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Aerosol characterization over the southeastern United States using high resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition, sources, and organic nitrates

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Aerosol characterization over the southeastern United States

L. Xu et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

ACPD

15, 10479–10552, 2015

Aerosol characterization over the southeastern United States

L. Xu et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

We deployed a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and an Aerosol Chemical Speciation Monitor (ACSM) to characterize the chemical composition of submicron non-refractory particles (NR-PM$_1$) in the southeastern US. Measurements were performed in both rural and urban sites in the greater Atlanta area, GA and Centreville, AL for approximately one year, as part of Southeastern Center of Air Pollution and Epidemiology study (SCAPE) and Southern Oxidant and Aerosol Study (SOAS). Organic aerosol (OA) accounts for more than half of NR-PM$_1$ mass concentration regardless of sampling sites and seasons. Positive matrix factorization (PMF) analysis of HR-ToF-AMS measurements identified various OA sources, depending on location and season. Hydrocarbon-like OA (HOA) and cooking OA (COA) have important but not dominant contributions to total OA in urban sites. Biomass burning OA (BBOA) concentration shows a distinct seasonal variation with a larger enhancement in winter than summer. We find a good correlation between BBOA and brown carbon, indicating biomass burning is an important source for brown carbon, although an additional, unidentified brown carbon source is likely present at the rural Yorkville site. Isoprene-derived OA (Isoprene-OA) is only deconvolved in warmer months and contributes 18–36 % of total OA. The presence of Isoprene-OA factor in urban sites is more likely from local production in the presence of NO$_x$ than transport from rural sites. More-oxidized and less-oxidized oxygenated organic aerosol (MO-OOA and LO-OOA, respectively) are dominant fractions (47–79 %) of OA in all sites. MO-OOA correlates well with ozone in summer, but not in winter, indicating MO-OOA sources may vary with seasons. LO-OOA, which reaches a daily maximum at night, correlates better with estimated nitrate functionality from organic nitrates than total nitrates.

Based on the HR-ToF-AMS measurements, we estimate that the nitrate functionality from organic nitrates contributes 63–100 % of total measured nitrates in summer. Further, the contribution of organic nitrates to total OA is estimated to be 5–12 % in summer, suggesting that organic nitrates are important components in the ambient

aerosol in the southeastern US. The spatial distribution of OA is investigated by comparing simultaneous HR-ToF-AMS measurements with ACSM measurements at two different sampling sites. OA is found to be spatially homogeneous in summer, possibly due to stagnant air mass and a dominant amount of regional SOA in the southeastern US. The homogeneity is less in winter, which is likely due to spatial variation of primary emissions.

We observed that the seasonality of OA concentration shows a clear urban/rural contrast. While OA exhibits weak seasonal variation in the urban sites, its concentration is higher in summer than winter for rural sites. This observation from our year-long measurements is consistent with 14 years of organic carbon (OC) data from the South-Eastern Aerosol Research and Characterization (SEARCH) network. The comparison between short-term measurements with advanced instruments and long-term measurements of basic air quality indicators not only tests the robustness of the short-term measurements but also provides insights in interpreting long-term measurements. We find that OA factors resolved from PMF analysis on HR-ToF-AMS measurements have distinctly different diurnal variations. The compensation of OA factors with different diurnal trends is one possible reason for the repeatedly observed, relatively flat OA diurnal profile in the southeastern US. In addition, analysis of long-term measurements shows that the correlation between OC and sulfate is substantially higher in summer than winter. This seasonality could be partly due to the effects of sulfate on isoprene SOA formation as revealed by the short-term, intensive measurements.

1 Introduction

The southeastern US has been an interesting region to study aerosol formation. Firstly, the fine particulate matter ($PM_{2.5}$) concentration is generally high and often exceeds the National Ambient Air Quality Standards (NAAQS) (Cohan et al., 2007; Blanchard et al., 2013). Secondly, the southeastern US is characterized by large emissions from both biogenic and anthropogenic sources, which makes it an ideal region to study

the biogenic/anthropogenic interactions on organic aerosol formation and air quality. Roughly, half of the land in the southeastern US is covered by forests, which emit large amounts of biogenic volatile organic compounds (VOCs) that are precursors for SOA formation (Geron et al., 2000; Guenther et al., 2006). Based on radiocarbon analysis,

5 Schichtel et al. (2008) showed that about 90 % of total carbon is biogenic in a rural site in Tennessee. Similarly, Weber et al. (2007) found that 70–80 % of the carbon in water soluble organic carbon (WSOC, a surrogate for SOA) is of biogenic origin in Atlanta, GA. However, recent studies revealed that the formation of SOA from biogenic VOCs is largely controlled by anthropogenic emissions in the southeastern US (We-

10 ber et al., 2007; Xu et al., 2015). Thirdly, a wide range of air quality data has been routinely collected by the SEARCH (SouthEastern Aerosol Research and Characterization) network, including multiple rural and urban sites in the southeastern US from 1999 to 2013 (Edgerton et al., 2005; Hansen et al., 2003; Hidy et al., 2014). Combining short-term field campaigns and long-term measurements is useful because short-term

15 field campaigns with state-of-the-art instruments can better characterize atmospheric processes and provide insights in interpreting the long-term observations. In turn, long-term measurements with basic variables of air quality are helpful to test the robustness of short-term field campaign results (Hidy et al., 2014).

A number of field studies have been conducted to understand the sources of OA in

20 the southeastern US. Lim and Turpin (2002) showed that ∼ 50 % of OC is secondary in urban Atlanta by using an EC tracer method. Blanchard et al. (2008) applied three different empirical models and estimated that the fraction of secondary OC (SOC) in OC is ∼ 20–60 % in the southeastern US, which is higher in rural sites and summer compared to urban sites and winter, respectively. The authors also showed that the es-

25 timated SOC/OC ratio highly depends on the estimation methods. By using WSOC as a surrogate for SOC, Weber et al. (2007) showed that SOC accounts for roughly 75 % of OC in Yorkville, a rural site in GA, while the contribution of SOC to OC decreases to about 65 % in urban site. However, these studies were based on bulk properties, such as OC and WSOC, which makes it challenging for OC source apportionment beyond

separating it into primary and secondary OC. Attempts have been made to apportion OC into different sources based on molecular makers. For example, by using a molecular maker-based chemical mass balance modeling (CMB-MM), Zheng et al. (2006) attributed OC into various primary emission sources such as wood combustion and gasoline engine exhaust. However, limited by the number of molecular markers included in the model, the CMB-MM method is insufficient to resolve SOC and often results in high percentages of unexplained OC (Zheng et al., 2002). Also, filter samples collected on a daily basis were used in most previous studies which limit the temporal resolution and could introduce uncertainty due to filter sampling artifacts. The Aerodyne Aerosol Mass Spectrometer (AMS) has been widely used to characterize the chemical composition of submicron non-refractory species with high temporal resolution (Canagaratna et al., 2007; Jayne et al., 2000). Budisulistiorini et al. (2013) deployed an Aerosol Chemical Speciation Monitor (ACSM) (Ng et al., 2011) at SEARCH Jefferson Street site in downtown Atlanta, GA. Various OA sources were identified by factor analysis in Budisulistiorini et al. (2013), including one source related to isoprene oxidation, indicating the versatility of PMF analysis in OA source apportionment. However, due to the lower resolving power of ACSM, PMF analysis on ACSM data might have difficulty in separating different primary sources such as cooking and vehicle emission, which have similar mass spectrum (Crippa et al., 2014; Mohr et al., 2009). In addition, measurements at both rural and urban sites are needed in order to investigate the spatial distribution of aerosol and various OA subtypes.

Organic nitrates are important species in the atmosphere as their fate could affect the nitrogen cycle and ozone production (Perring et al., 2013; Mao et al., 2012). Organic nitrates, which are primarily formed from VOCs oxidation by nitrate radicals or by ozone and hydroxyl radical in the presence of NO_x, have been shown to be an important component of organic aerosol. For example, Rollins et al. (2012) observed that organic nitrates contribute about 27–40 % of OA growth at night in Bakersfield, CA, by using the Thermal-Dissociation Laser-Induced-Fluorescence technique (TD-LIF) (Day et al., 2002). Multiple approaches have also been proposed to estimate organic nitrates

from indirect measurements. For example, Farmer et al. (2010) proposed that the concentration of the nitrate functionality (i.e., $-ONO_2$) in organic nitrates could be estimated based on the nitrate functionality fragmentation pattern in the AMS or the differences between AMS and ion-chromatography (IC) measurements.

In this study, we performed measurements by a suite of instrumentation in multiple sites in the greater Atlanta area, GA and Centerville, AL, with a focus on a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). Positive matrix factorization analysis is performed on HR-ToF-AMS data to identify distinct OA sources. The contribution of organic nitrates to total OA is estimated by different methods based on HR-ToF-AMS measurements. Measurements were performed in both rural and urban sites to investigate the spatial distribution of aerosol in the southeastern US. In addition, measurements spanning over a year allow us to evaluate the seasonal variation of aerosol composition. Our results are not only supported by the available long-term measurements from the SEARCH network, but also provide further insights into interpreting historic measurements.

2 Method

Measurements were conducted at the following sites as part of two field campaigns:

2.1 Southern Oxidant and Aerosol Study (SOAS)

The Southern Oxidant and Aerosol Study (SOAS, http://soas2013.rutgers.edu/) is a collaborative field campaign that took place from 1 June to 15 July 2013. The sampling site (32.94° N, 87.18° W) is a SEARCH network site near Centreville in rural Alabama, as shown in Fig. 1. The site is located in a forested area away from large urban cities (55 km SE of Tuscaloosa and 84 km SW of Birmingham, AL). Detailed meteorological conditions of the sampling site can be found in Hidy et al. (2014). In brief, the

sampling period was characterized by high relative humidity (> 50 % all the time), warm temperatures (daily maximum 28.6 °C at 15:00 LT), and light winds (Xu et al., 2015).

2.2 Southeastern Center of Air Pollution and Epidemiology study (SCAPE)

This extensive field study was part of the Southeastern Center for Air Pollution and Epidemiology (SCAPE, http://scape.gatech.edu/), which is an EPA-funded joint research center between Georgia Tech and Emory University, focusing on the study of air quality and the health effects of air pollutants (Verma et al., 2014; Winquist et al., 2014; Russell et al., 2014). Four sampling sites in both rural and urban areas are selected, as shown in Fig. 1. Detailed description of each sampling site can be found in Verma et al. (2014) and Hansen et al. (2003). Briefly,

- Roadside site (RS site) is on the Georgia Tech campus and adjacent (within 5 m) to the Interstate 75/85 (8 lines each direction). According to Georgia Department of Transportation, about 95 % of the traffic fleet on the Interstate 75/85 is light-duty gasoline vehicles.

- Georgia Tech site (GT site) is also on the Georgia Tech campus, but 840 m away from the roadside site. The GT site is located on the top floor of the Ford Environmental Science & Technology Building, which is 30–40 m above ground.

- Jefferson Street site (JST site) is a central SEARCH network site, which is about 2 km west of the Georgia Tech site. This site is situated in Atlanta's urban area and surrounded by a mixed residential and commercial neighborhood and is considered representative of the urban Atlanta.

- Yorkville site (YRK site) is the SEARCH rural pair to JST site and located approximately 80 km northwest of the JST site. This site is situated in a mixed forested – agricultural area and immediately surrounded by pastures for cattle grazing.

We outfitted a trailer with a large suite of instrumentation (described in Sect. 2.3) and conducted measurements from May 2012 to February 2013, with roughly one month

at each site and repeated it in different seasons. The sampling periods are listed in Table 1.

While the trailer was rotated between multiple sites, we also deployed an Aerosol Chemical Speciation Monitor (ACSM, described in Sect. 2.3.2) (Ng et al., 2011) at the Georgia Tech site from May 2012 to February 2013. The paired and simultaneous measurements using an ACSM at the Georgia Tech site and a High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, described in Sect. 2.3.1) rotating among four different sites allow for the investigation of the spatial distribution of aerosol loading and composition in the greater Atlanta area. It is noted that from 20 July to 4 September 2012, both the HR-ToF-AMS and the ACSM were deployed at the Georgia Tech site for instrument inter-comparison.

2.3 Instrumentation

2.3.1 High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS)

An Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) was rotated among different sites in this study to characterize the composition of ambient submicron non-refractory particulate matter (NR-PM$_1$). A detailed description of the HR-ToF-AMS can be found in literature (Canagaratna et al., 2007; DeCarlo et al., 2006). In brief, the HR-ToF-AMS focuses ambient particles with vacuum aerodynamic diameter smaller than 1 μm into a narrow beam by using an aerodynamic lens. The submicron particles are then impacted on a hot tungsten surface ($\sim 600\,°C$), where non-refractory species are flash evaporated. The resultant vapors are ionized using 70 eV electron impact ionization and analyzed by a time-of-flight mass spectrometer. During sampling, a PM$_1$ cyclone was used to remove coarse particles. A nafion-dryer was placed upstream of the HR-ToF-AMS to dry the particles (relative humidity < 20 %) in order to eliminate the potential influence of relative humidity on particle collection efficiency (CE) at the vaporizer (Matthew et al., 2008). Gas-phase interference was elimi-

nated by subtracting the signals when the HR-ToF-AMS sampled through a HEPA filter, which was performed regularly on a daily basis at different times of the day. Ionization efficiency (IE) calibration by using 300 nm ammonium nitrate particles was performed on a weekly basis and the composition-dependent CE was applied to the data based on Middlebrook et al. (2012). We operated the HR-ToF-AMS in both V mode and W mode, but only V mode data are reported in this study considering the low intensity of W mode data. The average sampling time was set at two minutes. The data analysis was performed using the standard AMS analysis toolkits SQUIRREL v1.53 and PIKA v1.12 in Igor Pro 6.34 (WaveMetrics Inc.). Elemental ratios, such as atomic oxygen-to-carbon ratio (O : C), hydrogen-to-carbon ratio (H : C), and organic mass-to-organic carbon ratio (OM : OC), are determined by following the latest procedures as recommended by Canagaratna et al. (2015). Canagaratna et al. (2015) improved the estimation from Aiken et al. (2008), which has been widely used in the literature to estimate elemental ratios, by including composition-dependent correction factors. Caution is required when comparing the elemental ratios in this study with values reported in literature, which typically used the Aiken estimation. Nitrate signals (NO^+ and NO_2^+) and sulfate signals (SO^+, SO_2^+, etc) are not included in the elemental ratios calculation. Oxidation state (OS) is calculated as $2 \times O : C - H : C$ (Kroll et al., 2011).

2.3.2 Aerosol Chemical Speciation Monitor (ACSM)

An Aerosol Chemical Speciation Monitor (ACSM) was stationary at the Georgia Tech site from 10 May 2012 to 28 February 2013. Similar to the HR-ToF-AMS, the ACSM also provides continuous, quantitative measurements of NR-PM$_1$ (Ng et al., 2011). The mass resolving power of ACSM (∼ 200) is lower than that of HR-ToF-AMS (∼ 2000 in V mode) due to the use of a low cost residual gas analyzer (RGA) quadrupole mass spectrometer in ACSM (Ng et al., 2011). In addition, the time resolution of ACSM (∼ 30 min) is longer than that of HR-ToF-AMS (∼ 2 min). The response factor (RF) of ACSM was also determined by using 300 nm ammonium nitrate particles (Ng et al., 2011). The relative ionization efficiency (RIE) values used for organics, nitrate, and chloride are

1.4, 1.1, and 1.3, respectively. RIE values of 4.18 and 0.59 were used for ammonium and sulfate, which were determined from IE calibrations by using ammonium nitrate and ammonium sulfate particles.

2.3.3 Co-located instruments

In addition to the HR-ToF-AMS, we deployed various instruments in the trailer while performing measurements at multiple sites (Verma et al., 2014). Instruments of interest to this study includes a PILS-LWCC-TOC system (Particle Into Liquid Sampler – Liquid Waveguide Capillary Cell – Total Organic Carbon analyzer), which was deployed to measure the light absorption spectra of water-soluble organic components. Detailed working principle of the PILS-LWCC-TOC system can be found in Hecobian et al. (2010). The average light absorption between 360 to 370 nm is used as a measure of brown carbon. Black carbon concentration was measured by either a seven-wavelength Aethalometer or a multi-angle absorption photometer (MAAP). For Aethalometer, the measurements under seven wavelengths (i.e., 370, 450, 571, 590, 660, 880, and 950 nm) were averaged to represent the black carbon concentration. The measured data were corrected for loading effects (Virkkula et al., 2007).

At the Jefferson Street site (JST) and Yorkville site (YRK), a suite of instruments was operated by the SEARCH Network. Detailed description about the collocated instruments can be found in Hansen et al. (2003) and Edgerton et al. (2005). In brief, O_3 concentration was measured by a UV-absorption analyzer. NO and NO_x were measured by a chemilumnescence analyzer, where the NO_2 concentration was calculated by subtracting NO from the total NO_x. $PM_{2.5}$ sulfate and OC were continuously measured by a Fe reduction/UV-fluorescence analyzer and an oxidative combustion (R&P 5400) analyzer, respectively. Meteorological conditions, such as temperature, relative humidity (RH), solar radiation, and wind speed were also recorded.

2.4 Positive Matrix Factorization (PMF) analysis

Positive Matrix Factorization (PMF) is a mathematical technique to solve bilinear un-mixing problems (Paatero, 1997; Paatero and Tapper, 1994). PMF analysis has been widely applied in the aerosol community for source apportionment (Ulbrich et al., 2009; Jimenez et al., 2009; Zhang et al., 2010; Lanz et al., 2007; Ng et al., 2010). For the data measured by AMS, PMF analysis represents the observed data matrix as a linear combination of various factors with constant mass spectrum but varying concentrations across the dataset (Ulbrich et al., 2009; Zhang et al., 2011). To determine the sources of organic aerosol, PMF analysis was performed on the high-resolution organic mass spectra (m/z 12–200) obtained by the HR-ToF-AMS for each sampling dataset. We generated the organic data matrix and error matrix from PIKA v1.12 and pretreated the error matrix by using PMF Evaluation Toolkit (PET) software and following the procedure described in Ulbrich et al. (2009). m/z's with signal-to-noise smaller than 0.2 are removed and m/z's with signal-to-noise ranging between 0.2 and 2 are downweighted by a factor of 2. We downweighted the errors of O^+, HO^+, H_2O^+, and CO^+, which are related to CO_2^+ organic ions, to avoid excessive weighting of CO_2^+. In addition, for four datasets (JST_May, CTR_June, YRK_July, and GT_August), the error of CHO^+ is downweighted by a factor of 4 because PIKA v1.12 appears to underestimate CHO^+ error, which is possibly caused by that the overlap of the CHO^+ (m/z 29.0027) ion with its adjacent N_2 isotope ion (j15NN, m/z 29.0032). For the other three datasets (JST_Nov, YRK_Dec, and RS_Jan), CHO^+ is not included in the PMF analysis due to its occasionally negative signals, which is likely caused by a low CHO^+ signal in winter. At times, the CHO^+ concentration is near the detection limit, so that a shift in threshold might cause the CHO^+ signal to be treated as noise. PMF solutions were carefully evaluated according to the procedure outlined in Zhang et al. (2011). For each dataset, the optimal solution was determined after examining the residuals of PMF fits, interpretability of factor's diurnal trend, factor correlation with external tracers, and characteristic signature in factor mass spectrum. The rotational ambiguity of solutions were

examined by changing the parameter FPEAK and the robustness of solutions were evaluated by starting PMF with different initial conditions (parameter SEED). The key diagnostic plots for all datasets are shown in Fig. S1. An FPEAK value of 0 is used for all datasets in our analysis, because the use of FPEAK values that are different from 0

5   do not improve the correlations between PMF factors with external tracers.

2.5 Estimation of organic nitrates contribution to ambient OA

As direct measurements of organic nitrates are not available, we estimate the concentration of particle-phase organic nitrates at each site based on HR-ToF-AMS measurements in this study. It is important to note that total nitrates measured by the HR-ToF-

10 AMS (denoted as $NO_{3,meas}$) is the nitrate functionality ($-ONO_2$) which could arise from both inorganic and organic nitrates. Here, we apply two independent methods in separating the measured total nitrates into nitrate functionality from inorganic and organic nitrates. In the following discussion, we use the subscripts $_{meas}$, $_{inorg}$, and $_{org}$ to denote nitrate functionality ($-ONO_2$) or fragments (NO^+ and NO_2^+) from total nitrates (mea-

15 sured), inorganic nitrates (calculated), and organic nitrates (calculated), respectively.

The first method is based on the NO^+/NO_2^+ ratio (denoted as NO_x^+ ratio method for discussions hereafter) in the AMS mass spectra (Farmer et al., 2010). Due to the extensive fragmentation caused by 70 eV electron ionization in the HR-ToF-AMS, the nitrate functionality ($-ONO_2$) fragments to produce NO^+ and NO_2^+ ions. Previous laboratory

20 studies have shown that the NO^+/NO_2^+ ratio in the aerosol mass spectrum is substantially higher for organic nitrates than ammonium nitrate (AN) (Bruns et al., 2010; Fry et al., 2009; Sato et al., 2010; Farmer et al., 2010; Boyd et al., 2015), which is the major source of PM_1 inorganic nitrates in the southeast US that can be detected by AMS (Guo et al., 2014; Allan et al., 2004). For example, while the NO^+/NO_2^+ ratio is about 2.4 for

25 ammonium nitrate, the ratio ranges from 5 to 10 for SOA derived from isoprene $+NO_3^\bullet$ and β-pinene $+NO_3^\bullet$ reactions, respectively (Bruns et al., 2010; Boyd et al., 2015). In addition to organic nitrates produced from biogenic VOC oxidation, Sato et al. (2010) showed that the NO_x^+ ratio of organic nitrates from the photooxidation of aromatic hy-

Title Page

Abstract   Introduction

Conclusions   References

Tables   Figures

|◀   ▶|

◀   ▶

Back   Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

drocarbons is also clearly higher than that of ammonium nitrate (3.8–5.8 vs. 1.1–2.8). Based on the differences in NO_x^+ ratio between organic and inorganic nitrates, Farmer et al. (2010) proposed that the concentrations of NO_{org} and $NO_{2,org}$ can be estimated from NO_{meas} and $NO_{2,meas}$ by Eqs. (1) and (2).

$$NO_{2,org} = \frac{NO_{2,meas} \times (R_{meas} - R_{AN})}{R_{ON} - R_{AN}} \quad (1)$$

$$NO_{org} = R_{ON} \times NO_{2,org} \quad (2)$$

R_{meas} is the NO_x^+ ratio from observation. R_{AN} is the NO_x^+ ratio for pure ammonium nitrate (AN), which has been reported to depend on instrument performance and vary between different instruments (Farmer et al., 2010; Rollins et al., 2010). In this study, we determine the R_{AN} of each dataset from Ionization Efficiency (IE) calibrations using 300 nm ammonium nitrate particles. We find that R_{AN} varies between 1.73 and 2.93 (Table 2), which is within the range (1.1–3.5) reported in literature (Sato et al., 2010; Farmer et al., 2010; Sun et al., 2012b; Fry et al., 2013). R_{ON} is the NO_x^+ ratio for organic nitrates. Similar to R_{AN}, R_{ON} also varies between instruments (Boyd et al., 2015; Bruns et al., 2010; Fry et al., 2009). Thus, the R_{ON} values reported in the literature cannot be directly applied in our datasets. In order to circumvent this issue, Fry et al. (2013) assumed that the R_{ON}/R_{AN} value is instrument independent. The authors further obtained R_{ON} by multiplying R_{AN} determined from in-field IE calibrations with R_{ON}/R_{AN} determined from six organic nitrate standards (average value = 2.25). However, the reported R_{ON}/R_{AN} values in the literature vary for different organic nitrates. For example, while the average R_{ON}/R_{AN} value is 2.25 for the organic nitrate standards in Farmer et al. (2010), the R_{ON}/R_{AN} ranges from 3.70 to 4.17 for organic nitrates produced from β-pinene oxidation by nitrate radicals (Boyd et al., 2015; Bruns et al., 2010; Fry et al., 2009). Considering the large variations in R_{ON}/R_{AN} values and unknown contributions from different organic nitrates, we apply the NO_x^+ ratio method to obtain an estimation range by using extreme R_{ON} values. We select organic nitrates formed from isoprene and monoterpene oxidations as representative because of their large abundance in

the southeastern US, potential to produce organic nitrates, and that they cover a wide range of R_{ON}/R_{AN} values (i.e., 2.08 for isoprene and 3.70–4.17 for β-pinene) (Boyd et al., 2015; Bruns et al., 2010; Fry et al., 2009). Though the photooxidation of aromatic VOCs could also produce organic nitrates, their R_{ON}/R_{AN} ratio is close to that of iso-
5 prene organic nitrates (Sato et al., 2010). Multiplying the average R_{AN} (i.e., 2.28 ± 0.40) of all datasets in this study by the average R_{ON}/R_{AN} ratio of isoprene (i.e., 2.08) and β-pinene organic nitrates (i.e., 3.99 ± 0.25) in the literature (Boyd et al., 2015; Bruns et al., 2010; Fry et al., 2009), within one SD we selected 5 (i.e., 4.74 ± 0.83) and 10 (i.e., 9.10 ± 1.69) as the lower and upper values of R_{ON}. It is important to note that
10 R_{ON} values of 5 and 10 likely correspond to upper and lower bounds of the $NO_{3,org}$ concentrations estimated by the NO_x^+ ratio method. The assumption that R_{ON}/R_{AN} is instrument independent warrants further study.

The second method is based on PMF analysis (denoted as PMF method). In addition to PMF analysis on organic mass spectra (denoted as PMF_{org}), we have also
15 performed PMF analysis on organic mass spectra together with NO^+ and NO_2^+ ions (denoted as PMF_{org+NO_3}). Such analysis could provide useful insights regarding the relative contributions of organic and inorganic nitrates. For instance, Sun et al. (2012b) and Hao et al. (2014) performed PMF analysis on merged mass spectra with both organic and inorganic signals from HR-ToF-AMS measurements. The authors showed
20 that the NO^+ and NO_2^+ fragments are distributed among a nitrate inorganic aerosol (NIA) factor and other organic aerosol factors.

In this study, the selection of optimal solutions for PMF analysis on the merged mass spectra (i.e. PMF_{org+NO_3}) is discussed in detail in the Supplement. In brief, in addition to examining the typical diagnostic plots (Fig. S3), the optimal solutions are se-
25 lected by comparing the time series (Fig. S5), mass spectrum (Fig. S5), and mass concentration (Fig. S6) with results from PMF_{org}. After determining the optimal solution of PMF_{org+NO_3}, the concentrations of "nitrate functionality from organic nitrates" (i.e., $NO_{3,org}$) are calculated by summing up the nitrate signals (i.e., NO^+ and NO_2^+) from all

OA factors by the following equations.

$$[NO^+_{org}] = \sum ([OA\ factor]_i \times f\_NO_i) \tag{3}$$

$$[NO^+_{2,org}] = \sum ([OA\ factor]_i \times f\_NO_{2,i}) \tag{4}$$

where $[OA\ factor]_i$ is the mass concentration of the ith OA factor, f_NO_i and $f\_NO_{2,i}$ are the mass fraction of NO^+ and NO^+_2, respectively, in ith OA factor. For both the NO^+_x ratio method and PMF method, we calculate the concentration of $NO_{3,inorg}$ (i.e., nitrate functionality from inorganic nitrates) by subtracting $NO_{3,org}$ (i.e., nitrate functionality from organic nitrates) from $NO_{3,meas}$ (i.e., total measured nitrates).

3   Results

Table 1 lists the meteorology parameters (temperature, relative humidity, and wind speed), gas-phase concentrations of NO, NO_2, and O_3, and aerosol compositions of the seven datasets reported in this study. The average RH is above 60 % for all the datasets with little seasonal variation, which is consistent with previous observations (Ford and Heald, 2013). The high RH in the southeastern US has direct impacts on par-ticle water content and particle acidity. Recently, Guo et al. (2014) showed that particle water and acidity are mainly driven by the variability of RH, although particle compo-sition also plays a role. The average wind speed is relatively constant (1.3–3.4 m s^{-1}) throughout the year at all sites. NO_x (NO and NO_2) and black carbon (BC), which are tracers for anthropogenic emissions, are lower in the rural Yorkville (YRK) site than the urban Jefferson Street (JST) site. In YRK, NO_x level is low (i.e., average concentra-tion < 0.3 ppb) in all seasons. In contrast, at the urban JST site, NO_x level is elevated in winter compared to summer, indicating more anthropogenic emissions in winter at urban sites.

Figure 2 shows the composition of non-refractory submicron particulate matter (NR-PM$_1$) of all datasets. Organics are the dominant components, which account for more

than 50 % of NR-PM$_1$ mass at all sites throughout the year. Although dominant, the concentration of organic aerosol varies substantially among sites and seasons. The seasonal variation of OA mass concentration is small for urban JST site (9.1 µg m^{-3} in May vs. 7.9 µg m^{-3} in November); however, OA concentration is about 4 times higher in summer than winter for rural YRK site (11.2 µg m^{-3} in July vs. 3.2 µg m^{-3} in December). The difference in seasonality of OA between urban and rural sites is likely due to the varying strength of different OA sources, which will be discussed in detail in Sect. 4.4.2. In terms of diurnal variation, OA reaches daily maximum in the early morning and evening for most datasets (except YRK_July) (Fig. 3). This diurnal variation in OA is likely caused by the changes in planetary boundary layer height and changes in contributions to total OA from various sources, which will be discussed in detail in Sect. 4.4.1. The campaign-average mass spectra of OA from all datasets are similar, as shown in Fig. S7. In order to assess the degree of oxidation of OA, average f_{44} (the ratio of m/z 44 to total OA signal) and f_{43} (the ratio of m/z 43 to total OA signal) of each dataset is plotted in the triangular space as defined by Ng et al. (2010) in Fig. 4. The OA from all datasets locate in the middle part of triangle, indicating they are moderately oxidized and have a similar degree of oxidation.

Following organics, sulfate (SO$_4$) has the second largest contribution to total NR-PM$_1$ mass at all sites. Average SO$_4$ concentration varies between 3.0 to 4.0 µg m^{-3} at different sites in summer and decreases to 1.4 ~ 1.7 µg m^{-3} in winter. The SO$_4$ concentration at most sites (except JST_Nov and RS_Jan) reaches a daily maximum in the afternoon (Fig. 3), which is likely caused by the strong photooxidation of SO$_2$ or sulfate entrainment from aloft when the boundary layer height is the highest in the afternoon (Weber, 2003). In contrast to SO$_4$ where the concentration is higher in summer, total nitrate concentration is elevated in winter. While the average concentration of total nitrates is 0.3–0.4 µg m^{-3} (2–3 % of total NR-PM$_1$, Fig. 2) in summer, it almost triples in winter (0.8–1.4 µg m^{-3}) with elevated mass fraction in total NR-PM$_1$ (10–16 %). The reason for the seasonal variation of the total nitrates will be discussed in Sect. 4.2.2.

Aerosol characterization over the southeastern United States

L. Xu et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

4 Discussion

4.1 OA source apportionment

In this section, we focus on the OA source apportionment based on results from PMF analysis on organic mass spectra only (i.e., PMF$_{org}$). We resolved various factors, including hydrocarbon-like OA (HOA), cooking OA (COA), biomass burning OA (BBOA), isoprene-derived OA (Isoprene-OA), more-oxidized oxygenated OA (MO-OOA), and less-oxidized oxygenated OA (LO-OOA) at multiple sites in different seasons.

4.1.1 HOA

Hydrocarbon-like organic aerosol (HOA) is a surrogate of primary OA from vehicle emissions. Among all the OA factors, HOA is the least oxidized with oxidation state (OS) ranging from -1.86 to -1.39 (Fig. 4). The mass spectrum of HOA is characterized by hydrocarbon-like ions (C$_x$H$_y$ family) as shown in Fig. S2, which is similar to the mass spectrum of freshly emitted traffic aerosol (Zhang et al., 2005). HOA is only identified in urban sites with evident morning and evening rush hour peaks (Fig. 6). HOA also shows good correlation with black carbon (R ranges from 0.70 to 0.83) (Fig. S2), further supporting the primary nature of this OA subtype.

For the sites where HOA is identified, HOA accounts for 9–15 % (daily average) of total OA (Fig. 5). Even for the roadside (RS) site, which is within 5 m to the Interstate 75/85, HOA only contributes 15 % of total OA. Low contributions of HOA to total OA near highways have been observed in several prior studies (Sun et al., 2012a; De-Witt et al., 2014). For example, DeWitt et al. (2014) found that HOA only comprised 20 % of total OA based on HR-ToF-AMS measurements in a high diesel environment (near a highway) in Paris, France. The small contribution of HOA could arise from the types of vehicles on road, the dilution of vehicle emissions, or the high level of regional background OA. Firstly, roughly 95 % of the traffic fleet on I75/85 is light-duty gasoline vehicles according to Georgia Department of Transportation. Unlike diesel vehicles

which have large emissions of POA and BC, gasoline vehicles have a larger emission of VOCs (e.g., toluene and benzene) (Platt et al., 2013). Secondly, in addition to vehicle type, the evaporation of POA emitted from vehicles would further decrease its mass concentration. Robinson et al. (2007) showed that POA from vehicle emission is indeed semi-volatile, which would evaporate substantially upon dilution from tailpipe to ambient conditions (a dilution ratio of 10^3 to 10^4). Thirdly, HOA tends to contribute a small fraction of OA because of the high level of regional background OA in the greater Atlanta area. For example, OOA factors (i.e., LO-OOA and MO-OOA) compromise 47–79 % of OA as shown in Fig. 5. The effect of wind direction on HOA concentration is expected to be small considering the close proximity of the roadside sampling site to the highway.

4.1.2 COA

The mass spectrum of cooking organic aerosol (COA) is characterized by prominent signal at ion $C_3H_5^+$ (m/z 41) and $C_4H_7^+$ (m/z 55) (Fig. S2), which could arise from the heating of seed oil (Allan et al., 2010). Another feature of COA is its clear and unique diurnal trend, which exhibits a small peak at lunch time and a large peak at dinner time (Fig. 6). The COA factor is identified in urban sites (JST site, GT site, and RS site) throughout the year, with the mass fraction varying from 12–20 %. A prior study by Zheng et al. (2002) estimated that meat cooking accounts for 5–12 % of $PM_{2.5}$ organic carbon in the southeastern US by using chemical mass balance receptor model. The range reported by Zheng et al. (2002) is similar to our study, considering the differences in sampling periods, particle size range, and estimation method. The COA factor has also been detected in many megacities around the world (Huang et al., 2010; Allan et al., 2010; Slowik et al., 2010; Mohr et al., 2012; Crippa et al., 2013), indicating cooking is an important OA source in megacities.

We note that the COA factor was not resolved in Budisulistiorini et al. (2013), in which the authors performed PMF analysis on the data collected by an Aerosol Chemical Speciation Monitor (ACSM) at the JST site in 2011 summer and fall. The lack of a COA factor in the analysis by Budisulistiorini et al. (2013) could be a result of the lower

resolution (unit mass resolution) of the ACSM compared to HR-ToF-AMS (Ng et al., 2011). Previous studies have suggested that COA is not easily differentiated from HOA due to the similarity of their mass spectra in unit mass resolution data (Crippa et al., 2014; Mohr et al., 2009).

4.1.3 Isoprene-OA

The Isoprene-OA factor is characterized by prominent signals at ion $C_4H_5^+$ (m/z 53) and $C_5H_6O^+$ (m/z 82) in its mass spectrum (Fig. S2), which resembles that of isoprene SOA formed via IEPOX uptake in the presence of hydrated sulfate in laboratory experiments (Lin et al., 2012; Budisulistiorini et al., 2013; Nguyen et al., 2014; Liu et al., 2014). For our datasets, Isoprene-OA is only identified in warmer months (May–August) and accounts for 18–36 % of total OA (Fig. 5). The seasonal variation of Isoprene-OA factor is consistent with that of isoprene emissions, which are high in summer and nearly zero in winter (Guenther et al., 2006). The identification of the Isoprene-OA factor could be further supported by its correlation with methytetrols, which are products formed from isoprene oxidation and likely via IEPOX uptake. For the Centreville dataset where methyltetrols were continuously measured by a semi-volatile thermal desorption aerosol gas chromatograph (SV-TAG) (Isaacman et al., 2014), the correlation (Pearson's R) between the Isoprene-OA factor and methyltetrols is found to be 0.68 (Xu et al., 2015).

The ratio of $C_5H_6O^+$ to total signal of isoprene-OA factor, $f_{C_5H_6O^+}$, which is used as a characteristic marker for SOA formed via IEPOX uptake in the literature, ranges from 0.9–2.3 % in this study. This range is similar to the values from other ambient data (Budisulistiorini et al., 2013; Chen et al., 2014; Robinson et al., 2011a; Slowik et al., 2011), but lower than that from laboratory-generated fresh SOA from IEPOX uptake (3.6 % from Liu et al., 2014). We note that the $f_{C_5H_6O^+}$ is higher at rural sites (1.9 % for YRK_July and 2.3 % for CTR_June) than urban sites (0.9 % for JST_May and 1.4 % for GT_August). Similarly, Liu et al. (2014) observed that the mass spectrum of laboratory-generated SOA from IEPOX uptake has a stronger correlation with that

of Isoprene-OA factor from remote regions (Amazon and Borneo) than urban regions (Atlanta, US). The identification of an Isoprene-OA factor at urban sites in the current study has interesting implications. The compound IEPOX is thought be an oxidation product of isoprene where the organic peroxy radicals react with hydroperoxy radicals (Paulot et al., 2009). In urban areas, one would expect the majority of organic peroxy radicals to react with NO_x, considering the relatively high NO_x level (~ 15.4 ppb for JST_May in Table 1). However, a recent laboratory study by Jacobs et al. (2014) found that the oxidation of isoprene-derived hydroxynitrates in the presence of NO_x could also produce IEPOX. Thus, Isoprene-OA observed in urban sites could be locally produced. Another possible source for Isoprene-OA at urban sites is advection from rural sites. This could explain the lower $f_{C_5H_6O^+}$ in the Isoprene-OA factor in urban sites, because the compounds which give rise to the $C_5H_6O^+$ signal can be further oxidized during transport. However, the lifetime of the Isoprene-OA factor and the changes in its mass spectral features with chemical aging are largely uncertain. The contribution of advection is probably small as it is unlikely that advection would result in a consistent diurnal profile of Isoprene-OA, which reaches a daily maximum in the afternoon observed not only in this study (Fig. 6), but also in other regions, such as Amazon (Chen et al., 2014) and Borneo forest (Janssen et al., 2013; Robinson et al., 2011a). In addition, Robinson et al. (2011a) only observed the Isoprene-OA factor in data obtained from afternoon flights, but not in morning flights through airborne measurements in the Borneo forest, implying that the Isoprene-OA formation is rapid and local.

For all the sites where an Isoprene-OA factor is resolved, the Isoprene-OA factor is found to be well-correlated with sulfate (R ranging from 0.73 to 0.88, Fig. S2). Xu et al. (2015) showed that the formation of isoprene-OA in the southeastern US is largely controlled by the abundance of sulfate, instead of the particle water content and/or particle acidity. While many prior laboratory studies show that particle acidity plays an important role in IEPOX uptake (Gaston et al., 2014; Surratt et al., 2007), results from ambient observations suggest that particle acidity is not the limiting factor in isoprene OA formation in the southeastern US, which is likely due to the consistently high particle

acidity in the southeastern US (Guo et al., 2014; Xu et al., 2015). Guo et al. (2014) showed that the daily average particle pH throughout the southeastern US ranges between 1.1 and 1.3 in summer time. In the afternoon, when isoprene mixing ratio is highest and photochemistry is strongest, the particle pH is even lower, ranging between 0 and 0.75. A recent chamber study (Gaston et al., 2014) showed that decreasing pH from 4.63 to 0.5 could greatly enhance IEPOX uptake by up to 150 times, but the enhancement is much weaker (a factor of 2) when furthering decreasing the pH from 0.5 to −0.27, the range of which is relevant to ambient particle pH (0–0.75) in the summer afternoon in the southeastern US (Guo et al., 2014). Similarly, another laboratory study also showed that the effect of particle acidity on IEPOX uptake is minor when the particle pH is low (Nguyen et al., 2014). By comparing the reactive uptake of IEPOX by using wet $(NH_4)_2SO_4$ seed (pH ∼ 3.5) and wet $MgSO_4 + H_2SO_4$ mixture seed (pH ∼ 0–1 with large uncertainty), Nguyen et al. (2014) found that the reaction partitioning coefficient of IEPOX increases by only 1.5 times as pH decreases from 3.5 to 1 ($H^+_{(aq)}$ increases by two or three orders of magnitude). Taken together, laboratory studies revealed that while increasing particle acidity could greatly enhance IEPOX uptake when pH is high, the sensitivity of IEPOX uptake to particle acidity is minor when pH is low. This is likely caused by isoprene OA formation from IEPOX uptake being limited by nucleophiles instead of catalyst activity under low pH (Eddingsaas et al., 2010; Piletic et al., 2013), although a low pH is needed to enhance these reactions. We also note that the co-variation between particle acidity and sulfate is not considered in previous laboratory studies (Gaston et al., 2014; Surratt et al., 2007), so the effect of particle acidity could possibly be confounded with the effect of sulfate and warrants further investigation.

4.1.4 BBOA

The mass spectrum of biomass burning organic aerosol (BBOA) is characterized by prominent signals at ion $C_2H_4O_2^+$ (*m/z* 60) and $C_3H_5O_2^+$ (*m/z* 73). These two ions are known to be produced by levoglucosan, which is formed from the breakdown of

cellulose in biomass burning (Schneider et al., 2006). In the greater Atlanta area, the BBOA factor is mainly resolved in winter datasets, which is consistent with the EPA reported Georgia fire season in late winter (January–March) (Hidy et al., 2014) and the large enhancement in levoglucosan concentrations in winter compared to summer in Georgia (Zhang et al., 2010). BBOA is also identified in JST_May, which may arise from residential wood burning near JST site.

BBOA accounts for 9–22 % of the OA at the sites where BBOA is identified (Fig. 5), which is smaller than the values reported in other studies. Zhang et al. (2010) estimated that biomass burning accounted for 27 % of $PM_{2.5}$ mass in winter over the southeastern US by performing PMF analysis on 10 species extracted from filter samples. The cause for the differences in biomass burning contribution to OA between this study and Zhang et al. (2010) is unclear at this point, but likely a result of different estimation methods and sampling years. It is important to note that the BBOA reported in this study likely only represents fresh OA from biomass burning. Recent laboratory studies revealed that the oxidation of levoglucosan is fast in both the gas phase and aqueous phase (Zhao et al., 2014; May et al., 2012; Hennigan et al., 2011). The fast oxidation of levoglucosan can result in the rapid decay of signals at $C_2H_4O_2^+$ (m/z 60) and $C_3H_5O_2^+$ (m/z 73), causing the mass spectrum of BBOA to lose its characteristic signature (Cubison et al., 2011). Hennigan et al. (2011) and Grieshop et al. (2009) showed that the mass spectrum of OA from biomass burning becomes increasingly similar to that of MO-OOA after aging by photooxidation. Thus, the aged OA from biomass burning could be apportioned to the MO-OOA factor (Bougiatioti et al., 2014) and the mass fraction of the BBOA factor likely serves as a lower bound of OA from biomass burning. The extent to which aged BBOA contributes to the MO-OOA factor warrants further investigation.

Recent studies have revealed that OA from biomass burning is an important source for brown carbon (Washenfelder et al., 2015; Andreae and Gelencsér, 2006; Zhang et al., 2010; Lack et al., 2013), which has important impacts on climate (Feng et al., 2013; J. Liu et al., 2014). For the four (out of five) datasets where BBOA is resolved

by PMF analysis in this study, the correlation between BBOA and brown carbon is greater than 0.69, with the best correlation observed at JST_Nov ($R = 0.90$) (Fig. 7). The correlation between BBOA and brown carbon is only 0.47 for YRK_Dec, which is likely caused by other brown carbon sources at the YRK site. This hypothesis could be supported by the summer measurements in YRK. In YRK_July, we observed a large abundance of brown carbon, which reaches daily maximum around 2 p.m. (Fig. S8); however, a BBOA factor is not resolved for YRK_July, indicating that brown carbon, in this case, could arise from sources other than biomass burning. Hecobian et al. (2010) suggested that SOA from aqueous phase reactions may be an important source for brown carbon in summer based on analysis on ~ 900 filters collected in 2007 in the southeastern US. A recent laboratory study showed that SOA from IEPOX reactive uptake could be light-absorbing and potentially an important source for brown carbon (Lin et al., 2014). However, Isoprene-OA factor, which is related to the IEPOX uptake pathway studied in Lin et al. (2014), only shows weak correlation (R ranges from 0.22 to 0.50) with brown carbon as shown in Fig. S9. As suggested by Washenfelder et al. (2015), the difference between ambient observation and laboratory studies might be due to that the IEPOX-derived absorbing chromophores do not dominate the Isoprene-OA mass. However, further studies are warranted to resolve this difference.

4.1.5 MO-OOA

Two oxygenated OA factors (MO-OOA and LO-OOA) with high, but differing O : C ratios, were identified in both rural and urban sites throughout the year. Based on their inferred volatility from O : C ratios, OOA factors are typically named as low-volatility OOA (higher O : C and lower volatility) and semi-volatile OOA (lower O : C and higher volatility) (Ng et al., 2010; Jimenez et al., 2009). However, recent studies showed that O : C ratios are not always well-correlated with aerosol volatility (Hildebrandt et al., 2010; Xu et al., 2014). Thus, in this study, we use the terms "more-oxidized OOA" (MO-OOA, O : C ranges between 0.66 and 1.05, with an average of 0.87) and "less-oxidized OOA" (LO-OOA, O : C ranges between 0.44 and 0.62, with an average of 0.54) (Fig. S10). This

terminology has been used in several previous studies (Setyan et al., 2012; Xu et al., 2015).

MO-OOA contributes 24–49 % of total OA mass (Fig. 5). This factor has the highest O : C ratio, indicating that it is highly oxidized. It has been shown that as OA ages in the atmospheric, the mass spectra of OA from different sources become increasingly similar to each other and resemble that of MO-OOA (Jimenez et al., 2009; Ng et al., 2010). Thus, MO-OOA likely represents highly aged organic aerosol from multiple sources, which causes the identification of MO-OOA to be challenging. In addition to a high degree of oxidation, other notable features of MO-OOA are its diurnal profile and ubiquitous presence. As shown in Fig. 6, in most datasets except RS_Jan, the diurnal profile of MO-OOA reaches a daily maximum in the afternoon. The daytime increase in MO-OOA would become more prominent after considering the dilution caused by boundary layer height expansion during the day. The similar diurnal profile has also been observed in a number of studies (Aiken et al., 2009; DeWitt et al., 2014; Hildebrandt et al., 2010; Huang et al., 2010; Setyan et al., 2012). Moreover, not only in this study in which MO-OOA is identified in different sites and seasons, MO-OOA (or the OOA factor in general) was also identified in datasets obtained at multiple sites around the world, pointing to the ubiquitous nature of this OA subtype (Jimenez et al., 2009; Ng et al., 2010).

Possible sources of this factor have been proposed in the literature. Firstly, a number of studies proposed that the source for MO-OOA is long-range transport (Li et al., 2015; Hayes et al., 2013; Robinson et al., 2011b; Raatikainen et al., 2010). This proposed mechanism could explain the high degree of oxidation of MO-OOA because the aerosol gets progressively more oxidized during advection, but it is unlikely to explain the well-defined diurnal profile of MO-OOA (peaks in the afternoon). Secondly, humic-like substances (HULIS) are proposed to be a source of MO-OOA because the mass spectrum and the degree of oxidation of HULIS resembles those of MO-OOA (Ng et al., 2010; El Haddad et al., 2013). A recent study by Paglione et al. (2014) performed factor analysis on NMR measurements of water-soluble organic carbon extracted from

filters collected in the Netherlands and resolved a factor with mass spectral features that are similar to HULIS. Further, the authors showed that this HUILS factor correlates with the most-oxidized OOA factor (O : C = 0.98) resolved from PMF analysis of their HR-ToF-AMS measurements, providing a linkage between HULIS and MO-OOA.

Thirdly, the oxidation of vehicle emission or fuel combustion in general might also contribute to MO-OOA mass, but such contribution is uncertain. On one hand, multiple studies have shown that the photooxidation of gas-phase species from direct vehicle emissions or POA evaporation could rapidly produce secondary OA, which resembles the mass spectrum of oxygenated OA factors and could be 1–2 orders of magnitude higher than the primary OA emissions (Nordin et al., 2013; Presto et al., 2014; Jathar et al., 2014; Platt et al., 2013). In addition, a previous study by Liu et al. (2011) showed that the carboxylic acids measured by FT-IR are exclusively associated with fossil fuel combustion and correlate with PMF resolved OOA factor from HR-ToF-AMS measurements in coastal California. On the other hand, Zotter et al. (2014) showed that > 69 % of MO-OOA originated from non-fossil sources in LA basin based on a combination of radiocarbon analysis and AMS PMF analysis. By using the same method, DeWitt et al. (2014) showed that the majority of carbon in OOA is non-fossil even in an environment heavily influenced by traffic emissions, suggesting the source of MO-OOA is not vehicle emissions. At last, aged biomass burning is also a possible source for MO-OOA as discussed above in Sect. 4.1.4.

One interesting observation in this study is that MO-OOA is well-correlated with ozone in summer ($R = 0.73$ for JST_May and YRK_July), but not in winter ($R = -0.059$ and -0.27 for JST_Nov and YRK_Dec, respectively) (Fig. 8), implying the sources of MO-OOA may vary with seasons. Considering the large biogenic VOC emissions in summer, the summer MO-OOA may be related to the oxidation of biogenic VOCs. Recently, Ehn et al. (2014) for the first time observed that monoterpenes oxidation could produce large amounts of extremely low-volatility vapors. As these compounds have very high O : C (~ 0.7), it is possible that they serve as an important source for MO-OOA. The identification of the sources of winter MO-OOA could be aided by the

10504

radiocarbon analysis. For example, if the majority of MO-OOA in winter has non-fossil sources, it could suggest that aged OA from biomass burning is an important source for MO-OOA, because biomass burning is enhanced and the emissions of biogenic VOCs are low in winter.

4.1.6 LO-OOA

Similar to MO-OOA, less-oxidized oxygenated organic aerosol (LO-OOA) is also observed in both rural and urban sites throughout the year. LO-OOA comprises 19–34 % of total OA (Fig. 5). A key feature of LO-OOA is that it consistently exhibits a daily maximum at early morning and night in all datasets (Fig. 6). The similar diurnal variation of LO-OOA has also been observed in previous field measurements and thought to be primarily driven by the semi-volatile nature of LO-OOA. The LO-OOA factor identified in multiple prior field measurements has been observed to correlate with ammonium nitrate, a semi-volatile species which mainly partitions into the particle phase at night when the temperature is relatively low (Jimenez et al., 2009; Sun et al., 2012a; Zhang et al., 2011; Ulbrich et al., 2009). However, in this study, LO-OOA only shows moderate correlation with total NO_3 (i.e., $NO_{3,meas}$) measured by the HR-ToF-AMS in summer datasets (R ranges between 0.56 and 0.76) and no correlation in winter datasets (R ranges between 0.14 and 0.46) (Fig. 9 and Table 2).

While LO-OOA only moderately or sometimes poorly correlates with $NO_{3,meas}$ in this study, we find improved correlation between LO-OOA and "nitrate functionality from organic nitrates" (i.e., $NO_{3,org}$) (Fig. 9 and Table 2). $NO_{3,org}$ is estimated by using NO_x^+ ratio method as described in Sect. 2.5. A R_{ON} value of 10 is applied since different R_{ON} values would only affect the estimated concentration of $NO_{3,org}$, but not the correlation between LO-OOA and $NO_{3,org}$, because estimated $NO_{3,org}$ has a linear relationship with R_{ON}. For most datasets, LO-OOA correlates better with $NO_{3,org}$ than total nitrates. The biggest improvement is seen in JST_Nov, where the correlation R increases from 0.14 to 0.63. However, we also note that the correlation becomes worse for YRK_Dec and RS_Jan, which is likely caused by the small contribution of organic nitrates to total

nitrates, resulting in a larger uncertainty in the NO_x^+ ratio method (Bruns et al., 2010). In addition, the correlations between LO-OOA and $NO_{3,org}$ for YRK_Dec and RS_Jan are weakened by the negative $NO_{3,org}$ concentration from estimation (Fig. 9), which is a result of smaller R_{meas} than R_{AN} at times (see Eq. 1), likely caused by contribution from inorganic nitrates other than ammonium nitrate or variation in instrument performance (Farmer et al., 2010; Rollins et al., 2010).

4.2 Nitrates source apportionment

4.2.1 Estimation of organic nitrates

NO_x^+ ratio method and PMF method are applied to estimate the concentration of "nitrate functionality from organic nitrates" (i.e., $NO_{3,org}$) at different sites. The concentration of $NO_{3,org}$ and the mass fraction of $NO_{3,org}$ in total measured NO_3 (i.e., $NO_{3,meas}$) estimated from both methods are shown in Fig. 10. Both the NO_x^+ ratio method and the PMF method show a similar seasonality of the contribution of $NO_{3,org}$ to $NO_{3,meas}$ (denoted as $NO_{3,org}/NO_{3,meas}$), which is higher in summer than winter. However, we observe noticeable differences between the two methods. In the following discussion, we first discuss the uncertainties associated with NO_x^+ ratio method and PMF method. Then, we discuss how the uncertainties affect the comparison between the two methods and provide a "best estimate" range of $NO_{3,org}$ based on the two methods. Lastly, we use the "best estimate" range of $NO_{3,org}$ to calculate the contribution of organic nitrates to OA by assuming the MW of organic nitrates.

For the PMF method, the uncertainty is mainly associated with the identification of a nitrate inorganic aerosol (NIA) factor. The NIA factor is resolved from most datasets except CTR_June and YRK_July. The mass spectrum of the NIA factor is similar to the corresponding factor in Sun et al. (2012b) (Fig. S4). Specifically, it is dominated by NO^+ and contains some organic signals such as CO_2^+ and $C_2H_3O^+$, indicating the NIA factor has potential interference from organics. The mass fraction of organic signals in the NIA factor varies across sites, with a higher value in warmer months ($\sim 70\%$

in JST_May and GT_August) than colder months (16–38 % in JST_Nov, YRK_Dec, and RS_Jan) (Fig. S11). The fact that the NO^+/NO_2^+ ratio of the NIA factor resolved from warmer months is higher than that of pure ammonium nitrate (Fig. S12) is also indicative of organic nitrate interference in the NIA factor. Conversely, the NO^+/NO_2^+

5 ratio of the NIA factor resolved from colder months is closer to that of pure ammonium nitrate, suggesting less interference from organics. Thus, for the sites where a NIA factor is identified, the presence of organic nitrates in the NIA factor would result in an underestimation of $NO_{3,org}$, and the underestimation is larger for warmer months (i.e., JST_May and GT_August). For CTR_June and YRK_July, the NIA factor is not resolved

10 from PMF_{org+NO_3} analysis, likely due to a small concentration of inorganic nitrates. For example, the concentrations of organics and total nitrates (i.e., $NO_{3,meas}$) are 5.0 and 0.1 $\mu g\,m^{-3}$, respectively, for CTR_June. Even if one assumes that all the measured nitrates arise from inorganic nitrates, the nitrates / organics ratios is only 2 %, making it difficult for PMF to retrieve the NIA factor accurately (Ulbrich et al., 2009). Thus,

15 for CTR_June and YRK_July, the small amount of $NO_{3,inorg}$, which is not retrievable by PMF, was attributed into OA factors so that the PMF method would slightly overestimate $NO_{3,org}$.

For the NO_x^+ ratio method, considering the large variation in NO_x^+ ratio for different organic nitrates, the largest uncertainty is associated with the value of R_{ON}. Ideally, the

20 time-dependent R_{ON} values should be applied. However, this is challenging because the determination of time-dependent R_{ON} requires measurements of every ambient organic nitrate species, which are not available. With this, we apply R_{ON} values of 5 and 10 in our analysis to provide the upper and lower bounds of the estimated $NO_{3,org}$ concentration for the NO_x^+ ratio method as discussed in Sect. 2.5. It is noted that for

25 Centreville, we applied a third method to calculate the concentration of $NO_{3,org}$, which is based on the differences between HR-ToF-AMS measurements (NO_3 from both organic and inorganic species) and PILS-IC measurements (NO_3 from inorganic species only) (Xu et al., 2015; Bae et al., 2007; Orsini et al., 2003). This method, denoted as AMS-IC method, is only applied for Centreville because PILS-IC was not deployed

in the SCAPE study. In order to match the HR-ToF-AMS particle cut size (i.e., PM_1), a PM_1 cyclone was deployed at the inlet of PILS-IC. However, due to the transmission efficiency of PM_1 cyclone, PILS-IC measurements might have interferences from particles larger than 1 μm (i.e., $NaNO_3$ in mineral dust). The interferences are expected to be small because the sodium concentration measured by PILS-IC with PM_1 cyclone is negligible and mostly below its detection limit (0.07 μg m^{-3}) (Fig. S13). As shown in Fig. 11, The $NO_{3,org}$ estimated by the AMS-IC method falls within the range of NO_x^+ ratio method, which is defined by R_{ON} values of 5 and 10, indicating the feasibility to use these two values as the upper and lower bounds to estimate $NO_{3,org}$ for the NO_x^+ ratio method.

Based on the uncertainties of the PMF method and the NO_x^+ ratio method, we could explain the differences between the two methods and further combine them in order to narrow the estimation range. According to the extent of agreement between the two methods, all seven datasets are grouped into three categories: summer months (CTR_June and YRK_July), transition months (JST_May and GT_August), and winter months (JST_Nov, YRK_Dec, and RS_Jan).

For winter months, the PMF method shows good agreement with the NO_x^+ ratio method with a R_{ON} value of 10 for JST_Nov and YRK_Dec. This is consistent with the observations that the interference of organic nitrates in the NIA factor is small in winter datasets (Figs. S11 and S12) and isoprene emission is negligible in winter (Guenther et al., 2006). Thus, results from the NO_x^+ ratio method with $R_{ON} = 5$ (i.e., isoprene organic nitrates) are likely unrealistic. With this, we combine the results from the PMF method and the NO_x^+ ratio method with $R_{ON} = 10$ as the "best estimate" range of organic nitrates for JST_Nov and YRK_Dec. For RS_Jan, the NO_x^+ ratio method predicts negative $NO_{3,org}$ due to R_{meas} being smaller than R_{AN} at times (Eq. 1). In this case, the PMF method is selected as the "best estimate". Taken together, the mass fraction of organic nitrates (i.e., $NO_{3,org}/NO_{3,meas}$) is 0.19–0.21, 0.11–0.21, and ~ 0.10 for JST_Nov, YRK_Dec, and RS_Jan, respectively.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

For summer months, the PMF method predicts that all the measured nitrates are from organic nitrates are (i.e., $NO_{3,org}/NO_{3,meas} = 1$, Fig. 10), because a NIA factor is not resolved from PMF analysis and that all the measured NO_3 are distributed in the OA factors. The $NO_{3,org}$ estimated from the PMF method falls within the upper (i.e., $R_{ON} = 5$) and lower bound (i.e., $R_{ON} = 10$) of the NO_x^+ ratio method (Fig. 10). For CTR_June, the NO_x^+ ratio method with R_{ON} value of 5 predicts a $NO_{3,org}/NO_{3,meas}$ ratio that is greater than 1, which results from the assumed R_{ON} value (i.e., 5) being smaller than R_{meas} at times (Eq. 1). Thus, the PMF method and the NO_x^+ ratio method with $R_{ON} = 10$ define the upper and lower bound, respectively. Accordingly, the "best estimate" range of $NO_{3,org}/NO_{3,meas}$ is 0.80–1 and 0.63–1 for CTR_June and YRK_July, respectively.

For transition months (i.e., JST_May and GT_Aug, the sampling periods of which were between summer and winter), the PMF method and the NO_x^+ ratio method show large discrepancies. Compared to PMF method, the NO_x^+ ratio method predicts 1.5–2.5 times higher $NO_{3,org}$ concentration depending on site and R_{ON} value. This is likely caused by the PMF method under-predicting $NO_{3,org}$ owing to the attribution of some organic nitrates to the NIA factor. Thus, we select the NO_x^+ ratio method with R_{ON} values of 5 and 10 as the "best estimate" range. Accordingly, $NO_{3,org}/NO_{3,meas}$ ranges 0.55–0.76 and 0.64–0.99 for JST_May and GT_Aug, respectively.

Further, we calculate the contribution of organic nitrate molecules to OA from "best-estimate" range of nitrate functionality (i.e., $NO_{3,org}$). We assume that particle-phase organic nitrates have an average molecule weight of 200 and 300 g mol^{-1} (Rollins et al., 2012), which provides an lower and upper bound for estimated concentration of organic nitrates. As shown in Fig. 10, organic nitrates contribute about 5–12 % of total OA for summer datasets (CTR_June and YRK_July) and 9–25 % of total OA for winter datasets (JST_Nov, YRK_Dec, and RS_Jan), suggesting that organic nitrates are important components of total OA in the southeastern US.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

4.2.2 Nitrate seasonal variation

As shown in Table 1 and Fig. 2, the total nitrate concentration is higher in winter (0.8–1.4 μg m^{-3}, 10–16 % of total NR-PM$_1$) than summer (0.3–0.4 μg m^{-3}, 2–3 % of total NR-PM$_1$). Based on the NO$_x^+$ ratio method, NO$_{3,inorg}$ is greatly enhanced in winter relative to summer. For example, the concentration of NO$_{3,inorg}$ increases from 0.22 μg m^{-3} (average of upper and lower bound of the NO$_x^+$ ratio method) in May to 1.6 μg m^{-3} in November for JST site. Similarly, NO$_{3,inorg}$ shows a 10-fold increase for YRK_Dec compared to YRK_July.

The seasonal variation of inorganic nitrates could possibly be caused by its semi-volatile nature and varying NO$_x$ emissions. Based on volatility measurements by a thermal denuder, Huffman et al. (2009) showed that ammonium nitrate is very volatile and its gas/particle partitioning is largely affected by temperature. The average temperature in summer is about 15 °C higher than that in winter (Table 1). According to laboratory measurements of ammonium nitrate volatility, a 15 °C increase in temperature would lead to the evaporation of 60 % of nitrate mass (Huffman et al., 2009). In addition to volatility, the winter enhancement of inorganic nitrates is related to higher NO$_x$ level, which is the major source for inorganic nitrates and largely elevated in winter in the southeastern US (Blanchard et al., 2013). For example, as shown in Table 1, the NO$_x$ concentration in JST_Nov (50.5 ppb) is 3.5 times higher than that in JST_May (14.4 ppb). Thus, the lower temperature and higher NO$_x$ level in winter than summer likely compensate the weaker photooxidation and result in the increase in inorganic nitrates. Interestingly, we observe a rush hour peak (around 9 a.m.) in the diurnal trend of total nitrates at urban sites in winter (JST_Nov and RS_Jan). This rush hour peak is primarily from inorganic nitrates supported by the following evidence: (1) the R_{meas} is close to R_{AN} during the rush hour period (Fig. S15), (2) the rush hour peak only exists in the diurnal profile of NO$_{3,inorg}$ (Fig. S16), and (3) the coincident peak in the diurnal trend of NH$_4$ (Fig. 3). Early morning peaks in inorganic nitrates were also consistently seen by a variety of online instruments as part of the Atlanta Supersite Experiment at

the JST site (Weber et al., 2003). In Mexico City, Hennigan et al. (2008) attributed the fast production of inorganic nitrates mainly to secondary formation from photooxidation of NO_x and subsequent partitioning of HNO_3. The rush hour peak of inorganic nitrates disappear rapidly, which is likely caused by evaporation and dilution as the planetary boundary layer height increases (Hennigan et al., 2008).

The concentration of $NO_{3,org}$ is slightly higher in summer, but its seasonal variation is not as strong as $NO_{3,inorg}$ (Table 2 and Fig. 10). This is likely due to compensating effects of source strength and gas/particle partitioning. The organic nitrates mainly originate from VOCs oxidation by the nitrate radical and/or photooxidation in the presence of NO_x. The VOC concentrations are higher in summer due to stronger biogenic emissions, which would provide sources for organic nitrates. However, the temperature is higher in summer than winter, which would hinder the partitioning of organic nitrates into the aerosol phase.

4.3 Aerosol spatial distribution

The spatial distribution of organics, sulfate, ammonium, and total nitrate in the greater Atlanta area is investigated by comparing ACSM measurements (stationary at the Georgia Tech site) with HR-ToF-AMS measurements (rotating among different sites). The HR-ToF-AMS and ACSM measurements between different sites are shown in Fig. S14 and the correlations (Pearson's R) of the four species are shown in Fig. 12. The ACSM and HR-ToF-AMS are compared side-by-side at the Georgia Tech (GT) site from 20 July to 4 September 2012 and the time series of the species measured by the two instruments are well correlated ($R = 0.95, 0.93, 0.82, 0.85$ for organics, sulfate, ammonium, and total nitrate, respectively) and agree within instrument uncertainty (i.e., 20–35 %) (Bahreini et al., 2009).

As expected, the correlation gets weaker as the distance between the GT site and other sampling sites increases. Surprisingly, the organic correlation in July is 0.92 between GT and YRK sites, which have considerable spatial separation (i.e., 70 km), indicating that the organics are uniformly distributed in the greater Atlanta area in summer

time. In contrast, the organic correlation between GT and YRK decreases to 0.66 in winter. Unlike organics, the correlation in SO_4 between GT and YRK is similarly good in both summer and winter ($R = 0.7$ and 0.85 for summer and winter, respectively). Our observation is generally consistent with the previous study by Zhang et al. (2012), who showed that WSOC, and to a less extent SO_4, are spatially homogeneous in the southeastern US based on results from daily-average filter measurements (one filter in every six days) in 2007. The authors attributed the uniform distribution of WSOC and SO_4 largely to stagnant air masses in southeastern US during summer time and both long-lived secondary WSOC and SO_4 eventually spread across the region. Hidy et al. (2014) also showed that secondary species, like SO_4, have weaker rural and urban contrast in the southeastern US, though only yearly average data were considered in that study.

Although meteorology plays an important role in the spatial distribution of aerosol, it alone cannot explain the seasonal variation of OA spatial distribution. For example, meteorology should have the same effect on the regional distribution of SO_4 and OA. However, while SO_4 is uniformly distributed in both summer and winter, OA is more uniform in summer than winter, suggesting other factors also influence the spatial distribution of OA. The seasonality of OA spatial distribution (i.e., highly spatially homogeneous in summer than winter) is probably affected by the seasonal variation of OA sources in addition to meteorology. As shown in Fig. 5, SOA is the dominant source for total OA (69–100 % of OA) in summer for both rural and urban sites. This likely arises from that biogenic VOCs, which are important precursors for SOA, are abundant and widely distributed in the southeastern US during summer time (Guenther et al., 2006). Thus, SOA is regional and the dominant component of OA, leading to the uniform distribution of OA. In contrast, POA concentration varies greatly between urban and rural sites. In winter, while the SOA still dominates total OA at rural sites, the POA is comparable with SOA at urban sites (Fig. 5). This is because the concentration of regional SOA decreases due to weaker photochemical activity and lower biogenic VOCs emissions in winter, but the concentration of POA (HOA + BBOA + COA) is relatively constant or

even increases. This is likely due to elevated emission from biomass burning and reduced evaporation and dilution, which are associated with lower temperatures in winter (Fig. 5). Thus, the fact that POA is not uniformly distributed and the concentration of POA is comparable to SOA possibly lead to the spatial non-uniformity of OA in winter.

4.4 Interpretation of long-term measurements

In this section, we compare our observations from short-term and extensive measurements with those from long-term and basic measurements to test the robustness of our conclusions. Further, based on our extensive measurements, we attempt to provide insights in interpreting long-term observations.

4.4.1 OA diurnal variation

By investigating the diurnal pattern of organic carbon (OC) from 1 June–15 July of each year (from 2000 to 2013) in Centreville, rural Alabama, Hidy et al. (2014) observed that OC shows consistently weak diurnal variability. Similarly, Zhang et al. (2012) observed that water-soluble organic carbon (WSOC), which is a surrogate for SOA, only shows moderate increase in the daytime in Jefferson Street and Yorkville, GA, during 2008 summer. In this study, we find that OA shows little diurnal variability in summer datasets (Fig. 3), which is consistent with long-term observations and previous studies in literature.

The lack of prominent daytime increase in the OA in summer could appear to discount the role of photochemistry-driven secondary OA formation. However, a number of factors need to be considered, such as the changes in planetary boundary layer height, contribution of various sources to OA, and temperature-dependent gas/particle partitioning. Firstly, the rapid expansion of boundary layer during the day may dilute the OA concentration. In Centreville, we observed that OA exhibits a distinct increase starting at noon after multiplying its diurnal profile by boundary layer height (Fig. 3d), which was measured by a ceilometer. For the cases where boundary layer height data

are not available, normalizing OA by CO is often utilized in literature to minimize the effect of dilution, considering CO as an inert species. By using this method, Blanchard et al. (2011) and Zhang et al. (2012) showed that OC/CO and WSOC/CO exhibit pronounced daytime increase, suggesting that the expansion of boundary layer would weaken the OA diurnal variation. The fact that both OC/CO and WSOC/CO peaks in the day implies that photochemistry-driven SOA production is an important source of OA.

Secondly, the time-dependent contributions of various sources to total OA could also affect its diurnal profile. As shown in Fig. 6, the various OA sources resolved by PMF analysis have distinctly different diurnal trends, indicating that their contributions to total OA vary throughout the day. Primary sources, such as HOA and COA, peak during rush hours and meal time, respectively. The contributions of Isoprene-OA and MO-OOA to total OA are largest in the afternoon and decrease after sunset. In contrast, another SOA source, LO-OOA, peaks in the early morning and at night, as the formation of LO-OOA is proposed to mainly correspond to nocturnal nitrate radical oxidation of biogenic VOCs in summer (Xu et al., 2015). Therefore, different diurnal trends of various OA sources compensate each other, which possibly results in the weak diurnal variation of total OA.

Specifically, LO-OOA, which exhibits a daily maximum at night, compensates the decrease of other OA sources after sunset and results in the relatively flat total OA diurnal profile. This has important implication in interpreting non-speciated OC measurements. For example, Hennigan et al. (2009) observed a substantial nocturnal increase of gas-phase WSOC, but not an accompanied increase in particle-phase WSOC in Atlanta during summer. The authors hypothesized that the differences between gas-phase and particle-phase WSOC are caused by the oxidation of α-pinene and isoprene by $NO_3^{\bullet}$ radical producing substantial amount of gas-phase WSOC but little particle-phase WSOC. Though it is plausible that α-pinene $+NO_3^{\bullet}$ and isoprene $+NO_3^{\bullet}$ reactions produce more volatile products than low-volatility products, our study shows that there is indeed substantial nocturnal SOA production (i.e., LO-OOA), which likely corresponds

to the nocturnal increase in gas-phase WSOC in Hennigan et al. (2009) but not clearly discernible in particle-phase WSOC due to the compensation by the decreasing concentrations of other OA sources at night.

In addition, temperature-dependent gas/particle partitioning also plays a role in OA diurnal variation. As the temperature is higher during day, the gas/particle partitioning would favor gas-phase and hence lower the particle-phase concentration. Taken together, the weak diurnal variation of OA in summer is likely caused by changes in boundary layer height and varying contribution of various OA sources throughout the day, which does not contradict the importance of photochemistry-driven SOA production. Especially, LO-OOA, which is likely related to $NO_3^{\bullet}$ chemistry, peaks at night and compensates the nocturnal decrease of other SOA sources. In fact, the importance of photochemistry can be gained by comparing OA diurnal profile of summer and winter. As the photochemistry is relatively weaker in winter, daytime SOA production is suppressed, which results that OA reaches daily minimum during daytime in winter datasets (Fig. 3).

4.4.2 Urban and rural contrast of OA seasonality

In this study, we observed that the seasonality of OA behaves differently between urban and rural sites. For example, while the OA concentration is relatively constant between summer and winter for urban JST site ($9.1\,\mu g\,m^{-3}$ in May vs. $7.9\,\mu g\,m^{-3}$ in November), OA concentration is ~ 4 times higher in summer than winter for rural YRK site ($11.2\,\mu g\,m^{-3}$ in July vs. $3.2\,\mu g\,m^{-3}$ in December). Our observations are consistent with the long term measurements from the SEARCH network. Figure 13 shows the seasonal average OC concentration measured in JST and YRK sites from 1999 to 2013. Despite of the decreasing trend of OC in the past 14 years, which has been noted and discussed extensively in Hidy et al. (2014), we note that the OC concentration is similar between summer and winter at the JST site, but OC is elevated in summer compared to winter for the YRK site. The urban and rural contrast of OA seasonality is likely caused by that OA sources are different at urban and rural sites. As shown by PMF analysis

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

on our short-term measurements, the total OA in rural YRK site is dominant by SOA in both summer and winter (SOA/OA = 100 and 78 % for summer and winter, respectively, Fig. 5), but the concentration of SOA is lower in winter when the SOA formation is depressed due to low biogenic VOCs emissions and weak photochemical activity. For the urban JST site, in contrast, POA accounts for a large fraction of total OA (30–48 %, depending on the month). Though the SOA formation is also depressed in winter at urban sites, the decrease in SOA concentration is compensated by the increase in POA concentration from vehicles and cooking (Fig. 5). Thus, the OA in JST is relatively constant between summer and winter. The fairly flat seasonal trend in OA or OC at urban sites has not been captured by current models. All 31 models reviewed in a recent study by Tsigaridis et al. (2014) predicted higher OC concentration in summer than winter for urban monitoring sites in Georgia. One possible reason is that the anthropogenic emission inventories applied in current models do not take seasonal variation into account, resulting under-prediction of the pollution levels in urban area.

4.4.3 Correlation between OC and sulfate

Based on the OC and sulfate measurements (2005–2010) from three SEARCH network sites (Centreville, Jefferson Street, and Yorkville), we find that regardless of the sampling sites, the correlation between OC and sulfate has distinct seasonal variation, with the best correlation in summer (R ranging 0.47–0.69) and worst in winter (R ranging 0.01–0.33) (Fig. 14). Since sulfate is mostly secondary in the southeastern US, one possible explanation for the seasonality of the correlation between OC and sulfate is that the majority of OC is secondary in summer, but not in winter, which is supported by the OA source apportionment in this study. It is also likely that sulfate is directly involved in the OA production in summer. Specifically, Xu et al. (2015) found that sulfate directly and largely mediates the formation of isoprene OA (18–36 % of total OA in summer) in the southeastern US, instead of particle water content and/or particle acidity as previous studies have suggested.

5   Conclusions

Nearly one-year measurements were performed across multiple sites in the southeastern US with a variety of online instruments, with the focus on HR-ToF-AMS data in this study. We find that organics are the dominant components of the NR-PM$_1$ at both rural and urban sites throughout the year. The OA diurnal profile shows little variation in summer and peaks at night in winter datasets. The lack of midday enhancement in OA diurnal profile is likely caused by the expansion of boundary layer in the day and compensating effects of various OA factors. The OA measured at different sampling sites and seasons has a similar degree of oxidation. Sulfate contributes the second highest to NR-PM$_1$. Sulfate concentration is higher in summer (3.0 to 4.0 $\mu g\,m^{-3}$) than winter (1.4 to 1.7 $\mu g\,m^{-3}$), probably due to stronger photochemistry in summer. In contrast to sulfate, inorganic nitrate concentration is estimated to be tripled in winter than summer. This is likely caused by higher NO$_x$ levels in winter, which serves as the source for inorganic nitrates and the semi-volatile nature of inorganic nitrates, which tend to partitions into the particle phase when the temperature is low.

Positive Matrix Factorization (PMF) analysis revealed that the organic aerosol has various sources in the southeastern US, which changes between seasons and sampling sites (rural vs. urban). Hydrocarbon-like organic aerosol (HOA) and cooking organic aerosol (COA), which arise from primary vehicle emissions and cooking, respectively, are important but not dominant OA sources for urban sites. Biomass burning OA (BBOA) concentrations shows clear enhancements in winter compared to summer. In addition, biomass burning is found to be an important, but not exclusive, source for brown carbon in the southeastern US. Isoprene-derived OA (Isoprene-OA), which is from the reactive uptake of isoprene epoxides in the presence of hydrated sulfate, only exists in warmer months (May–August) when the isoprene emission is substantial. In addition to rural sites, Isoprene-OA is resolved from urban sites where the majority of peroxy radicals are believed to react with NO$_x$. We note that $f_{C_5H_6O^+}$, which has been used as a marker for Isoprene-OA, ranges from 0.9–2.3 % and is higher in the Isoprene-

OA factor from rural sites than urban sites. One possible source of Isoprene-OA in urban sites is transport. However, transport would unlikely result in the reproducible diurnal profile of Isoprene-OA, which peaks in early afternoon. Instead, Isoprene-OA in urban sites more likely comes from local production as a recent study showed that IEPOX could be produced in the presence of NO_x (Jacobs et al., 2014). Less-oxidized oxygenated OA (LO-OOA) and more-oxidized oxygenated OA (MO-OOA) are resolved from both rural and urban sites throughout the year. LO-OOA shows improved correlation with estimated "nitrate functionality from organic nitrates" (i.e., $NO_{3,org}$) than total nitrates. In addition, both LO-OOA and estimated $NO_{3,org}$ peaks at night (Figs. 6 and S16), implying that LO-OOA could arise from nighttime oxidation of biogenic VOCs by nitrate radicals. Unlike isoprene, monoterpene emission is year-around and continues into the nights. The prevalent presence of the LO-OOA factor at all sites year-around points to the important contribution of monoterpene SOA to the total OA budget in the Southeastern US. As the most oxidized OA factor, MO-OOA reaches a daily maximum in the afternoon and likely contains aged OA from various sources, such as vehicle emission, biomass burning, and aged OA from biogenic VOCs. We find that the correlation between MO-OOA and ozone is substantially better in summer than winter, suggesting that the sources of MO-OOA might vary with season.

In order to estimate the organic nitrate contribution to OA, we applied and evaluated three methods, i.e., the NO_x^+ ratio method, the PMF method, and AMS-IC method. Despite the uncertainty of NO_x^+ ratio method (i.e., the values of R_{ON} and R_{AN}) and PMF method (i.e., the separation of pure NIA factor), both methods provide reasonable results in separating the measured total nitrates into nitrate functionality from inorganic and organic nitrates. The "nitrate functionality from organic nitrates" (i.e., $NO_{3,org}$) accounts for about 63–100 and 10–20 % of total measured nitrate (i.e., $NO_{3,meas}$) in summer and winter, respectively. Further, we estimate the contribution of organic nitrates to total OA based on estimated $NO_{3,org}$ and assumed MW of bulk organic nitrates. Depending on location, season and estimation method, organic nitrates account for about

5–25 % of total OA, which indicates that organic nitrates are important components in the ambient aerosol.

The spatial distribution of OA is investigated by comparing ACSM measurements (stationary at the Georgia Tech site) and HR-ToF-AMS measurements (rotating among different sites). In summer, OA is spatially homogeneous as suggested by the good correlation ($R = 0.92$) in July between the GT and YRK sites, which are 70 km apart. The spatial homogeneity of OA in summer is likely caused by SOA being the dominant source of OA for both urban and rural sites. The parameters such as temperature, solar radiation, and precursor VOCs, which have great influences on SOA formation, are similar between urban and rural sites. Compared to summer, the OA is less spatially homogenous in winter. The correlation of OA between GT and YRK decreases to 0.66 in winter. This is likely due to the elevated contribution from POA to total OA in winter and the spatially inhomogeneous distribution of POA. Meteorology also plays a role in the OA spatial distribution, but alone is unlikely to explain the observation.

We show that short-term and extensive measurements can help interpret long-term basic measurements. For example, consistent with long-term (1999–2013) OC measurements from the SEARCH network, we also observed that the seasonal variation of OA has some urban and rural contrasts. While the OA concentration is similar between summer and winter for the urban JST site, it increases 4 times from winter to summer for the rural YRK site according to our year-long observation. PMF analysis suggests that the different OA seasonality between urban and rural sites is likely due to varying strength of OA sources. For rural sites, SOA represents the dominant fraction of OA in both summer and winter, but SOA concentration is much lower in winter. For urban sites, in contrast, the decrease in SOA concentration in winter is compensated by the increase in POA concentration, leading to a relatively constant total OA concentration compared to summer. In addition, analysis of long-term OC and sulfate measurement from the SEARCH network shows that the correlation between OC and sulfate is substantially better in summer than winter, consistent with our source apportionment results that the majority of OA is secondary in summer. The better correlation

of OC and sulfate in summer also supports that sulfate directly mediates the formation of isoprene SOA (Xu et al., 2015), which is only present in warmer months.

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Aerosol characterization over the southeastern United States

L. Xu et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Aerosol characterization over the southeastern United States

L. Xu et al.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures

◀	▶
◀	▶

| Back | Close |

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

ACPD

15, 10479–10552, 2015

Aerosol characterization over the southeastern United States

L. Xu et al.

Title Page

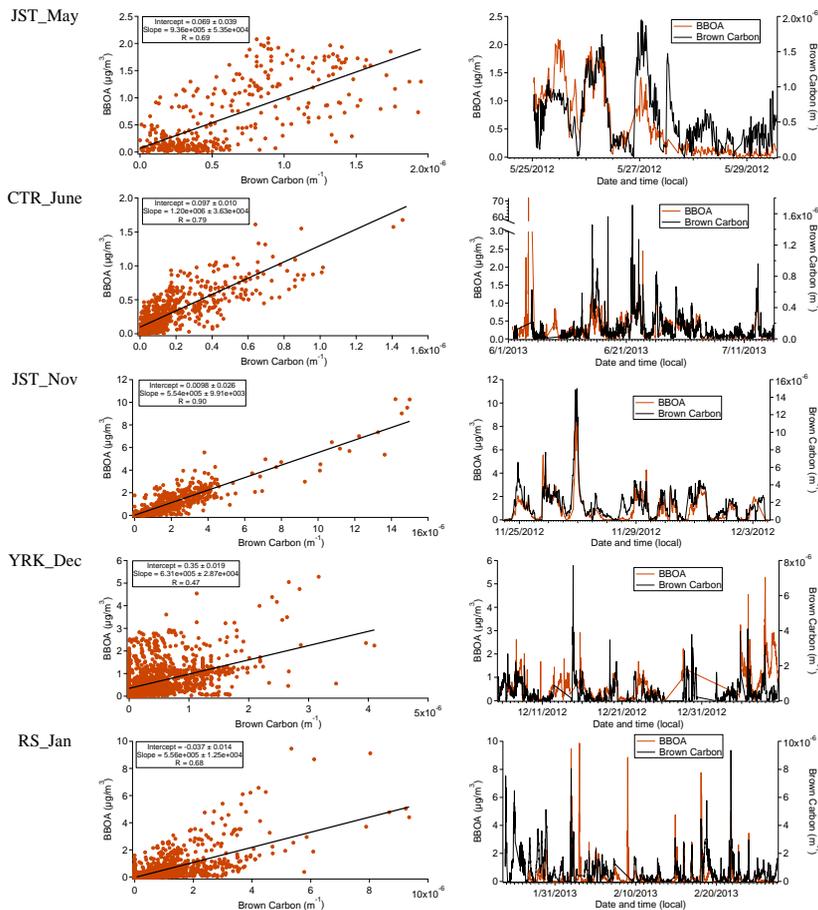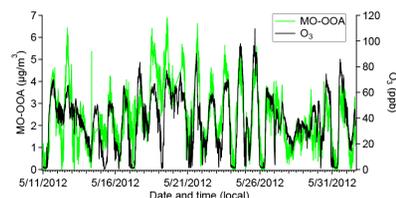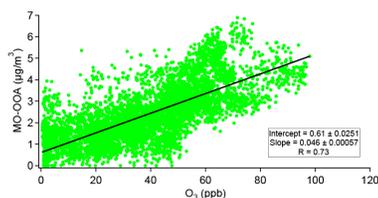Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Sampling sites and periods for the SCAPE and SOAS studies. Meteorological conditions, mixing ratios of gas-phase species, and mass concentrations of black carbon and NR-PM_1 species for all datasets. Average ± one standard deviation are reported.

AMS sampling site Sampling period Abbreviation		Jefferson Street 10 May 2012– 2 Jun 2012 JST_May	Centreville 1 Jun 2013– 15 Jul 2013 CTR_June	Yorkville 26 Jun 2012– 20 Jul 2012 YRK_July	Georgia Tech 20 Jul 2012– 4 Sep 2012 GT_Aug	Jefferson Street 6 Nov 2012– 4 Dec 2012 JST_Nov	Yorkville 5 Dec 2012– 10 Jan 2013 YRK_Dec	Roadside 26 Jan 2013– 28 Feb 2013 RS_Jan
Met[a]	T (°C)	23.0 ± 4.3	24.7 ± 4.3	26.9 ± 4.5	26.1 ± 3.5	11.3 ± 5.0	7.8 ± 5.5	8.1 ± 4.8
	RH (%)	65.8 ± 19.3	82.9 ± 15.3	61.9 ± 18.5	71.2 ± 17.2	64.5 ± 20.6	74.2 ± 20.1	64.6 ± 25.3
	WS (m s^{-1})	1.6 ± 1.1	1.9 ± 0.9	2.3 ± 1.1	1.3 ± 0.8	1.3 ± 0.9	3.4 ± 1.7	2.1 ± 1.4
Gas (ppb)	NO	4.1 ± 13.0	0.1 ± 0.2	0.1 ± 0.1	N/A	32.1 ± 60.2	0.3 ± 0.8	N/A
	NO_2	10.3 ± 10.3	0.6 ± 0.6	1.1 ± 0.8	N/A	18.4 ± 12.8	3.0 ± 3.0	N/A
	SO_2	0.4 ± 0.7	0.3 ± 0.7	0.4 ± 0.5	N/A	1.2 ± 1.7	0.6 ± 1.1	N/A
	O_3	39.0 ± 21.9	26.4 ± 12.4	41.1 ± 17.0	N/A	18.8 ± 14.5	28.8 ± 8.3	N/A
$PM_{2.5}$ (µg m^{-3})	BC[b]	N/A	0.2 ± 0.2	N/A	0.9 ± 0.6	0.9 ± 0.9	0.4 ± 0.3	1.3 ± 1.0
NR-PM_1 (µg m^{-3})	SO_4	3.0 ± 1.5	1.9 ± 1.4	3.5 ± 1.8	4.0 ± 2.1	1.7 ± 0.9	1.4 ± 1.0	1.6 ± 1.2
	NO_3	0.4 ± 0.3	0.1 ± 0.1	0.3 ± 0.2	0.4 ± 0.4	1.2 ± 1.1	0.8 ± 0.8	1.4 ± 1.3
	NH_4	1.1 ± 0.5	0.4 ± 0.3	1.1 ± 0.5	1.2 ± 0.6	0.9 ± 0.6	0.6 ± 0.5	0.9 ± 0.6
	Chl	0.03 ± 0.03	0.01 ± 0.01	0.03 ± 0.03	0.02 ± 0.01	0.06 ± 0.07	0.04 ± 0.07	0.06 ± 0.11
	Org	9.1 ± 4.3	5.0 ± 4.0	11.2 ± 6.4	9.6 ± 4.4	7.9 ± 5.1	3.2 ± 2.3	4.7 ± 3.6

[a] Meteorological data at JST and YRK are recorded by Atmospheric Research & Analysis (ARA). Meteorological data at GT and RS are from JST during the same periods.
[b] Black carbon concentration was measured by a seven-wavelength Aethalometer at GT_Aug and JST_Nov and by a multi-angle absorption photometer (MAAP) at CTR_June, YRK_Dec, and RS_Jan.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 2. A summary of organic nitrates estimation from NO_x^+ ratio method. R_{AN} represents the NO_x^+ ratio (= NO^+/NO_2^+) for pure ammonium nitrate (AN). R_{meas} represents the NO_x^+ ratio from observation. $NO_{3,meas}$ represents the total nitrate functionality (from both organic and inorganic nitrates) as measured by the HR-ToF-AMS. $NO_{3,org}$ represents the nitrate functionality from organic nitrates, which is estimated from the NO_x^+ ratio method. ON and OA represent organic nitrate and organic aerosol, respectively.

Site	R_{AN}[a]	R_{meas}	R with LO-OOA		$NO_{3,org}$ conc. ($\mu g\,m^{-3}$)[d]		$NO_{3,org}/NO_{3,meas}$		ON/OA[e]	
			$NO_{3,meas}$	$NO_{3,org}$[b]	lower	upper	lower	upper	lower	upper
JST_May	1.73	4.47	0.68	0.78	0.19	0.27	0.55	0.68	0.07	0.14
CTR_June[c]	2.93	7.10	0.76	0.84	0.06	0.08	0.80	1.00	0.06	0.10
YRK_July	2.24	5.45	0.66	0.83	0.18	0.28	0.63	1.00	0.05	0.12
GT_Aug	2.26	6.17	0.56	0.70	0.21	0.33	0.64	0.99	0.07	0.16
JST_Nov	1.95	3.12	0.14	0.63	0.23	0.25	0.19	0.21	0.09	0.15
YRK_Dec	2.24	3.16	0.29	0.08	0.09	0.16	0.11	0.21	0.09	0.25
RS_Jan	2.62	2.78	0.46	−0.22	0.13	0.13	0.10	0.10	0.09	0.13

[a] R_{AN} is determined from IE calibrations at each site.

[b] The correlation (Pearson' R) between LO-OOA and $NO_{3,org}$ are obtained by using $R_{ON} = 10$ in the NO_x^+ ratio method.

[c] For CTR_June, only 24 June–15 July data are reported in order to compare with results from AMS-IC method where a PM_1 cyclone was used.

[d] For CTR_June and YRK_July, the NO_x^+ ratio method with $R_{ON} = 10$ and PMF method define the lower and upper bound for $NO_{3,org}$, respectively; for JST_Nov, YRK_Dec, the PMF method and NO_x^+ ratio method with $R_{ON} = 10$ define the lower and upper bound, respectively; for RS_Jan, the PMF method defines both the lower and upper bound; for JST_May and GT_Aug, the NO_x^+ ratio method with $R_{ON} = 10$ and 5 defines the lower and upper bound, respectively.

[e] The lower and upper bounds correspond to an assumed MW of organic nitrates of 200 and 300 $g\,mol^{-1}$.
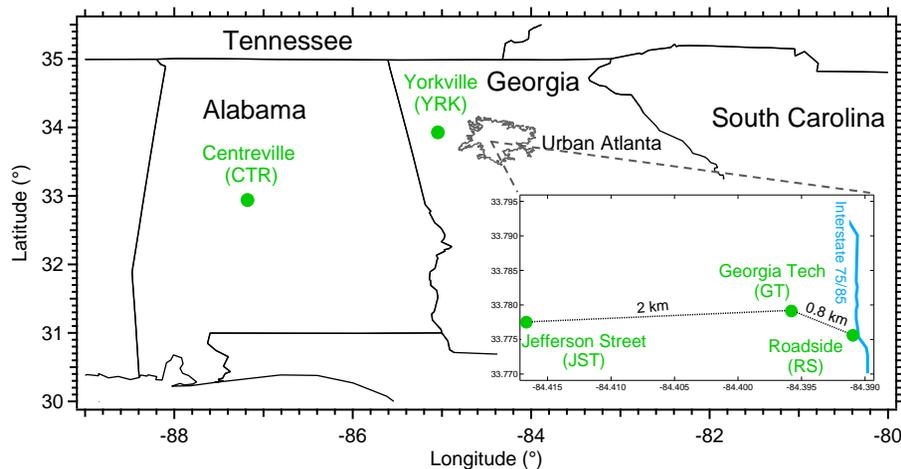
Figure 1. Sampling sites of SCAPE and SOAS studies. The gray circled region represents urban Atlanta.
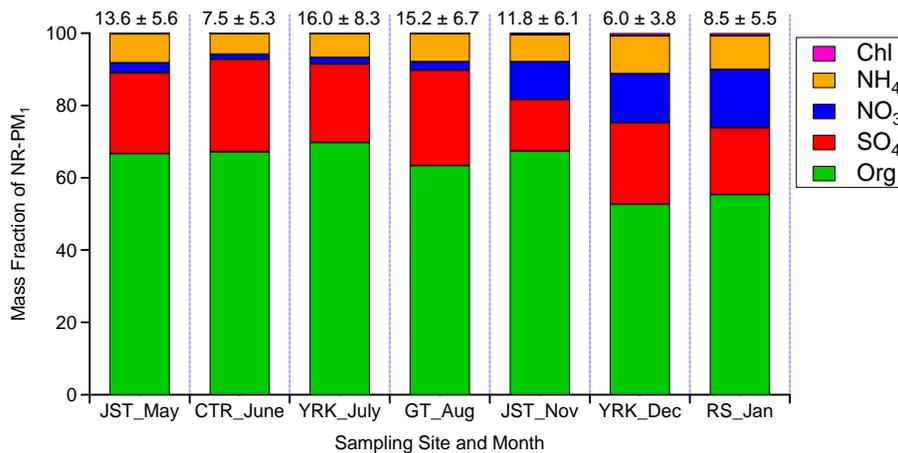
Figure 2. The mass fractions of non-refractory PM_1 (NR-PM_1) species measured by HR-ToF-AMS. The campaign average concentrations ($\mu g\,m^{-3}$) with one SD of total NR-PM_1 are listed at the top of the bar charts.
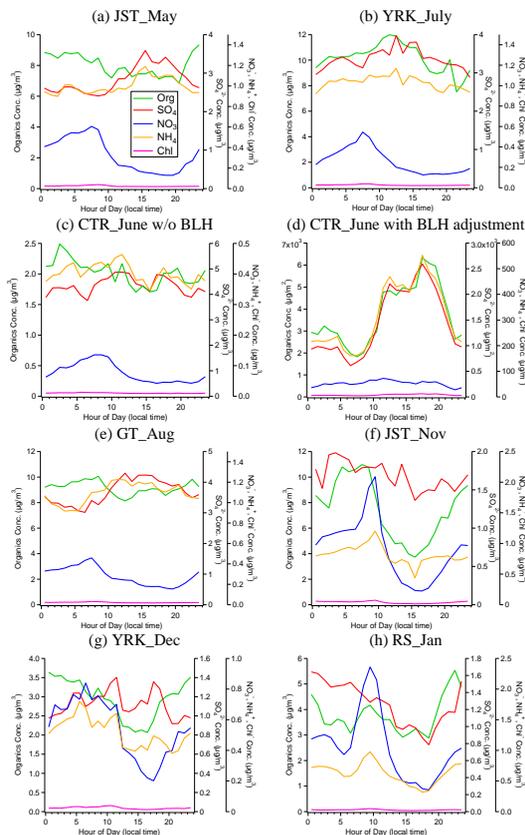
Figure 3. The diurnal profiles of non-refractory PM_1 (NR-PM_1) species measured by HR-ToF-AMS. Panel **(d)** shows the diurnal profiles of NR-PM_1 species after multiplying by the boundary layer height for the Centreville site.
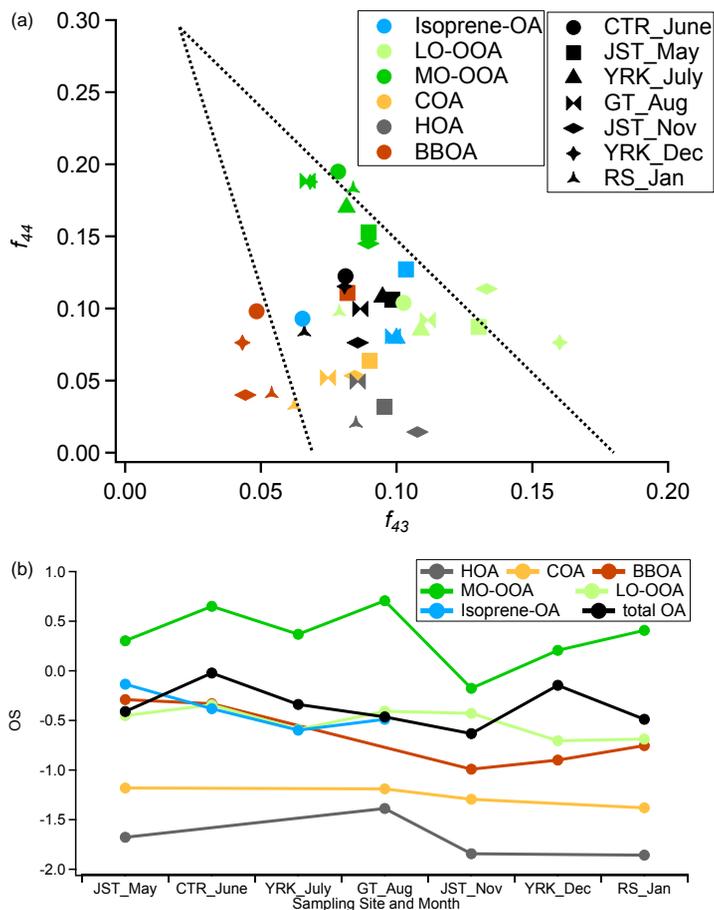
Figure 4. (a) f_{44} vs. f_{43} for total OA and OA factors resolved from PMF analysis. **(b)** The oxidation state of OA factors.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
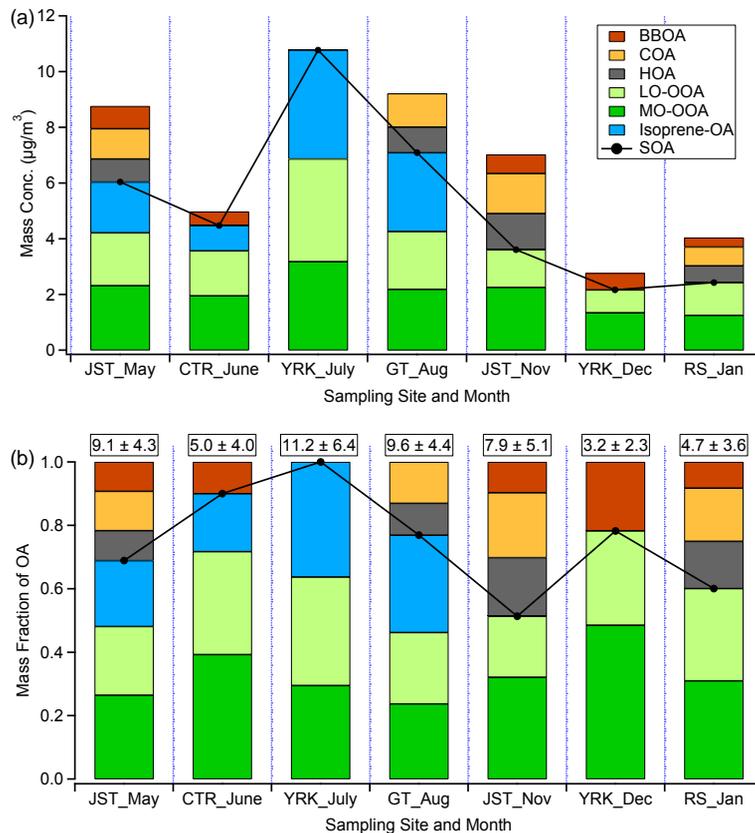
Figure 5. (a) The compaign average mass concentrations of OA factors resolved from PMF analysis. **(b)** The mass fractions of OA factors resolved from PMF analysis. The campaign average concentrations ($\mu g\,m^{-3}$) with one SD of total OA are listed at the top of the bar charts. SOA is the sum of Isoprene-OA, MO-OOA, and LO-OOA. POA is the sum of HOA, COA, and BBOA.
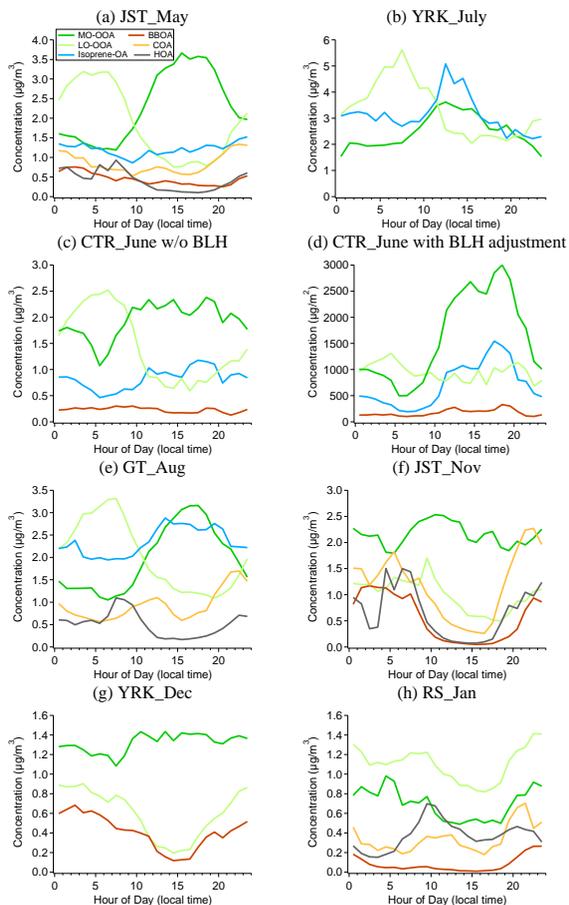
Figure 6. The diurnal profiles of OA factors resolved from PMF analysis. **(d)** shows the diurnal profiles of OA factors after multiplying by the boundary layer height for the Centreville site.

Figure 7. The scatter plot (left panel) and the time series (right panel) of BBOA and brown carbon for the datasets where BBOA factor is resolved.
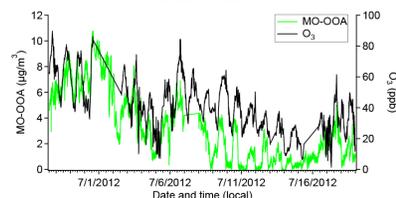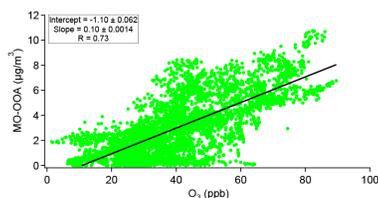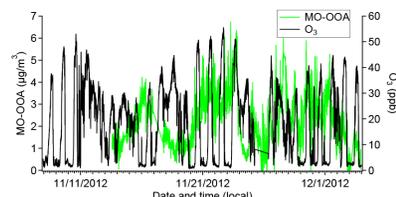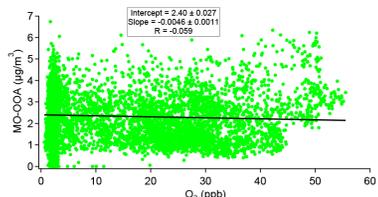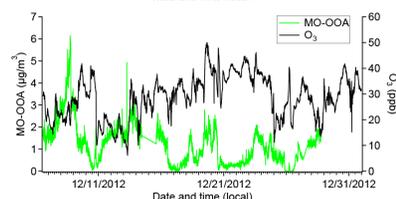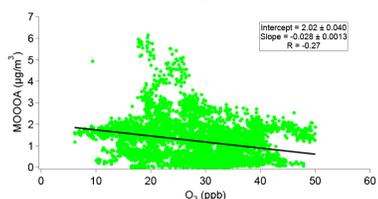
Figure 8. The scatter plot (left panel) and the time series (right panel) of MO-OOA and ozone.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
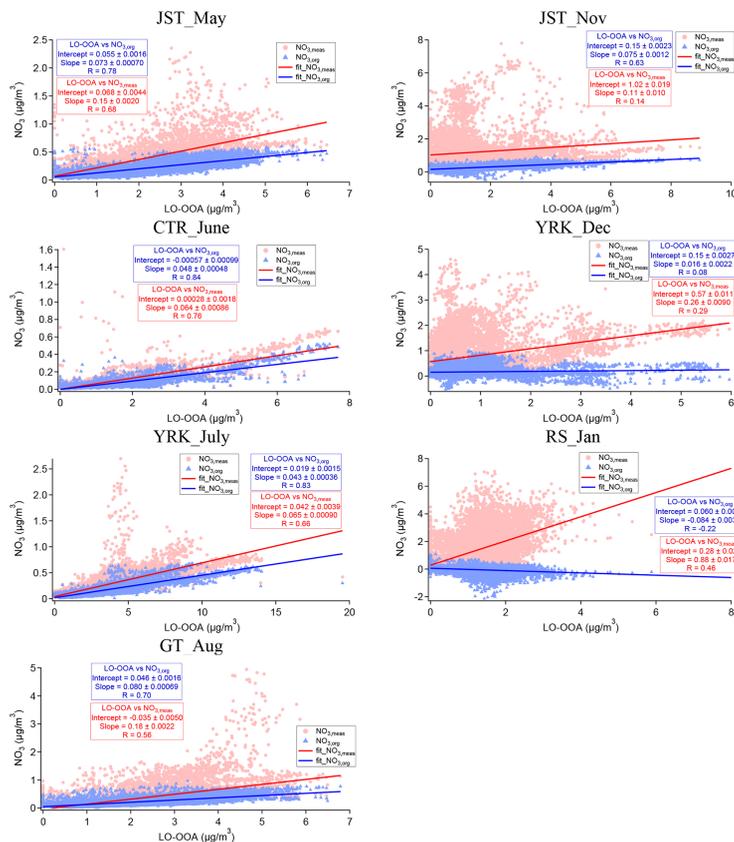
Figure 9. The scatter plot of LO-OOA vs. the total measured nitrates (i.e., $NO_{3,meas}$) and LO-OOA vs. estimated concentration of "nitrate funcionality from organic nitrates" (i.e., $NO_{3,org}$) by using $R_{ON} = 10$ in the NO_x^+ ratio method.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶

◀ | ▶

Back | Close

Full Screen / Esc
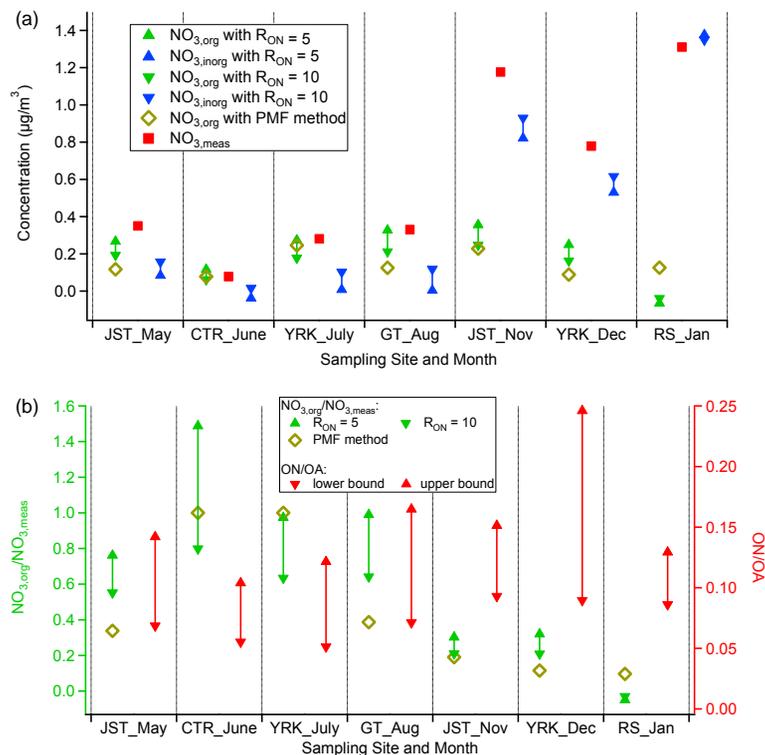
Figure 10. **(a)** The concentrations of total measured NO_3 (i.e., $NO_{3,meas}$), estimated "nitrate functional group from organic nitrates" (i.e., $NO_{3,org}$) by the NO_x^+ ratio method and the PMF method. **(b)** The contribution of $NO_{3,org}$ to $NO_{3,meas}$ (i.e., $NO_{3,org}/NO_{3,meas}$) from the NO_x^+ ratio method and the PMF method. Also shown are the estimated contribution of organic nitrates to total OA from the "best estimate" range of $NO_{3,org}$ and by assuming a MW of 200 and 300 g mol^{-1} of organic nitrates.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
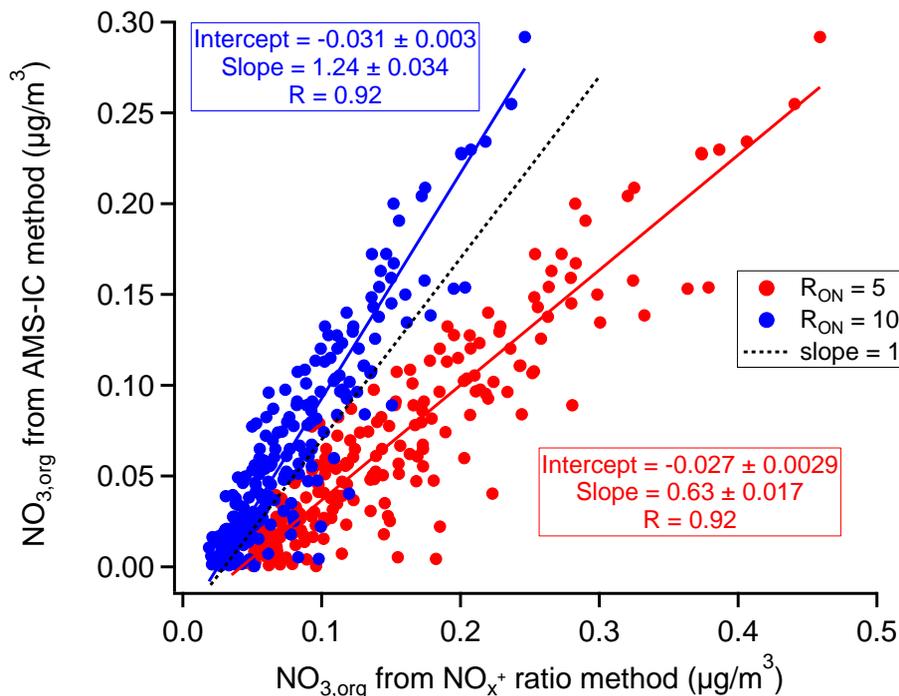
Figure 11. The comparison of estimated concentration of "nitrate functionality from organic nitrates" (i.e., $NO_{3,org}$) at Centreville site between the AMS-IC method and NO_x^+ ratio method with R_{ON} values of 5 and 10. The intercept and slope are obtained by orthogonal fit which considers the measurement errors in both dependent and independent variables. The correlation R is obtained by linear least-squares fit. The intercepts are within to the detection limit of PILS-IC nitrate (i.e., $0.03\,\mu g\,m^{-3}$). The 1 : 1 line is offset by the dection limit of PILS-IC nitrate (i.e., $-0.03\,\mu g\,m^{-3}$).
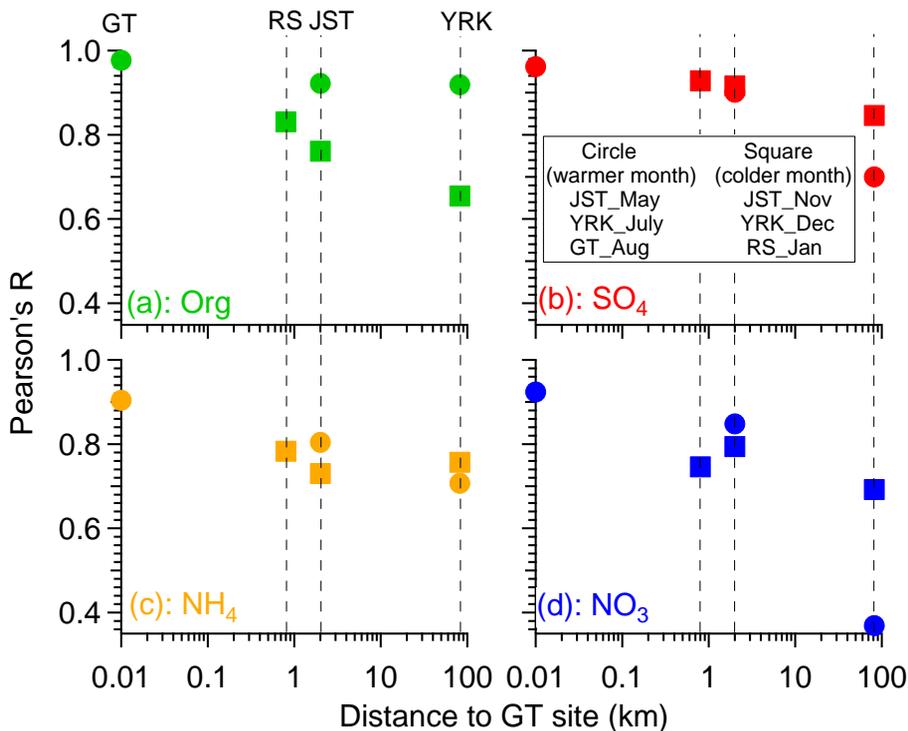
Figure 12. The correlations for NR-PM$_1$ species between ACSM measurements (stationary at the Georgia Tech site) and HR-ToF-AMS measuremens (rotating among different sites). The dotted lines represent the sampling sites where the HR-ToF-AMS measurements were made.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
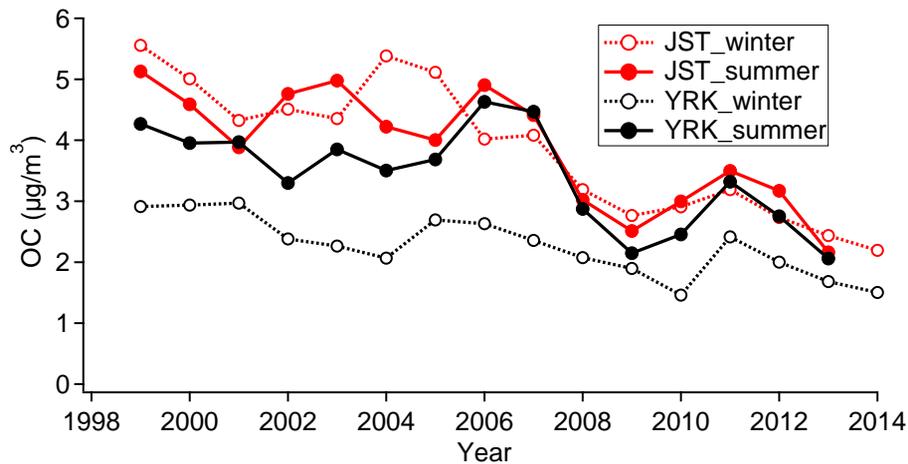
Figure 13. Mean seasonal concentrations of organic carbon at the Jefferson Street site and the Yorkville site. Summer: June–August. Winter: December–February.
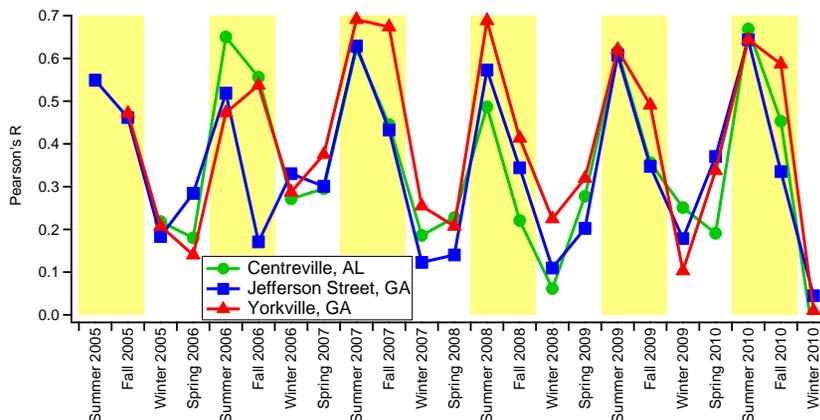
Figure 14. The seasonality of the correlation between organic carbon and sulfate at the Jefferson Street, Yorkville, and Centreville site. Seasons are by grouped by calendar months (Spring: March–May, Summer: June–August, Fall: September–November, and Winter: December–February).