheric wet aerosol and cloud/fog droplets in relation to their organic carbon content and chemical composition. *Atmos. Environ.* **2000**, *34* (28), 4853–4857.

(11) Hecobian, A.; Zhang, X.; Zheng, M.; Frank, N.; Edgerton, E. S.; Weber, R. J. Water-soluble organic aerosol material and the light-absorption characteristics of aqueous extracts measured over the southeastern United States. *Atmos. Chem. Phys.* **2010**, *10* (13), 5965–5977.

(12) Graham, B.; Mayol-Bracero, O. L.; Guyon, P.; Roberts, G. C.; Decesari, S.; Facchini, M. C.; Artaxo, P.; Maenhaut, W.; Koll, P.; Andreae, M. O. Water-soluble organic compounds in biomass burning aerosols over Amazonia —1. Characterization by NMR and GC—MS. *J. Geophys. Res.-Atmos.* **2002**, *107* (D20), 8047.

(13) Decesari, S.; Fuzzi, S.; Facchini, M. C.; Mircea, M.; Emblico, L.; Cavalli, F.; Maenhaut, W.; Chi, X.; Schkolnik, G.; Falkovich, A.; Rudich, Y.; Claeys, M.; Pashynska, V.; Vas, G.; Kourtchev, I.; Vermeylen, R.; Hoffer, A.; Andreae, M. O.; Tagliavini, E.; Moretti, F.; Artaxo, P. Characterization of the organic composition of aerosols from Rondônia, Brazil, during the LBA-SMOCC 2002 experiment and its representation through model compounds. *Atmos. Chem. Phys.* **2006**, *6* (2), 375–402.

(14) Zhang, Q.; Anastasio, C. Free and combined amino compounds in atmospheric fine particles ($PM_{2.5}$) and fog waters from Northern California. *Atmos. Environ.* **2003**, *37*, 2247–2258.

(15) Decesari, S.; Facchini, M. C.; Fuzzi, S.; McFiggans, G. B.; Coe, H.; Bower, K. N. The water-soluble organic component of size-segregated aerosol, cloud water and wet depositions from Jeju Island during ACE-Asia. *Atmos. Environ.* **2005**, *39* (2), 211–222.

(16) Sannigrahi, P.; Sullivan, A. P.; Weber, R. J.; Ingall, E. D. Characterization of water-soluble organic carbon in urban atmospheric aerosols using solid-state 13C NMR spectroscopy. *Environ. Sci. Technol.* **2005**, *40* (3), 666–672.

(17) Kiss, G.; Varga, B.; Galambos, I.; Ganszky, I. Characterization of water-soluble organic matter isolated from atmospheric fine aerosol. *J. Geophys. Res.* **2002**, *107*, 8339.

(18) Canagaratna, M.; Jayne, J.; Jimenez, J. L.; Allan, J. A.; Alfarra, R.; Zhang, Q.; Onasch, T.; Drewnick, F.; Coe, H.; Middlebrook, A.; Delia, A.; Williams, L.; Trimborn, A.; Northway, M.; Kolb, C.; Davidovits, P.; Worsnop, D. Chemical and microphysical characterization of aerosols via aerosol mass spectrometry. *Mass Spectrom. Rev.* **2007**, *26*, 185–222.

(19) Aiken, A. C.; DeCarlo, P. F.; Kroll, J. H.; Worsnop, D. R.; Huffman, J. A.; Docherty, K. S.; Ulbrich, I. M.; Mohr, C.; Kimmel, J. R.; Sueper, D.; Sun, Y.; Zhang, Q.; Trimborn, A.; Northway, M.; Ziemann, P. J.; Canagaratna, M. R.; Onasch, T. B.; Alfarra, M. R.; Prevot, A. S. H.; Dommen, J.; Duplissy, J.; Metzger, A.; Baltensperger, U.; Jimenez, J. L. O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. *Environ. Sci. Technol.* **2008**, *42* (12), 4478–4485.

(20) DeCarlo, P. F.; Kimmel, J. R.; Trimborn, A.; Northway, M. J.; Jayne, J. T.; Aiken, A. C.; Gonin, M.; Fuhrer, K.; Horvath, T.; Docherty, K. S.; Worsnop, D. R.; Jimenez, J. L. Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. *Anal. Chem.* **2006**, *78*, 8281–8289.

(21) Kroll, J. H.; Donahue, N. M.; Jimenez, J. L.; Kessler, S. H.; Canagaratna, M. R.; Wilson, K. R.; Altieri, K. E.; Mazzoleni, L. R.; Wozniak, A. S.; Bluhm, H.; Mysak, E. R.; Smith, J. D.; Kolb, C. E.; Worsnop, D. R. Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol. *Nature Chem.* **2011**, *3* (2), 133–139.

(22) Sun, Y. L.; Zhang, Q.; Anastasio, C.; Sun, J. Insights into secondary organic aerosol formed via aqueous-phase reactions of phenolic compounds based on high resolution mass spectrometry. *Atmos. Chem. Phys.* **2010**, *10* (10), 4809–4822.

(23) Zheng, M.; Cass, G. R.; Schauer, J. J.; Edgerton, E. S. Source apportionment of $PM_{2.5}$ in the southeastern United States using solvent-extractable organic compounds as tracers. *Environ. Sci. Technol.* **2002**, *36* (11), 2361–2371.

(24) Sueper, D. ToF-AMS analysis software online available at: http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html. 2010.

(25) Ding, X.; Zheng, M.; Yu, L.; Zhang, X.; Weber, R. J.; Yan, B.; Russell, A. G.; Edgerton, E. S.; Wang, X. Spatial and seasonal trends in biogenic secondary organic aerosol tracers and water-soluble organic carbon in the southeastern United States. *Environ. Sci. Technol.* **2008**, *42* (14), 5171–5176.

(26) Mohr, C.; Huffman, J. A.; Cubison, M. J.; Aiken, A. C.; Docherty, K. S.; Kimmel, J. R.; Ulbrich, I. M.; Hannigan, M.; Jimenez, J. L. Characterization of primary organic aerosol emissions from meat cooking, trash burning, and motor vehicles with high-resolution aerosol mass spectrometry and comparison with ambient and chamber observations. *Environ. Sci. Technol.* **2009**, *43* (7), 2443–2449.

(27) Turpin, B. J.; Lim, H. J. Species contributions to $PM_{2.5}$ mass concentrations: Revisiting common assumptions for estimating organic mass. *Aerosol Sci. Technol.* **2001**, *35* (1), 602–610.

(28) Paatero, P.; Tapper, U. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* **1994**, *5*, 111–126.

(29) Ulbrich, I. M.; Canagaratna, M. R.; Zhang, Q.; Worsnop, D. R.; Jimenez, J. L. Interpretation of organic components from positive matrix factorization of aerosol mass spectrometric data. *Atmos. Chem. Phys.* **2009**, *9* (9), 2891–2918.

(30) Turpin, B. J.; Huntzicker, J. J. Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS. *Atmos. Environ.* **1995**, *29* (23), 3527–3544.

(31) Saylor, R. D.; Edgerton, E. S.; Hartsell, B. E. Linear regression techniques for use in the EC tracer method of secondary organic aerosol estimation. *Atmos. Environ.* **2006**, *40* (39), 7546–7556.

(32) Claeys, M.; Graham, B.; Vas, G.; Wang, W.; Vermeylen, R.; Pashynska, V.; Cafmeyer, J.; Guyon, P.; Andreae, M. O.; Artaxo, P.; Maenhaut, W. Formation of secondary organic aerosols through photo-oxidation of isoprene. *Science* **2004**, *303* (5661), 1173–1176.

(33) Lee, S.; Kim, H. K.; Yan, B.; Cobb, C. E.; Hennigan, C.; Nichols, S.; Chamber, M.; Edgerton, E. S.; Jansen, J. J.; Hu, Y.; Zheng, M.; Weber, R. J.; Russell, A. G. Diagnosis of aged prescribed burning plumes impacting an urban area. *Environ. Sci. Technol.* **2008**, *42* (5), 1438–1444.

(34) Zhang, Q.; Jimenez, J. L.; Canagaratna, M. R.; Allan, J. D.; Coe, H.; Ulbrich, I.; Alfarra, M. R.; Takami, A.; Middlebrook, A. M.; Sun, Y. L.; Dzepina, K.; Dunlea, E.; Docherty, K.; DeCarlo, P. F.; Salcedo, D.; Onasch, T.; Jayne, J. T.; Miyoshi, T.; Shimono, A.; Hatakeyama, S.; Takegawa, N.; Kondo, Y.; Schneider, J.; Drewnick, F.; Weimer, S.; Demerjian, K.; Williams, P.; Bower, K.; Bahreini, R.; Cottrell, L.; Griffin, R. J.; Rautiainen, J.; Sun, J. Y.; Zhang, Y. M.; Worsnop, D. R. Ubiquity and dominance of oxygenated species in organic aerosols in anthro-pogenically-influenced northern hemisphere mid-latitudes. *Geophys. Res. Lett.* **2007**, *34*, L13801, doi:10.1029/2007GL029979.

(35) Zhang, Q.; Alfarra, M. R.; Worsnop, D. R.; Allan, J. D.; Coe, H.; Canagaratna, M. R.; Jimenez, J. L. Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry. *Environ. Sci. Technol.* **2005**, *39*, (13), 4938−4952, doi:10.1021/es048568l.

(36) Ng, N. L.; Canagaratna, M. R.; Zhang, Q.; Jimenez, J. L.; Tian, J.; Ulbrich, I. M.; Kroll, J. H.; Docherty, K. S.; Chhabra, P. S.; Bahreini, R.; Murphy, S. M.; Seinfeld, J. H.; Hildebrandt, L.; Donahue, N. M.; DeCarlo, P. F.; Lanz, V. A.; Prévôt, A. S. H.; Dinar, E.; Rudich, Y.; Worsnop, D. R. Organic aerosol components observed in Northern Hemispheric datasets from aerosol mass spectrometry. *Atmos. Chem. Phys.* **2010**, *10* (10), 4625–4641.

(37) Jimenez, J. L.; Canagaratna, M. R.; Donahue, N. M.; Prevot, A. S. H.; Zhang, Q.; Kroll, J. H.; DeCarlo, P. F.; Allan, J. D.; Coe, H.; Ng, N. L.; Aiken, A. C.; Docherty, K. S.; Ulbrich, I. M.; Grieshop, A. P.; Robinson, A. L.; Duplissy, J.; Smith, J. D.; Wilson, K. R.; Lanz, V. A.; Hueglin, C.; Sun, Y. L.; Tian, J.; Laaksonen, A.; Raatikainen, T.; Rautiainen, J.; Vaattovaara, P.; Ehn, M.; Kulmala, M.; Tomlinson, J. M.; Collins, D. R.; Cubison, M. J. E.; Dunlea, J.; Huffman, J. A.; Onasch, T. B.; Alfarra, M. R.; Williams, P. I.; Bower, K.; Kondo, Y.; Schneider, J.; Drewnick, F.; Borrmann, S.; Weimer, S.; Demerjian, K.; Salcedo, D.; Cottrell, L.; Griffin, R.; Takami, A.; Miyoshi, T.; Hatakeyama, S.; Shimono, A.; Sun, J. Y.; Zhang, Y. M.; Dzepina, K.; Kimmel, J. R.; Sueper, D.; Jayne, J. T.; Herndon, S. C.; Trimborn, A. M.; Williams, L. R.; Wood, E. C.; Middlebrook, A. M.; Kolb, C. E.; Baltensperger, U.; Worsnop, D. R. Evolution of organic aerosols in the atmosphere. *Science* **2009**, *326* (5959), 1525–1529.

(38) Sun, Y. L.; Zhang, Q.; Macdonald, A. M.; Hayden, K.; Li, S. M.; Liggio, J.; Liu, P. S. K.; Anlauf, K. G.; Leaitch, W. R.; Steffen, A.; Cubison, M.; Worsnop, D. R.; van Donkelaar, A.; Martin, R. V. Size-resolved aerosol chemistry on Whistler Mountain, Canada with a high-resolution aerosol mass spectrometer during INTEX-B. *Atmos. Chem. Phys.* **2009**, *9* (9), 3095–3111.

(39) Sun, Y. L.; Zhang, Q.; Schwab, J. J.; Demerjian, K. L.; Chen, W. N.; Bae, M. S.; Hung, H. M.; Hogrefe, O.; Frank, B.; Rattigan, O. V.; Lin, Y. C. Characterization of the sources and processes of organic and inorganic aerosols in New York city with a high-resolution time-of-flight aerosol mass spectrometer. *Atmos. Chem. Phys.* **2011**, *11* (4), 1581–1602.

(40) Alfarra, M. R.; Prévôt, A. S. H.; Szidat, S.; Sandradewi, J.; Weimer, S.; Lanz, V. A.; Schreiber, D.; Mohr, M.; Baltensperger, U. Identification of the mass spectral signature of organic aerosols from wood burning emissions. *Environ. Sci. Technol.* **2007**, *41* (16), 5770–5777.

(41) Kiendler-Scharr, A.; Zhang, Q.; Hohaus, T.; Kleist, E.; Mensah, A.; Mentel, T.; Spindler, C.; Uerlings, R.; Tillmann, R.; Wildt, J. Aerosol mass spectrometric features of biogenic SOA: Observations from a plant chamber and in a rural atmospheric environment. *Environ. Sci. Technol.* **2009**, *43*, 8166–8172.

(42) Chhabra, P. S.; Flagan, R. C.; Seinfeld, J. H. Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer. *Atmos. Chem. Phys.* **2010**, *10* (9), 4111–4131.

(43) Chen, Q.; Farmer, D. K.; Schneider, J.; Zorn, S. R.; Heald, C. L.; Karl, T. G.; Guenther, A.; Allan, J. D.; Robinson, N.; Coe, H.; Kimmel, J. R.; Pauliquevis, T.; Borrmann, S.; Poschl, U.; Andreae, M. O.; Artaxo, P.; Jimenez, J. L.; Martin, S. T. Mass spectral characterization of submicron biogenic organic particles in the Amazon Basin. *Geophys. Res. Lett.* **2009**, *36*, L20806.

(44) Sakulyanontvittaya, T.; Duhl, T.; Wiedinmyer, C.; Helmig, D.; Matsunaga, S.; Potosnak, M.; Milford, J.; Guenther, A. Monoterpene and sesquiterpene emission estimates for the United States. *Environ. Sci. Technol.* **2008**, *42* (5), 1623–1629.

(45) Kleindienst, T. E.; Jaoui, M.; Lewandowski, M.; Offenberg, J. H.; Lewis, C. W.; Bhave, P. V.; Edney, E. O. Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern U.S. location. *Atmos. Environ.* **2007**, *41* (37), 8288–8300.

(46) McLafferty, F. W.; Turecek, F. *Interpretation of Mass Spectra*; University Science Books: Mill Valley, CA, 1993.

(47) Lee, S.; Baumann, K.; Schauer, J. J.; Sheesley, R. J.; Naeher, L. P.; Meinardi, S.; Blake, D. R.; Edgerton, E. S.; Russell, A. G.; Clements, M. Gaseous and particulate emissions from prescribed burning in Georgia. *Environ. Sci. Technol.* **2005**, *39* (23), 9049–9056.

(48) Zhang, X.; Hecobian, A.; Zheng, M.; Frank, N. H.; Weber, R. J. 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. *Atmos. Chem. Phys.* **2010**, *10* (14), 6839–6853.

(49) Zheng, M.; Ke, L.; Edgerton, E. S.; Schauer, J. J.; Dong, M.; Russell, A. G. Spatial distribution of carbonaceous aerosol in the southeastern United States using molecular markers and carbon isotope data. *J. Geophys. Res* **2006**, *111*, (D10), D10S06, doi:10.1029/2005JD006777.

(50) Grieshop, A. P.; Donahue, N. M.; Robinson, A. L. Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 2: Analysis of aerosol mass spectrometer data. *Atmos. Chem. Phys.* **2009**, *9* (6), 2227–2240.

(51) Aiken, A. C.; Salcedo, D.; Cubison, M. J.; Huffman, J. A.; DeCarlo, P. F.; Ulbrich, I. M.; Docherty, K. S.; Sueper, D.; Kimmel, J. R.; Worsnop, D. R.; Trimborn, A.; Northway, M.; Stone, E. A.; Schauer, J. J.; Volkamer, R. M.; Fortner, E.; de Foy, B.; Wang, J.; Laskin, A.; Shutthanandan, V.; Zheng, J.; Zhang, R.; Gaffney, J.; Marley, N. A.; Paredes-Miranda, G.; Arnott, W. P.; Molina, L. T.; Sosa, G.; Jimenez, J. L. Mexico City aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0)—Part 1: Fine particle composition and organic source apportionment. *Atmos. Chem. Phys.* **2009**, *9* (17), 6633–6653.

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