Specific comments:

(1) Page 22385, line 17-21: Perma Pure PD-50T isn’t designed for flows containing particles. Have the authors tested the particle loss through the dryer?

We did not test the Nafion dryer ourselves. Aerodyne tested Perma Pure PD-200T (more tubes than 50T model) and found particle losses was less than 10%. ACSM setup requires a high sampling flow rate (3 L/min), which cannot to be achieved using the MD series. Therefore, the PD series was used in the ACSM sampling setup.

(2) Page 22385 to 22386: The slope obtained from ACSM NR-PM1 + BC and SEMS PM1 is complicated with the CE value. Although a CE value of 0.5 was chosen, substantial differences exist when comparing the ACSM results with other measurements at the sites studied herein (Budisulistiorini et al., 2014). Given the large uncertainty of CE (as well as other uncertainties in the ACSM quantification of mass concentration), I don’t think it is meaningful to derive the particle density by this method. Also, the authors estimated the particle density based on average composition. It is perhaps better to use 1.4 instead of 1.2 g cm$^{-3}$ for organic material based on our current understanding (Hallquist et al., 2009; Kuwata et al., 2012). Nevertheless, to me, 1.48 in Table S3 and 1.75 for summer JST are quite different. The question is what is the reasonable tolerance for density estimates.

We agree that the derived particle densities are not very useful for discussion in this study. As a result, we removed this part from the paragraph.

The estimation of dry densities was done to examine if CE of 0.5 was yielding reasonable total submicron aerosol density. For the estimation of particle density, we calculated again using density of 1.4 g/cm$^3$ for organic and updated the table.

We revised the sentences as follow:

“We estimated dry density of ambient PM$_1$ based on average particle composition for each season, and the assumption of organic, inorganic, and EC densities are 1.4 (Hallquist et al., 2009), 1.77 (Turpin and Lim, 2001), and 1.77 g cm$^{-3}$ (Park et al., 2004), respectively. The estimated dry aerosol densities at both the JST and LRK sites are 1.55 g cm$^{-3}$ on average (Table S3), which is about 10–20% from density of 1.75 at JST (Budisulistiorini et al., 2014) and 1.52 g cm$^{-3}$ at LRK (Budisulistiorini et al., 2015) during summer at LRK. If a CE of 1 was applied to JST and LRK datasets, the estimated aerosol density is <1 g cm$^{-3}$, which is much lower than the suggested organic aerosol density of 1.4 g cm$^{-3}$ (Hallquist et al., 2009) and inorganic aerosol density of 1.77 g cm$^{-3}$ (Cross et al., 2007). Therefore, we applied a CE value of 0.5 on all seasonal datasets.”

(3) Page 22386, last paragraph: The determination of the “best” PMF solution for each case
seems quite subjective. Although Figures S2-S9 are provided for the PMF diagnostics, there is no description about them. It was mentioned that the uncertainties of selected solutions were investigated with the seed, fpeak, and bootstrapping tests. But I can’t find any further information. The authors should provide the details about the best-solution determination and the uncertainty analysis. Some questions regarding the PMF diagnostics are listed below.

– The Q/Q\text{exp} values are not near 1, and are different for the JST (2-3) and the LRK (~0.2) best solutions. Have the errors of the input data and the downweighting treated properly? If the Q/Q\text{exp} contributions are dominated by a few temporal spikes or plumes, test PMF runs excluding those time periods should be performed and analyzed. It is not unlikely that certain plume events represent source profiles very different from the long-term profiles. The authors should make sure those events won’t bias the PMF solutions.

The Q/Q\text{exp} values >> 1 in JST PMF analysis suggests that errors were underestimated. We have omitted the temporal spikes in all datasets and downweighted the bad and weak ions. In doing so, JST datasets were left with quite large number of missing datapoints that variability could not be modeled. LRK datasets were treated in similar manner, i.e., omission of temporal spikes and downweighting of bad and weak ions. The low Q/Q\text{exp} values in LRK PMF analysis suggest that errors were overestimated. Overall, OA concentration in LRK was lower than JST, and for some periods the concentrations could be less than detection limit of ACSM instrument (0.3 \(\mu\text{g/m}^3\)). The low OA at LRK could result in lower signal-to-noise ratio and overestimation in errors.

– Figure S2: It looks like there are significant Q/Q\text{exp} contributions from marker ions of m/z 41 to 60. What does the 5 factor solution look like?

The five-factor solution of JST winter 2012 PMF analysis resulted in a split factor, which has SV-OOA and BBOA time series and profiles characteristics. The 5\text{th} factor time series is correlated with BBOA and SV-OOA (R \sim 0.7). Adding the 5\text{th} factor yielded a lower correlation (R < 0.6) of BBOA with primary emission tracers (i.e., CO and BC), SV-OOA with NO3. Moreover, reduction in overall Q/Q\text{exp} value is < 10% for the five-factor solution. Thus, we will keep the four-factor solution for JST winter 2012.

– There are still some patterns in the residual time series for the “best” solutions that need to be checked, for example, March in Fig. S2, April in Fig. S3, earlier October and December in Fig. S5, and mid March in Fig. S6. Those features may indicate that more factors are needed to explain the data. Besides, the season separation may not be ideal and adjustments may be needed.

We have examined adding number of factors for those cases. At each case, additional factor yielded split factor(s) that correlate with other factors time series or mass spectra. The additional factor(s) also show lack of correlation with external gas- and/or particle-phase tracers, which cause difficulties in chemically characterizing the factor(s). We acknowledge that comprehensive collocated particle-phase tracers analysis was unavailable, thus limiting PMF factor analysis.

– The chosen of a particular rotation (e.g., fpeak = -0.15 for LRK spring in Fig. S7 and -0.1 for LRK fall in Fig. S9) needs to be well explained. It looks like the factor mass spectra are highly correlated for those cases. Tuning rotation to obtain more distinct markers like m/z 82 and 91 would bias the PMF analysis.
When we tuned fpeak, we were checking and making sure the rotation did not significantly change factors mass spectra. The fpeak was selected based on correlation of factors time series to external tracers (e.g., SO4, NO3, CO, BC, etc). We have been careful in tuning the mass spectra (positive fpeak) to avoid obtaining more distinct ion markers that would bias the PMF analysis. We added explanation about the selected rotation in the SI section.

(3) Page 22388, line 22: It should be clarified in the text or figure caption that some of the data are published in Budisulistiorini et al., 2015.

We added this information in Method section.

“We added this information in Method section.

“Organic and inorganic species characterizations during 2013 Southern Oxidant Aerosol Study (SOAS) published in Budisulistiorini et al. (2015) were included in the analysis of the summer season at the LRK site of this study.”

(4) Page 22389, line 12-14: How big could the under-prediction be if organosulfates are considered? Studies suggest organosulfates accounted for up to 30% of the organic mass and 4-14% of total sulfate (Lin et al., 2012 and references therein). Have the authors done any analysis on the ambient samples at the sites to quantify the amount of organosulfates?

We quantified isoprene- and monoterpenes-derived organosulfates using authentic standard of 2-methyltetrols sulfate (m/z 216) and α-pinene sulfate (m/z 250). Quantification of isoprene-derived organosulfates has been published in Budisulistiorini et al. (2015). The isoprene OS accounted ~3.5% and ~9.5% of the OA and sulfate mass measured by ACSM, respectively. In contrast to East Asia findings in Lin et al. (2012), monoterpane OS were very low (0.012 µg/m³) and no sesquiterpene OS were found at LRK. Aerosol acidity estimation is influenced by concentrations of inorganic aerosol constituents as well as organic water content. We could not estimate contribution of OS to aerosol liquid water content using the available data.

(5) Page 22391, line 22-30: The production of SOA may be balanced out by the loss and hence appeared as day-time valley. It looks like all OOA-factors and inorganic species show similar diurnal patterns that decrease during the day. Could the authors show data like the diurnal PBL height and other meteorological parameters to specify the main driver of the day-time decrease? Why do the minimum concentrations of nitrate, organic material, sulfate, and ammonium appear at different time (Fig.4a)?

We, unfortunately, did not have LIDAR measurements at JST and LRK, and thus we could not provide PBL height profile. Acknowledgement of the missing PBL height profile has been added to OA characterization section.

“Due to lack of measurements, the potential role of planetary boundary layer (PBL) height to diurnal variation of PMF factors was not accounted for in this study. However, it is acknowledged here that diurnal PBL dynamics or loss processes (e.g. deposition) could influence diurnal patterns observed here for the PMF factors.”

The difference in minimum concentration of inorganic species and organic matter could be influenced by not only PBL height but also different characteristics of each species. Sulfate increased in the afternoon, likely due to increasing photochemistry. Since nitrate is semi-
volatile, it most likely decreases when temperature was higher. Diurnal profiles of ammonium were quite insignificant, except those during winter and fall season. Organic diurnal profiles were highly influenced by sources and atmospheric processing.

(6) Page 22392, line 19-30: I would argue that the 91Fac reported in Robinson et al., 2011 (Supplementary) is more likely the HOA factor (see the high R2 values in Table S1). The f43/f44 ratio for the Robinson 91Fac factor (1.2) is also much greater than the ratio herein (0.12). The caveat is that f43/f44 is also sensitive (usually) to the rotation. Overall, I tend to agree with the assignment of this factor at LRK as 91Fac, similar to those identified in Budisulistiorini et al., 2015 and Chen et al., 2015. But at JST spring (summer as well), because the small mass fractions of the 91Fac, noisy temporal variations (Fig. 3a), and the high correlation of the mass spectrum of this factor with LV-OOA. I think it is more likely a “split” factor, which needs to be carefully reanalyzed.

As pointed out by referee, temporal variation of 91Fac resolved from PMF analysis of JST spring and summer 2012 are noisy. Re-analysis of JST spring and summer 2012 suggested that at least three-factor solution is needed to explain OA from spring and summer datasets. Four factor solution yielded a factor with noisy temporal variation as previously resolved. Five factor solution also yielded factors with noisy temporal variation. In conclusion, three-factor solution was selected as the best fit based on correlation of factors’ time series and profiles with external tracers and references, respectively.

(7) Page 22393, line 7-13: The 82 marker seems not present in the IEPOX-OA factor here (Fig. 2b). The spectrum is highly correlated with LV-OOA (R2 ~0.9) but less correlated with lab IEPOX SOA (Tables S1-S2). How confident do the authors believe this is not a “split” factor, or something else (e.g., some type of SV-OOA), but a real IEPOX-OA factor? Similarly for the fall, relatively high 82 and m/z 53 (associated with the 82 peak (Budisulistiorini et al., 2013; Chen et al., 2015; Robinson et al., 2011) are missing (Fig. 2d). The authors should carefully check the PMF analysis for the spring and fall.

Mass spectrum of 82Fac (Robinson et al., 2011) is correlated (r2 = 0.84) with LV-OOA (Ng et al., 2011). Thus, it is somewhat expected that IEPOX-OA from both JST spring and spring are well correlated (r2 ~0.9) with reference LV-OOA (Ng et al., 2011). Correlations of JST spring and summer IEPOX-OA with IEPOX-OA resolved from Atlanta 2011 and SOAS 2013 (Budisulistiorini et al., 2013 and 2015) are very strong (r2 ≥ 0.9). Laboratory-generated IEPOX SOA is better correlated with JST spring and summer IEPOX-OA (r2 0.5-0.6) than with LV-OOA (r2 = 0.37). Thus, we are confident that the IEPOX-OA resolved from JST spring and summer PMF analysis is a real factor associated with IEPOX SOA.

JST fall 2012 PMF analysis did not resolve IEPOX-OA factor, and only at LRK site we resolved IEPOX-OA factor in fall season.

Signal of m/z 82 varied seasonally, which was likely related to isoprene emission variation. At LRK during spring and fall 2013, the m/z 82 signal of IEPOX-OA was much lower than that in summer. This suggests variation in source of IEPOX-OA factor. Ion fragment at m/z 53 (mostly C4H5+) was recommended by Lin et al. (2012) to aid in PMF factor identification. However, in this study we found that this ion did not strongly correspond to m/z 82 fragment.

IEPOX-OA from LRK spring and fall 2013 PMF analysis are strongly correlated (r2 0.8-1.0) with IEPOX-OA from Atlanta 2011 and SOAS 2013 (Budisulistiorini et al., 2013 and 2015).
Laboratory-generated IEPOX SOA is better correlated with LRK fall 2013 IEPOX-OA ($r^2 \approx 0.5$) than with LV-OOA ($r^2 0.2-0.3$). Thus, we are confident that IEPOX-OA resolved from LRK spring and fall PMF analysis is a real factor.

(8) Page 22395, line 1-6: The 91Fac for LRK fall seems being mixed with HOA although $f_{44}$ is high. The CxHy+ ion series clearly present, and in particular, m/z 57 stands out. For comparison, biogenic-related 91 factors are expected to have a m/z 53-55 pattern (Chen et al., 2015).

Correlation of LRK fall 2013 91Fac mass spectrum vs. reference HOA is low ($r^2 \approx 0.2$), while correlations with Borneo and SOAS 2013 (Robinson et al., 2011 and Budisulistiorini et al., 2015) are stronger ($r^2 0.6 – 0.8$). In addition to distinct ion fragment at m/z 91, Robinson et al. (2011) and Budisulistiorini et al., (2015) observed distinct m/z 55 and 57 fragment from 91Fac in forested areas. Chen et al. (2015) observed significant m/z 53 and 55 signals from laboratory experiment with biogenic SOA. We also observed differences between laboratory-generated IEPOX SOA (distinct m/z 82 and 100 fragments, Lin et al., 2012) and field IEPOX-OA factor (distinct m/z 101 fragment than m/z 100, Budisulistiorini et al. 2013, 2015). The differences in mass spectra obtained from laboratory experiments and field observations could be attributed to complex atmospheric processes.

(9) Given the differences in the mass spectra and diurnal profiles of one factor for different seasons (Fig.2), PMF analysis for combined datasets of different seasons should be done to test if the results are robust and meaningful.

We have done PMF analysis of combined datasets. Some factors resolved in separate datasets were note able to be resolved in the combined datasets. Signal of these factor(s) might be low and/or specific to certain period (for example BBOA and biogenic SOA), and have similar characteristics (for example SV-OOA and IEPOX-OA). By combining the datasets, these factors are averaged over long period, and lose their distinct characteristics. This issue might be specific to low-time resolution instruments such as the ACSM.

Technical remarks:
Page 22388, line 26: It is better to specify here as “non-refractory chloride”.

It has been revised as follows:

“Average non-refractory chloride loadings were low (<0.1 µg m$^{-3}$), indicating that it is not a significant contributor to inorganic aerosol mass in this region.”

Page 22393, line 1 and p22399, line 3: “Chen et al., 2014” should be “Chen et al., 2015”.

The reference has been revised.

Figure 2. The signals for ions above m/z 60 are too low to see. Ion markers (e.g., 82 and 91) are difficult to tell. Either additional figures or amplified right axes are needed.

We separated mass spectra from JST and LRK into Fig. 3 and 4, respectively. Thus, the ion signals are now more readable.
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Anonymous Referee #2
Received and published: 15 October 2015

General comments The manuscript by Budisulistiorini et al. presents new and interesting data from two years of measurements using ACSM at an urban and a rural site in south-eastern USA. This is a very large dataset and the analysis presents important and new findings. Unfortunately the manuscript needs considerable editing, before submission should be considered. There are numerous spelling errors and grammatical errors, which must be corrected. I have identified some, but it is not the task of the reviewers to correct spelling and standard grammatical errors. My only other major point is that the authors should remember the limitations of the study, namely that the measurements were performed during two different years. This should be written much more clearly in the discussion of the data. Generally the figures look very good, but they are too small and should be divided into more separate figures to enhance readability. Please describe and use a uniform description of the r2 values (high/low/moderate/low).

Specific comments.
Page 22383 line 4: Please include a reference to the statements of sources to sulfate, nitrate and OA.

We removed the statement and re-phrased the paragraph.

Page 22383 line 9-10: Please add a reference to the discussion of POA/SOA variation during the day.

We revised the statement and add reference.
“Contribution of hydrocarbon-like OA (HOA) associated with POA to urban OA mass may be significant during morning traffic, while oxygenated OA (OOA) associated with SOA exceeds POA at midday or in the afternoon (Zhang et al., 2005).”

Page 22383 lines 13-16: Please add a reference here.

We removed the statement and re-phrased the paragraph.

Page 22383 line 29: Anthropogenic sources might be low in rural areas, but they are not "absent".

We revised it to “low”.

Page 22384 Lines 7-8: Please clarify this sentence.
What is the distance between the sites?

The current and previous studies were located at the same site. We revised the sentence as follows.
“Moreover, OC at LRK is the primary component of SOA in summer, while POA from wood burning can contribute significantly during fall.”

Page 22384 Line 16: collocated -> co-located.

Both words are appropriate according to Oxford dictionary. We will keep “collocated”.

Page 22385 Line 23: Please state how often the calibration procedure was done.
We added the number of calibrations performed. The sentence has been revised as follows:

“The ACSM was tuned for ionizer and electronic offset and calibrated for ionization efficiency on site (5 – 7 times) throughout each year of sampling at each site.”

Page 22387: The results and discussion should start with a somewhat broader presentation to introduce the data, including some average concentrations.

We separated the results and discussion into different sections. We re-organized the paragraphs so that there is a general introduction to the results section.

Page 22388 line 11: Please correct language here. How close are the coal-fired power plants? Given the time-scale for sulfate formation, would you expect them to contribute to sulfate at your sites?

The closest coal-fired power plant is ~7 km from JST and ≥100 km from LRK. These power plants contributed to regional sulfate variability in the southeast region, and thus, sulfate concentration measured at the site.

We have revised the sentence and paragraphs as follows:

“Average OA contributions to NR-PM$_1$ were higher in spring and summer at JST and LRK, suggesting that biogenic SOA plays significant role during these periods. OA characterization is further discussed in section 3.2.”

“Average sulfate concentrations were highest in summer for LRK (2.1 µg m$^{-3}$) and fall for JST (~2 µg m$^{-3}$) as illustrated in Fig. 1. The enhanced sulfate concentrations coincided with increased OA concentration, which is consistent with prior studies that sulfate may contribute to enhanced SOA formation (Lin et al., 2013a, Xu et al., 2015, Budisulistiorini et al., 2015). Changes of sulfate concentrations at LRK are likely affected by changes in SO$_2$ emissions from electrical generating units in the region (Tanner et al., 2015). At JST, SO$_2$ emissions from coal-fired power plants nearby Atlanta contributed to the spatial variability of sulfate concentrations (Peltier et al., 2007).”

Page 22389: in accord with -> in accordance with? The word “correlation” should only be used if you actually calculated the correlation of the data. did you do that? Which technique did Guo et al. use – please state.

“in accord with” and “in accordance with” are both appropriate English phrase based on Oxford dictionary. We keep “in accord with”.

We did calculate correlation between aerosol pH and organic. The sentence has been revised to include correlation value:

“No direct correlation ($r^2<$0.1) was observed between aerosol pH and OA at both sites.”

Guo et al. (2015) used CCN measurements to calculate organic hygroscopic parameter, which was then used to calculate organic water. The sentence has been revised as follows:

“It should be noted that the possible LWC contributions from OA are not included because cloud condensation nuclei (CCN) measurements, such as that recently used by Guo et al. (2015) to
measure this quantity, are lacking at our sites.”

Page 22390
Line 14:Specify “during fall and winter”. Is this only referring to JST site?

The original text referred to winter season only and comparing trend at night and day. We clarified the text into:

“The BBOA factor concentration increased during the night and decreased during the day at both sites (Fig. 8)…”

Line 20-21: $r^2 = 0.2-0.5$ is not moderate, but low.

It has been revised.
“The time series of BBOA showed low to moderate correlation ($r^2 0.4-0.5$ at JST and $r^2 0.2-0.4$ at LRK; Tables S2–S3) with BC, suggesting that it is likely influenced by some local sources (e.g., fires).”

Page 22391
line 19: “most abundant component of OA”

It has been revised as follows:
“SV-OOA, which was observed only in urban OA, is the most abundant component of OA.”

Lines 25-: Please correct and clarify this sentence.

We rephrased the sentence as follows:

“Since isoprene emission is expected to be negligible during winter season, SV-OOA might not relate to IEPOX-derived SOA.”

Page 22393 lines 10-12: This sentence needs further editing to be clear.

We rephrased the sentences as follow:

“The average IEPOX- OA concentration was slightly higher at LRK than at JST, which is expected due to abundant emissions of isoprene at the forested site.”

Page 22394 line 2: $r^2$ of 0.2 is very weak, approaching non-existent.

It has been revised as follows:

“The time series of LV-OOA was weakly correlated with sulfate ($r^2 \sim 0.2$) at JST, but more strongly correlated with sulfate at LRK ($r^2 = 0.6-0.7$) (Table S3).”

Page 22394 lines 20-21: What do you mean here?

We rephrased the sentences as follow:

“Average concentration of IEPOX-OA at JST and LRK increased during summer. At LRK, the average concentration of IEPOX-OA reached a maximum in summer, but its relative contribution
to total OA mass was lower due to the increasing concentration of 91Fac.”

*Page 22395 line 4: Please clarify/use correct language.*

We rephrased the sentence as follow:

“At JST, PMF analysis of fall OA resulted in a four-factor solution (i.e., HOA, BBOA, SV-OOA, and LV-OOA), while at LRK a three-factor solution was resolved (i.e., LV-OOA, 91Fac, and IEPOX-OA).”

*Page 22396: Avoid repeating the results presented in the very long section above. Furthermore the discussion should reflect the fact that the data were collected in two different years.*

We re-organized the results and discussion and added information about measurement period for the two sites.

*Page 22397 line 13: The argument about “loss of foliage as a major source of isoprene emissions” is unclear.*

We rephrased the argument as follows:

“Decrease of IEPOX-OA concentration in fall season is consistent with loss of tree foliage as a major source of isoprene emission. Additionally, IEPOX-OA was not observed during winter suggesting that isoprene emission was negligible.”

*Line 23: What are “sources datasets”?*

The “sources datasets” refers to OA mass spectra datasets from field and experiment measurements. We revised the sentence as follows:

“The IEPOX-OA component has been observed in chamber experiments and field OA (Hu et al., 2015).”

*Page 22398 lines 18- . Please remove and replace “we offer” with eg, “the study presents”.*

It has been revised.

“Although parameterizations of IEPOX-OA factor based on its markers (Hu et al., 2015) was not done in this study, this study presents some insights of role of the m/z 82 fragment ion over different seasons in southeastern U.S. “

*line 22: identification -> detection.*

It has been revised.

“Observation of the m/z 75 fragment ion variation over different seasons indicates its potential as an additional marker ion for IEPOX-OA detection.”

*Page 22399 lines 9-14: This is very speculative, given the quite similar correlations.*
We rephrased the argument as follow:
“SOA tracers of isoprene ozonolysis were moderately correlated ($r^2 = 0.2–0.5$) with both IEPOX-OA and 91Fac, adding to fair correlation between 91Fac component and monoterpane SOA tracers reported in Budisulistiorini et al. (2015).”

Figure 6 does not provide enough information to include it in the main manuscript. Please move to SI or leave out.

We moved Fig. 6 to SI.
This manuscript reports the real-time characterization of non-refractory submicron aerosol in an urban and rural site in SE USA using the ACSM. Source apportionments of the organic aerosol were made at each site during different seasons. The results presented in this manuscript fall within the scope of this journal, but major revisions need to be made before this manuscript can be accepted.

General comments:
1. There are numerous grammatical and punctuation errors in this manuscript. This needs to be corrected. The inappropriate use of semi-colons in certain sentences in this manuscript makes it particularly difficult to understand the message that the authors are trying to convey.

2. The figures need to be bigger and clearer. Currently, it is hard to make comparisons between datasets obtained at the two sites. I suggest making separate figures for the two sites (especially Fig 2).

3. This is a two year study. This needs to be stated more clearly in the discussion section, and kept in mind when the authors discuss their results. Currently, the discussion reads like it is a direct comparison between the two sites during the same time period.

Specific comments:
Pg 22384 line 20: More details need to be provided on the two sites. For example, how far are the power plants away from the measurement sites? (especially since this is later discussed in the discussion)

We have added details about power plants location nearby the two sites.
“Plant McDonough is the closest coal-fired power plant to JST site of about 7.4 km northwest (Edgerton et al., 2006)....”
“LRK site is located quite far from coal-fired power plants. Some of the operating coal-fired power plants (Frost et al., 2006) are located of about 300 – 400 km northwest of the site.”

Pg 22386 line 16: Please specify the months that are classified as spring, summer, fall and winter. A more detailed explanation on the choice of factors is also needed. This can be placed in the supporting information.

We added a table (Table 1) that provide data analysis period for each site.

Table 1. Seasonal classification period of measurements at JST and LRK

<table>
<thead>
<tr>
<th>Season</th>
<th>JST</th>
<th>LRK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter</td>
<td>22/12/2011 – 19/03/2012</td>
<td>18/01/2013 – 19/03/2013</td>
</tr>
<tr>
<td>Spring</td>
<td>20/03/2012 – 19/06/2012</td>
<td>20/03/2013 – 31/05/2013</td>
</tr>
<tr>
<td>Summer</td>
<td>20/06/2012 – 21/09/2012</td>
<td>01/06/2013 – 21/09/2013</td>
</tr>
<tr>
<td>Fall</td>
<td>22/19/2012 – 20/12/2012</td>
<td>22/09/2013 – 20/12/2013</td>
</tr>
</tbody>
</table>

* Measurements in summer at Look Rock coincided with 2013 SOAS campaign from 1 June to 17 of July 2013. Thus, summer season for LRK was classified to include SOAS.

Pg 22387 line 6: More details on the parameters used in ISORROPIA is needed. For example, was forward or reverse mode used and why?

We used forward mode because it estimate the thermodynamic equilibrium between gas- and particle-phase. We added the information into the text:

“The thermodynamic model, ISORROPIA-II in forward mode (Fountoukis and Nenes, 2007, Nenes et al., 1999), was used to estimate aerosol pH.”

Pg 22387 line 16: Do you mean Eq. (1) in Budisulistiorini et al. (2015)?
Yes, it is Eq. 1 in Budisulistiorini et al. (2015). We revised the text accordingly.

Pg 22389 line 16-17: A brief description of the method used by Guo et al. is needed here, in order to better understand the limitations of the authors’ calculation of aerosol pH and liquid water content.

We added the information as suggested.

“It should be noted that the possible LWC contributions from OA are not included because organic hygroscopicity parameter estimated from observed cloud condensation nuclei (CCN) activities of OA (Guo et al., 2015) is lacking at our sites.”

Pg 22389 line 21: “pH prediction using ISORROPIA-II based on inorganic ions alone was found to give a reasonable estimate” Are you referring to the study by Guo et al. (2015) or this study? How do the findings reported by Guo et al. (2015) apply to your study? This needs to be explained more clearly.

The finding was referred to Guo et al. (2015) study. We clarified the sentence as:

“Although organic water fraction in total LWC was found to be significant, Guo et al. (2015) suggested that pH prediction using ISORROPIA-II based on inorganic ions alone gave a reasonable estimate.”

Pg 22389 line 22-25: “Hence, the lack of correlation in this study between OA and LWC based only on inorganic water suggests that LWC is not a limiting factor in OA production in this region.” How did the authors draw this conclusion from the previous statement? Please explain.

This is related to previous comment. We clarified the sentence to reflect changes made to the overall statement.

“The lack of correlations between OA and pH as well as LWC indicate that pH and LWC may not be limiting factors in OA production in this region. It should be noted that this study did not include contribution of organic water into pH estimation, which could contribute to the relationship between pH and OA.”

Pg 22390 line 21: $r^2 = 0.2 \ldots 0.5$ is a low correlation, not moderate. Also, the authors need to specify in the manuscript what they mean by moderate and high correlation.

We have addressed similar question from Referee #2.

Pg 22391 line 12: The paper by Henry and Donahue (2012) is a chamber study where the normalization of organics to sulfate is used to account for wall loss. The authors need to justify more clearly why the same methodology can be used in this field study.

We cited the incorrect reference. The sentence has been clarified as follow:

“Variability in organic-to-sulfate ratio could indicate different photochemical conditions that could affect concentrations of OA and sulfate (Hildebrandt et al., 2010).”

Pg 22392 line 1-3: “It is noted here that we acknowledge the potential role of diurnal PBL dynamics or loss processes (e.g. deposition) in contributing to diurnal patterns observed here for the PMF factors.” This needs to be stated earlier in the discussion, specifically before the discussion of the PMF factors.

We moved this sentence before discussion of PMF factors.

Pg 22397 line 22: I do not agree with the authors’ suggestion that m/z 75 can be used as a marker ion for IEPOX-OA. This mass peak does not appear to be significant in the IEPOX-OA mass spectra shown by the authors (in Fig. 2) and Budisulistiorini et al. (2013).
The ion fragment at m/z 75 along with m/z 53, 82, and 100 were recommended by Lin et al. (2012) to aid in identification of IEPOX SOA of PMF analysis. Here, we examined contribution of those ions to IEPOX-OA factor over different seasons and sites. The m/z 75 might not be prominent ion in the mass spectra; however, its time trend is well correlated with m/z 82. Therefore, m/z 75 and 82 could be used to identify of IEPOX-OA factor, which is consistent to the Lin et al. (2012) recommendation.

Pg 22398 line 24: I do not agree with the authors’ assessment that 91Fac, which is characterized by a prominent mass peak at m/z 91, is attributed to isoprene chemistry. First, given that the authors have an ACSM with unit mass resolution, the m/z 91 fragment ion in their mass spectra may not necessarily be C3H7O+, as strongly implied by the authors. Second, the chamber study by Surrattt et al. (2006), which was cited by the authors to justify their discussion that the m/z 91 fragment ion correlates with isoprene chemistry, was not performed using a high resolution ToF-AMS. Consequently the m/z 91 fragment ion was only suggested to be C3H7O+ in that paper. Third, high resolution ToF-AMS data collected by Xu et al. (2015) at different rural and urban sites in SE US, which includes data collected at JST, showed that the m/z 91 fragment ion is primarily a CxHy fragment in all the mass spectra. Fourth, the m/z 91 fragment ion may be C7H7+, a marker ion for SOA formed from monoterpene chemistry (Boyd et al. 2015). While the authors acknowledge this possibility at the end of this section, this needs to be brought up earlier in this discussion section and the authors need to be more circumspect when correlating the 91Fac to isoprene chemistry.

We thank the referee for the discussion. We have clarified in the current text that isoprene is not the sole source of 91Fac. It might have not been clearly stated in the previous version. We acknowledged that other biogenic emissions could potentially be associated to 91Fac, as what we found from tracers correlations. Some parts of the discussion have been re-phrased as follows:

“The moderate correlations with isoprene ozonolysis and photooxidation tracers suggest that 91Fac could be related to isoprene chemistry but not specifically related to the IEPOX pathway. However, the fair correlations of 91Fac with monoterpene SOA tracers suggest multiple sources could contribute to its formation. Laboratory studies found that combined isoprene-, α-pinene-, and β-caryophyllene-derived SOA mass (Chen et al., 2015) as well as β-pinene+NO3 SOA mass spectra (Boyd et al., 2015) produced an intense signal at m/z 91 associated with C7H7+. Due to limitation in unit mass resolution of ACSM measurements, we could not identify composition of m/z 91 fragment ion. Thus, contributions of C7H7+ and C3H7O3+ could not be examined from this study. Additionally, SOA tracers from monoterpene chemistry were found to fairly correlate with 91Fac from Look Rock, USA (Budisulistiorini et al., 2015). However at LRK, isoprene was more abundant (~2 ppb) than monoterpenes (<1 ppb) during the 2013 SOAS campaign as measured by online high-resolution proton transfer reaction time-of-flight mass spectrometry (HR-PTR-TOFMS) (Budisulistiorini et al., 2015). Thus, isoprene chemistry could be more influential in formation of 91Fac at LRK.”

Fig. 2: Please separate the JST and LRK datasets into individual figures. It is currently hard to understand. This is especially the case for 91Fac from the LRK site since its color is similar to 91Fac from the JST site.

We have separated figures of mass spectra from JST and LRK sites into Fig. 2 and Fig. 3, respectively.

References
Seasonal Characterization of Submicron Aerosol Chemical Composition and Organic Aerosol Sources in the Southeastern United States: Atlanta, Georgia and Look Rock, Tennessee

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Abstract

A yearlong near-real-time characterization of non-refractory submicron aerosol (NR-PM$_1$) was conducted at an urban (Atlanta, Georgia in 2012) and rural (Look Rock, Tennessee in 2013) site in the southeastern U.S. using the Aerodyne aerosol chemical speciation monitor (ACSM) collocated with established air-monitoring network measurements. Seasonal variations in organic aerosol (OA) and inorganic aerosol species are attributed to meteorological conditions as well as anthropogenic and biogenic emissions in this region. The highest concentrations of NR-PM$_1$ were observed during winter and fall seasons at the urban site and during spring and summer at the rural site. Across all seasons and at both sites, NR-PM$_1$ was composed largely of OA (50–76%) and inorganic sulfate (12–31%). Six distinct OA sources were resolved by positive matrix factorization applied to the ACSM organic mass spectral data collected from the two sites over the one year of near-continuous measurements at each site: hydrocarbon-like OA (HOA), biomass burning OA (BBOA), semi-volatile oxygenated OA (SV-OOA), low-volatility oxygenated OA (OOA), isoprene-derived epoxydiol (IEPOX) OA (IEPOX-OA), and 91Fac OA (a factor dominated by a distinct ion at m/z 91 fragment ion previously observed in biogenic influenced areas). LV-OOA was observed throughout the year at both sites and contributed 30–66% of total OA mass. HOA was also observed during the entire year only at the urban site (15-24% of OA mass). BBOA (15-33% of OA mass) was observed during winter and fall, likely dominated by local residential wood burning emission. Although SV-OOA contributes quite significantly (~27%), it was observed only at the urban site during colder seasons. IEPOX-OA was a major component (27-41%) of OA at both sites, particularly in spring and summer. An ion fragment at m/z 75 is proposed as an additional marker for IEPOX-OA, as it is shown to correlate well with the m/z 82 ion associated with the aerosol mass spectrum of...
IEPOX-derived secondary organic aerosol (SOA). The contribution of 91Fac to the total OA mass was quite low at the urban site (~9%), but was significant (21-23%) at the rural site during warmer months. Comparison of 91Fac OA time series with SOA tracers measured from filter samples collected at Look Rock suggests that isoprene oxidation through a pathway other than IEPOX SOA chemistry may contribute to its formation. Other biogenic sources could also contribute to 91Fac, but there remains a need to resolve the exact source of this factor based on its significant contribution to rural OA mass.
1 Introduction

Characterization of the chemical composition of atmospheric fine aerosol is important, because of its adverse human health effects (Pope III and Dockery, 2006) and possible impacts on the Earth’s climate system (Forster et al., 2007). Aerosol with aerodynamic diameters ≤1 μm (PM$_1$) play a significant role in scattering and/or absorbing solar radiation as well as cloud formation (IPCC, 2013). Long-term regional characterizations of ambient PM$_1$ is required to understand their sources, formation, and aging mechanisms, as well as their atmospheric lifetimes. This information will lead to more accurately constrained air quality models for making regulatory decisions to mitigate the potential adverse impacts of PM$_1$.

Over the past decade, online aerosol mass spectrometry (AMS) has been used to extensively characterize ambient non-refractory (NR)-PM$_1$ (Zhang et al., 2007, Jimenez et al., 2009, Ng et al., 2010, Crippa et al., 2014); however, prior studies were limited by short measurement periods (weeks to a several months) because the need for intensive instrument maintenance required the continuous on-site presence of skilled personnel in order to generate high quality data. The Aerodyne aerosol chemical speciation monitor (ACSM) based on the AMS technology have been modified to allow for long-term operation with less maintenance (Ng et al., 2011b). The ACSM has been recently used for long-term NR-PM$_1$ measurements (Petit et al., 2015, Ripoll et al., 2015, Parworth et al., 2015, Zhang et al., 2015) and shown to be durable and comparable to data collected from existing fine aerosol monitoring networks (Budisulistiorini et al., 2014).

Worldwide studies have shown that tropospheric PM$_1$ mass is dominated by organic aerosol (OA) (Zhang et al., 2007, Jimenez et al., 2009). While inorganic aerosol constituents, such as sulfate and nitrate, are largely anthropogenic in origin, both anthropogenic and
biogenic sources can contribute to OA. OA consists of aerosol directly emitted into the atmosphere, primary organic aerosol (POA), and aerosol formed from atmospheric oxidation of volatile organic compounds (VOCs), secondary organic aerosol (SOA). POA sources include fossil fuel combustion from vehicles, power generation, and residential burning (cooking and heating) as well as forest fires (Kanakidou et al., 2005). Contribution of hydrocarbon-like OA (HOA) associated with POA Although POA contributions to urban OA mass may be significant during morning traffic, while oxygenated OA (OOA) associated with SOA exceeds POA, especially at midday or in the afternoon (Zhang et al., 2005). SOA has been observed to contribute upwards of 90% to the total OA mass (Docherty et al., 2008), indicating the critical role of photochemical processes in SOA formation.

Anthropogenic emissions are the predominant sources of ambient aerosol in urban areas, whereas a regional component that is comprised of a combination of anthropogenic and biogenic contributions can also be significant, especially urban areas surrounded by dense forests, such as Atlanta, Georgia (GA). Studies in Atlanta, Georgia have characterized the chemical components of ambient aerosol collected during different seasons (Lee et al., 2002, Kim et al., 2003, Butler et al., 2003); however, they were limited by low-time or -mass resolution. A recent study reported that non-fossil carbon derived from modern sources (e.g., biogenic) accounts for 50% of carbon at two urban sites and 70%–100% of carbon at 10 near-urban or remote sites in the U.S. (Schichtel et al., 2008). Additionally, isoprene-derived SOA has been recently observed to contribute substantially to SOA in downtown Atlanta during summer (Budisulistiorini et al., 2013, Xu et al., 2015). The isoprene-derived SOA was attributed to the heterogeneous chemistry of isomeric isoprene epoxydiols (IEPOX), known oxidation products of isoprene under both low- (Paulot et al., 2009) and high-NO (Jacobs et
Biogenic hydrocarbons and their oxidation products are major contributors to ambient fine aerosol in rural areas where anthropogenic sources are absent (Budisulistiorini et al., 2015). In summer 2001, the fraction of non-fossil carbon was reported to vary from 66-80% of total carbon at Look Rock (LRK), Great Smoky Mountains National Park (GSMNP), TN, indicating the likely importance of photochemical oxidation of biogenic VOCs (BVOCs) (Tanner et al., 2004a). Sulfate did not show significant diurnal variability at LRK, TN, suggesting that local meteorological conditions are minimally influential in determining concentrations of long-lived species (Tanner et al., 2005). Moreover, OC at LRK is the primary component of SOA in summer, while POA from wood burning can contribute significantly during fall (Ke et al., 2007).

Because previous studies on detailed OA composition in the southeastern U.S. are limited by low-time resolution, we undertook a two-year study comparing near-real-time chemical characterizations of NR-PM$_1$ collected for one-year at the urban Jefferson Street (JST) site in downtown Atlanta, GA and a subsequent year at the rural LRK site located in the GSMNP, TN. NR-PM$_1$ was sampled, chemically characterized and quantified over a two-year period spanning 2012–2013 using the ACSM. OA sources were seasonally analyzed by positive matrix factorization (PMF). OA factors resolved by PMF were compared with collocated data collected from both air-monitoring sites in order to associate them with specific types of OA sources.
2 Methods

2.1 Fine Aerosol Sampling and Data Analysis

Real-time continuous chemical measurements were conducted during 2012–2013 at a downtown urban site (JST) in Atlanta, GA, and during 2013 at a rural/forested site (LRK) in GSMNP, TN, respectively. Analysis of data obtained from measurements at JST and LRK was classified into seasons (Table 1). Organic and inorganic species characterizations during 2013 Southern Oxidant Aerosol Study (SOAS) (Budisulistiorini et al., 2015) were included in analysis of summer season at LRK site of this study. Detailed descriptions of both sites have been published (Budisulistiorini et al. 2013, 2015). Briefly, the JST site is one of several research sites of the Southeastern Aerosol Research and Characterization (SEARCH) network. The JST site is located in a mixed industrial-residential area about 4.2 km northwest of downtown Atlanta and within approximately 200 m of a bus maintenance yard and several warehouse facilities to the south and southwest (Hansen et al., 2003, Solomon et al., 2003), and ~53 km of coal-fired power plant (Plant Bowen) (Edgerton et al., 2006). Recent study has shown decreases of sulfate as well as non-methane organic carbon (NMOC) have been observed from 1999–2013 at SEARCH network sites (including JST) (Hidy et al., 2014). The LRK site is located on a ridge-top on the northwestern edge of the GSMNP downwind of urban areas, such as Knoxville and Maryville, TN, and small farms with animal grazing areas. Coal-fired power plants Kingston and Bull Run are located within 50–60 km northwest of LRK site (Tennessee Valley Authority, 2015). In summer, up-slope flow carries pollutants emitted in the valley during early morning to the LRK site by mid-morning, and in the evening down-slope flow accompanies a shift of wind direction to the south and east that could isolate the site from fresh primary emissions from the valley and allows aged secondary
species to accumulate (Tanner et al., 2005). Decreases of PM$_{2.5}$ mass from 1999–2013 at LRK was attributed to decline in sulfate and OC concentrations (Tanner et al., 2015).

Ambient NR-PM$_1$ was analyzed using the Aerodyne ACSM in a similar manner at both sites. Details of NR-PM$_1$ sampling at the JST and LRK sites have been described in Budisulistiorini et al. (2013, 2015). Briefly, the ACSM was operated with a sampling flow rate of 3 L min$^{-1}$, resulting in a residence time of <2 s for PM$_{2.5}$ in the sampling line. The aerodynamic lens mounted on the ACSM inlet continuously samples PM$_1$ from the bypass PM$_{2.5}$ sampling line (Ng et al., 2011b). Particle-laden air was dried using a 50-tube Nafion dryer (Perma Pure PD-50T-24SS) in which a dry-air system delivered 7 L min$^{-1}$ of dry sheath of dry-air to keep the sample air relative humidity (RH) well below 10%, preventing condensation within the sampling line that could adversely affect the collection efficiency (CE) of PM$_1$ and clog the ACSM sampling inlet. The ACSM was tuned for ionizer and electronic offset and calibrated for ionization efficiency on site (5–7 times) periodically every season throughout each year of sampling at each site. Mass calculation of aerosol constituents is described in detail elsewhere (Ng et al., 2011b). At both sites, a CE value of 0.5 for all species was used based on evaluation of composition dependent CE as described in Budisulistiorini et al. (2013, 2015).

Correlations of combined aerosol mass concentrations of ACSM NR-PM$_1$ and collocated elemental carbon (EC; Sunset Labs) at JST and black carbon (BC; Magee Sci. Model AE 21 Aethalometer) at LRK, with aerosol volume concentrations of PM$_1$ measured by the Scanning Electrical Mobility System Mixing Condensation Particle Counter (SEMS-MCPC, Brechtel Manufacturing Inc.) were strong ($r^2 > 0.8$), suggesting an aerosol density of 1.75 g cm$^{-3}$ at JST (Budisulistiorini et al., 2014) and 1.52 g cm$^{-3}$ at LRK (Budisulistiorini et al., 2015) during summer, and a density of 1.46 g cm$^{-3}$ (Fig. S1) during winter at LRK. Operational issues, prevented measurements by the SEMS-MCPC during
other seasons at both the JST and LRK sites. Therefore, we estimated dry density of ambient PM$_1$ based on average particle composition for each season, and the assumption of organic, inorganic, and EC densities are 1.4 (Hallquist et al., 2009), 1.77 (Turpin and Lim, 2001), and 1.77 g cm$^{-3}$ (Park et al., 2004) respectively. The estimated dry aerosol densities at both the JST and LRK sites are on average provided in (Table S13), which is about 10–20% from density of 1.75 at JST (Budisulistiorini et al., 2014) and 1.52 g cm$^{-3}$ at LRK (Budisulistiorini et al., 2015) during summer, and a density of 1.46 g cm$^{-3}$ (Fig. S1) during winter at LRK. If a CE of 1 was used applied to JST and LRK datasets, the estimated aerosol density is <1 g cm$^{-3}$, which is much lower than the suggested bulk-organic of 1.4 g cm$^{-3}$ (Hallquist et al., 2009) and inorganic aerosol densities of 1.27 g cm$^{-3}$ and 1.77 g cm$^{-3}$, respectively (Cross et al., 2007).

Estimated values for winter and summer at the LRK site and summer at the JST site were close to measured values (within 10–20%). Therefore, we applied a CE value of 0.5 on all seasonal datasets.

If a CE of 1 is used, the estimated aerosol density is <1 g cm$^{-3}$, which is much lower than the suggested bulk-organic and inorganic aerosol densities of 1.27 g cm$^{-3}$ and 1.77 g cm$^{-3}$ respectively (Cross et al., 2007).

2.2 Organic Aerosol Characterization by PMF

Details of PMF analysis of the organic mass fraction have been described previously (Lanz et al., 2007, Ulbrich et al., 2009, Zhang, 2011). The PMF2 algorithm (Paatero and Tapper, 1994) was used in robust mode via PMF Evaluation Tool panel (PET v2.04) using the methods outlined in Ulbrich et al. (2009) and Zhang et al. (2011). Only the mass range $m/z$ 12–120 was utilized for PMF because no organic fragment ions are possible at $m/z$ <12 and
low transmission efficiency for ions with $m/z > 120$ (Ng et al., 2011b), which results in low signal-to-noise ratios as well as possible interferences from naphthalene at $m/z$ 128 signal.

PMF analysis was performed separately for winter, spring, summer and fall seasons at both the JST and LRK sites. Solutions were chosen based on the quality of PMF fits as well as interpretability when compared to reference mass spectra (Ng et al., 2011a, Robinson et al., 2011) and independent gas- and particle-phase measurements (Budisulistiorini et al., 2013, Budisulistiorini et al., 2015). For each analysis, uncertainty of selected factor solutions was investigated with different seeds (SEED parameter varied from 0 to 100, in steps of 5), FPEAK parameters, and 100 bootstrapping runs. PMF analysis of each season are detailed in Figures S1–S24 and correlations of selected PMF factors with external tracers and reference mass spectra are provided in Tables S21–S32, and PMF factors diagnostics are provided in Figs. S2–S9.

2.3 Estimation of Aerosol Acidity by ISORROPIA

The thermodynamic model, ISORROPIA-II in forward mode (Fountoukis and Nenes, 2007, Nenes et al., 1999), was used to estimate aerosol pH. Inputs for the model include aerosol-phase sulfate, nitrate, and ammonium as $\mu$mol m$^{-3}$, measured by the ACSM under ambient conditions. In addition, RH and temperature obtained from the SEARCH network and the National Park Service (NPS) for JST and LRK sites, respectively, were used as inputs. Inputs of gas-phase ammonia for the JST site were obtained from SEARCH and for LRK site, from the Ammonia Monitoring Network (AMoN; TN01/Great Smoky Mountains National Park – Look Rock). ISORROPIA-II predicted particle hydronium ion concentration per volume of air ($H^+$, $\mu$g m$^{-3}$) and aerosol liquid water content (LWC, mol L$^{-1}$). Calculation of aerosol pH follows that of Eq. 14 in Budisulistiorini et al. (2015).
3 Results and Discussion

3.1 Seasonal Submicron Aerosol Chemical Composition, pH, and LWC

Seasonally averaged NR-PM$_1$ was typically higher at JST in 2012 (~6–13 μg m$^{-3}$) compared to LRK in 2013 (~5–8 μg m$^{-3}$), especially during colder seasons (fall and winter) when anthropogenic primary emissions are higher. However, during warmer seasons (spring and summer) the average NR-PM$_1$ concentrations were similar at both sites (Fig. 1, Table 2). The highest average seasonal concentration of urban-NR-PM$_1$ at JST was observed during the fall (12.5 μg m$^{-3}$), whereas the summer season yielded the highest average NR-PM$_1$ concentration at the rural LRK site (8.4 μg m$^{-3}$). Interestingly, these patterns correspond to OA and sulfate seasonal trends, suggesting the important roles of these species to total NR-PM$_1$ mass at urban and rural sites across the southeastern U.S.

3.1 Submicron Aerosol Chemical Composition

At the LRK site, average OA loadings increased from spring (~3.2 μg m$^{-3}$) to summer (~5.3 μg m$^{-3}$), and then decreased in fall (~2.8 μg m$^{-3}$), which is likely related to BVOC emissions that depend on leaf surface area, solar radiation, and ambient temperature (Guenther et al., 2006). A different pattern was observed at the urban site, where average OA loadings were highest during the fall (8.2 μg m$^{-3}$) and winter (7.2 μg m$^{-3}$) seasons, suggesting contributions from biomass burning-related OA and non-biogenic sources. Generally, average OA contributions to NR-PM$_1$ were higher in spring and summer at both urban and rural sites, implying that the role of biogenic SOA formation increased during these periods. Contributions of POA and SOA OA characterization are further discussed in section 3.2 below.
Average sulfate concentrations were highest in summer for LRK (2.1 μg m⁻³) and fall for JST (~2 μg m⁻³), when OA concentrations also reached a maximum (Fig. 2). This suggests that sulfate which may contribute to enhanced SOA formation in this region (Lin et al., 2013a, Xu et al., 2015, Budisulistiorini et al., 2015). Changes in sulfate concentrations at LRK were suggested to be mainly affected by changes in SO₂ emissions that occur from electrical-generating units in the region nearby and/or further upwind (Tanner et al., 2015). At JST, SO₂ emissions from nearby coal-fired power plants nearby Atlanta could contribute to spatial variability of sulfate concentration (Peltier et al., 2007). The average contribution of sulfate to NR-PM₁ loading was quite significant throughout the year, ranging from 12–17% at JST and 21–31% at LRK (Table 2). Average concentrations of ammonium and nitrate were <1 μg m⁻³ at JST and <0.5 μg m⁻³ at LRK, seed aerosol to provide a surface for heterogeneous acid-catalyzed reactions leading to enhancement of SOA. The average ammonium and nitrate contribution to seasonal average NR-PM₁ loadings is small compared to those of OA and sulfate (Table 2). Both ammonium and nitrate species showed similar trends at the urban JST site, where they were highest during colder seasons (i.e., winter and fall), while showing no significant fluctuations during the duration of the study at LRK. This observation is consistent with previous studies (Tanner et al., 2004b, Olszyna et al., 2005) reporting that average contributions of ammonium and nitrate are not significant for rural PM₁. Average non-refractory chloride loadings were low (<0.1 μg m⁻³), indicating that chloride is not a significant contributor to inorganic aerosol mass in this region. The increasing average contributions from the sum of sulfate, ammonium, and nitrate in winter and fall at JST suggests the important role of inorganics in NR-PM₁, in accord with observations in other major urban areas (Sun et al., 2011b, Petit et al., 2015).
The lowest seasonal average pH was observed in summer (1.45) for JST and in fall (1.53) for LRK, as illustrated in Fig. 2. On the other hand, the highest seasonal average pH was 2.01 for JST and 1.81 for LRK, which were observed during winter. Overall, seasonal aerosol pH was 1.5–2.0 at both sites, indicating that NR-PM$_1$ in the southeastern U.S. is acidic year round. This is consistent with a recent study by Guo et al. (2015).

Fig. 1 shows that no direct correlation ($r^2 < 0.1$) was observed between aerosol pH and OA at both sites. However, this does not necessarily rule out the potential role of aerosol acidity in enhancing SOA formation in light of laboratory studies demonstrating a significant pH effect (Gao et al., 2004, Surratt et al., 2007, Lin et al., 2013b). Uncertainty of aerosol acidity estimation by ISORROPIA-II by omission of organic sulfate as input (Lin et al., 2014) could lead to under-prediction of aerosol acidity and the observed lack of correlation with OA. Seasonal averages of LWC were highest during summer at both JST (33.97 mol L$^{-1}$ of aerosol) and LRK (38.17 mol L$^{-1}$) sites. It should be noted that the possible LWC contributions from OA are not included because organic hygroscopicity parameter estimated from observed cloud condensation nuclei (CCN) activities of OA (Guo et al., 2015) such as that recently used by Guo et al. (2015) to measure this quantity was lacking in this study at our sites. Studies have suggested that reactive uptake decreases with enhanced RH (Nguyen et al., 2014, Gaston et al., 2014); however, some isoprene-derived SOA tracers were elevated by high RH (Zhang et al., 2011). Although organic water fraction in total LWC was found to be significant, by Guo et al. (2015) suggested that pH prediction using ISORROPIA-II based on inorganic ions alone was found to give a reasonable estimate. The lack of correlations between OA and pH as well as LWC indicate that pH and LWC might not be limiting factors in OA production in...
It should be noted that this study did not include contribution of organic water into pH estimation, which could contribute to relationship between pH and OA.

3.2 Seasonal-OA Characterizations

The seasonal mass spectra of and time series of OA factors resolved from PMF analysis at both JST in 2012 and LRK in 2013 sites are depicted in Figs. 2a and 3a, respectively. More PMF factors were resolved from JST OA than from LRK OA, which could be due to more OA sources in urban area. Each factor has a distinctive time trend throughout 2012 (Fig. 5) at JST and 2013 at LRK (Fig. 6). OA measured at JST in 2012 and LRK in 2013 mainly composed of low-volatility oxygenated OA (LV-OOA) and IEPOX-derived OA factor (IEPOX-OA). Concentrations of LV-OOA and IEPOX-OA at both sites were on average 1.9 and 1.6 μg m⁻³, respectively (Fig. 7). Hydrocarbon-like OA (HOA) and semi-volatile oxygenated OA (SV-OOA) concentrations varied between 1–2 μg m⁻³ at JST and biomass-burning OA (BBOA) was ~1 μg m⁻³ at both sites. A biogenically influenced factor (91Fac) was observed only at LRK and accounted ~1 μg m⁻³. Due to lack of measurements, the potential role of planetary boundary layer (PBL) height to diurnal variation of PMF factors was not accounted in this study. However, it is noted that we acknowledge the potential role of diurnal planetary boundary layer (PBL) dynamics or loss processes (e.g. deposition) could influence in contributing to diurnal patterns observed here for the PMF factors.

3.2.1 Winter

Seasonal mass spectra and time series of OA factors resolved from PMF analysis at both JST and LRK sites are depicted in Figs. 2a and 3a, respectively. PMF analysis of winter
OA yielded a four-factor solution at JST (Fig. 3a) and a two-factor solution at LRK (Fig. 4a).

Hydrocarbon-like OA (HOA), biomass burning OA (BBOA), semi-volatile oxygenated OA (SV-OOA), and low-volatility oxygenated OA (LV-OOA) factors (Ng et al., 2011a) were resolved from the JST dataset, whereas only the BBOA and LV-OOA factors were resolved from the LRK dataset. The temporal variation of the HOA factor correlates well ($r^2 > 0.7$) with black carbon (BC), carbon monoxide (CO), and reactive nitrogen species (NO$_x$) (Tables S21). Moreover, its diurnal variation (Fig. 84b) showed a morning peak, consistent with an expected contribution from vehicular emissions (Zhang et al., 2007).

The BBOA factor concentration increased during the night and decreased during the day at both sites (Fig. 84a), which could be related to residential and non-residential wood burning as well as planetary boundary layer (PBL) dynamics. BBOA at the LRK site also showed a large nighttime peak with a gradual decrease during the day. The large peak appears to result from a short period of intense biomass burning that occurred in 15–18 March 2013. Since a source for this event could not be identified, we do not report it specifically in this study. The time series of BBOA showed low to moderate correlation ($r^2 = 0.24$–0.5 at JST and $r^2 = 0.2$–0.4 at LRK; Tables S24–S32) with BC, suggesting that it is likely influenced by some local sources (e.g., fires). BBOA mass spectra from JST and LRK were highly correlated ($r^2 ~0.7$), indicating similarity of the sources. Comparisons of the BBOA mass spectra with reference mass spectra showed correlation with other OOA factors (Tables S1 and S2), a known caveat in resolution of BBOA based on unit mass resolution (UMR) data such as that from ACSM measurements (Wood et al., 2010). The similarity of BBOA and OOA factors mass spectra could indicate aged BBOA factor, which was observed to have enhanced signals at $m/z$ 18, 29 and 44 ions and low signals at $m/z$ 60 and 73 ions (Bougiatioti et al., 2014). However, the BBOA factor observed at JST and LRK...
displayed enhanced signal at m/z 44 ion but retained signals at m/z 60 and 73 ions, suggesting that it was not as oxidized as the aged BBOA factor.

LV-OOA is characterized by high fraction of total ion intensity at m/z 44 ($f_{44}$) resulting from high oxygen content (Ng et al., 2011a). LV-OOA is characterized by high fraction of total ion intensity at m/z 44 ($f_{44}$) resulting from high oxygen content (Ng et al., 2011a) and is the most abundant OA type at both JST and LRK (Table 24). Maxima around midnight at JST and in the mid-afternoon at LRK (Fig. 84b) were not significant, indicating that LV-OOA concentration is relatively constant throughout the day in this region. LV-OOA has been shown to correlate with non-volatile secondary species (Jimenez et al., 2009). Lack of temporal correlation between LV-OOA and sulfate has been observed to depend on oxidation degree of urban ambient aerosol (Sun et al. 2011a). We observed weak correlations ($r^2 < 0.2$) between LV-OOA and sulfate at both sites. Variability in Ratio of organic-to-sulfate ratio was used to track different photochemical aging conditions that could affect concentrations of OA and sulfate (Hildebrandt et al., 2010) of biogenic SOA (Henry and Donahue, 2012). Large variability of LV-OOA:sulfate ratio (Fig. S10S25) at LRK and JST could indicate gradual photochemical aging process in winter. This might cause lack of correlation with sulfate, as previously seen in New York City (Sun et al., 2011a). On the other hand, the mass spectral comparison of LV-OOA from both sites were strongly correlated ($r^2 \sim 1$, Fig. S2611), possibly suggesting similar sources of LV-OOA at these sites.

SV-OOA, which was observed only in urban OA, is the most abundant component of OA. An $f_{44}$ smaller than that of LV-OOA indicates the factor is less oxidized and thus semi-volatile (Ng et al., 2011a). The temporal variation of SV-OOA was moderately correlated ($r^2 \sim 0.4$) with nitrate (Fig. 84a; Table S24) while the mass spectrum was well correlated with previously resolved 82Fac and IEPOX-OA factors (82Fac and IEPOX-OA are equivalent and are characterized by a distinct ion at m/z 82) (Robinson et al., 2011;
Budisulistiorini et al., 2013; Budisulistiorini et al., 2015). Since isoprene emission is expected to be negligible during winter season, SV-OOA might not relate to IEPOX-derived SOA. However, low isoprene emissions during winter do not support the association of the SV-OOA factor is associated with IEPOX-derived SOA. The diurnal profile of SV-OOA showed an increase in the evening and decrease in the morning, similar to the BBOA profile and HOA factors. This variability suggests an influence of nitrate-radical chemistry on nighttime SOA formation (Xu et al., 2015). It is noted here that we acknowledge the potential role of diurnal planetary boundary layer (PBL) dynamics or loss processes (e.g., deposition) in contributing to diurnal patterns observed here for the PMF factors.

### 3.2.2 Spring

PMF analysis of spring OA resulted in a four-factor solution (i.e., HOA, LV-OOA, 91Fac, and IEPOX-OA) for the JST site (Fig. 3b) and a three-factor solution (i.e., LV-OOA, 91Fac, and IEPOX-OA) for the LRK site (Fig. 4b). The average concentration of HOA in Atlanta was significantly lower in spring (0.755 μg m$^{-3}$) than in winter (1.769 μg m$^{-3}$), but the diurnal pattern was similar (Figs. 3a and 4b) and temporal correlation with primary species ($r^2 \sim 0.6$) was strong ($r^2 \sim 0.6$, Table S1). Average LV-OOA concentration at JST also was the lowest in spring (1.42 μg m$^{-3}$), which might be attributed to warming temperatures that elevate the PBL and enhance atmospheric mixing. Diurnal variation of rural LV-OOA showed a small diurnal maximum in the afternoon, whereas no variation was observed for JST LV-OOA (Fig. 4b). LRK LV-OOA showed moderate correlation with sulfate ($r^2 > 0.4$; Table S2). Although, while no correlation was found for JST LV-OOA versus sulfate, comparison of mass spectra revealed the same strong correlation ($r^2 \sim 1$, Fig. 23).
S2611) between JST and LRK LV-OOA factors observed in winter, suggesting possible similar sources over regional scale.

A third factor resolved from Atlanta OA was assigned as 91Fac rather than SV-OOA based on a higher oxidation level \( \left( \frac{f_43/f_44}{f_43/f_44} = 0.12 \right) \) and better correlation \( (r^2 = 0.44) \) with the 91Fac reference mass spectrum (Robinson et al., 2011) than with SV-OOA \( (r^2 < 0.4) \). Average mass contributions of 91Fac to total OA are lower at JST \( (< 10\%) \) than LRK \( (21\%) \), and do not vary substantially throughout the day (Fig. 4b). The JST and LRK 91Fac were highly correlated \( (r^2 \sim 1) \), indicating nearly identical composition. During spring and summer, the average 91Fac was resolved concentration at the LRK site and accounted \( (0.7–1.2 \mu g m^{-3}) \) is slightly higher than at JST \( (0.3–0.6 \mu g m^{-3}) \) (Fig. 3a), suggesting a higher emission sources at the rural site. 91Fac has been attributed to various sources: monoterpenes-derived SOA (Budisulistiorini et al., 2015) and biogenic SOA (Chen et al., 2015) (Chen et al., 2014). 91Fac had also been attributed to aged BBOA (Robinson et al., 2011), however, a recent field study identified ions at \( m/z \) 18, 29, and 44 as markers for aged BBOA but not \( m/z \) 91 ion (Bougiatioti et al., 2014) (Bougiatioti et al., 2014). Since BBOA was not resolved from OA measurements at either location in spring, aging of BBOA seems unlikely to be the source of 91Fac in this study, although it cannot be definitely ruled out. 91Fac will be further discussed in section 4.2.3.5.

The IEPOX-OA factor, attributed to IEPOX heterogeneous chemistry (Budisulistiorini et al., 2013, Lin et al., 2012) (Budisulistiorini et al., 2013, Lin et al., 2012), was resolved from datasets at both JST and LRK. It was the second most abundant OA type after LV-OOA at JST, but the most abundant at LRK (Table 24). The average IEPOX-OA concentration was slightly higher at LRK than at JST, which is expected due to abundant emissions of isoprene at the forested site, consistent with increasing isoprene emission during spring, with higher
concentrations near densely forested areas like at GSMNSP, TN. Diurnal patterns of IEPOX-OA are different at JST and LRK. At LRK, IEPOX-OA increased in the afternoon and remained high until evening, suggesting that this factor is driven by photooxidation of isoprene. At JST, the diurnal pattern of IEPOX-OA followed that of total OA, where it slightly decreased during the day before it increased again in the evening, which is different from previous observations at JST during summer 2011 (Budisulistiorini et al., 2013). Nevertheless, the mass spectra of IEPOX-OA at JST and LRK are tightly correlated ($r^2 \sim 1$), indicative of similar composition.

3.2.3 Summer

PMF analysis of summer OA resolved the same factors as spring at both sites: HOA, LV-OOA, 91Fac, and IEPOX-OA factors at JST (Fig. 3c), and LV-OOA, 91Fac, and IEPOX-OA factors at LRK (Fig. 4c). Average HOA mass concentration at JST increased in summer to $\sim 1.1 \mu g m^{-3}$, but its contribution to total OA was lower than from spring (Fig. 73, Table 1). Temporal variation of HOA was well correlated ($r^2 \sim 0.6$) with BC, CO, and NO$_x$ (Table S21) and the diurnal pattern was similar to that of spring (Fig. 84b).

Average LV-OOA concentrations at both sites also increased in summer; however, the proportional contribution decreased as a result of a larger contribution of IEPOX-OA at JST and 91Fac at LRK (Fig. 73, Table 21). The time series of LV-OOA correlated with sulfate ($r^2 \sim 0.2$) at JST, but more strongly correlated with sulfate at LRK ($r^2 = 0.6$–0.7) (Tables S2–S3). The diurnal profile of rural LV-OOA showed a local maximum in mid-afternoon tracking with the sulfate diurnal profile (Fig. 84). At JST, LV-OOA and sulfate increased slightly during mid-morning, and while LV-OOA remained high, sulfate decreased in the evening. Comparison of JST and LRK LV-OOA mass spectra revealed a strong correlation ($r^2 = 0.945$). Ratios of LV-OOA:sulfate at both sites were on average $>1$. 
suggesting the LV-OOA was aged. The large variability of LV-OOA:sulfate ratio at LRK in summer could indicate that LV-OOA was aging gradually.

Average concentrations of the 91Fac OA at both sites LRK were higher in summer than spring. The relative contribution of 91Fac to total OA OA remained constant at JST, but increased at LRK (Table 21, Fig. 3) and its The diurnal profile of 91Fac at LRK showed a local maximum around noon, whereas no diurnal variation was observed at JST. No correlation was observed for time series of 91Fac with inorganics in Atlanta, but a moderate correlation of 91Fac with nitrate ($r^2 \sim 0.5$) with nitrate was observed at LRK (Tables S2). Correlation of the mass spectra at the two sites was slightly less ($r^2 \sim 0.9$) than in spring.

91Fac at both sites were less aged compared to LV-OOA based on average ratios of 91Fac:sulfate $< 1$ (Fig. S25) suggest that 91Fac was a less oxidized factor. Variability of LRK 91Fac, however, was large suggesting that it was gradually aged in both spring and summer seasons during spring.

Both concentration of IEPOX-OA and relative contribution to total OA mass increased at JST and LRK increased during summer. At LRK, the average concentration of IEPOX-OA reached a maximum in summer, but its relative contribution to total OA mass was lower due to the increasing contribution from 91Fac. Concentrations of IEPOX-OA at both sites are comparable (Fig. 73c), suggesting that in summer this factor may become spatially homogeneous in the southeastern U.S. Since measurements at JST and LRK were conducted at different years, meteorological changes might play role in site-to-site comparison. At LRK, IEPOX-OA showed a small increase around noon, while at JST there was a local maximum in the mid-afternoon, suggesting an influx of IEPOX-OA likely transported from surrounding forested areas. The time series of IEPOX-OA was moderately correlated with nitrate ($r^2 \sim 0.4$) at JST, whereas at

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LRK, stronger correlations ($r^2 > 0.5$) with inorganics (i.e., sulfate, nitrate and ammonium) were observed.

### 3.2.4 Fall

At JST, PMF analysis of fall OA resulted in a four-factor solution similar to that of winter OA (i.e., HOA, BBOA, SV-OOA, and LV-OOA), while at LRK a three-factor solution was resolved (i.e., LV-OOA, 91Fac, and IEPOX-OA) (Figs. 3d and 4d, respectively). The concentration of HOA increased to a level comparable to that in winter (Fig. 73). The correlations of the time series of HOA with BC, CO, and NOx ($r^2 > 0.7$) were similar to spring and summer and slightly stronger than in winter (Table S1). The diurnal profile of HOA appears similar to that in winter (Fig. 84).

At JST, the BBOA factor was resolved again from OA in fall with average concentration and fractional contribution to total OA less than from winter. BBOA was not resolved from OA at LRK. The diurnal profile of BBOA during fall at JST appeared similar to that in winter, suggesting similar emission sources as well as possible PBL effect during these two colder seasons. SV-OOA was also resolved from JST OA in fall with slightly higher average concentration and fractional contribution than in winter. The diurnal profile of fall SV-OOA was similar to that in winter, suggesting similar sources and role of PBL.

LV-OOA was resolved from OA at both JST and LRK. Average concentrations of LV-OOA remained relatively constant from summer to fall at both the urban and rural sites (Fig. 74). However, the contribution of LV-OOA to total OA at LRK increased due to decreasing concentrations of other OA factors (i.e., IEPOX-OA and 91Fac) (Table 24). JST LV-OOA did not show diurnal variation, whereas LRK LV-OOA increased in mid-morning and reached a maximum around mid-afternoon. Temporal variation of LV-OOA was weakly correlated ($r^2 \approx 0.2$) with inorganics at JST, but moderately correlated ($r^2 = 0.4\rightarrow0.5$) at LRK.
Strong correlation of LV-OOA mass spectra ($r^2$ ~1, slope = 0.8–1.1; Fig. S1S26) at JST and LRK indicates a similar or identical source.

The concentration and fractional contribution of 91Fac resolved from OA at LRK were much lower in fall than summer (Fig. 73, Table 21). No significant diurnal variation or correlations with inorganics was observed. IEPOX-OA concentration decreased in fall as expected from reduced isoprene emissions. Time series of IEPOX-OA were not correlated with any secondary species. The diurnal profile of IEPOX-OA showed a small peak around noon, suggesting that SOA formation was still occurring.

### 3.3.3. Seasonal Changes and Contribution of OA Sources

Figs. 3a and 3b illustrate annual temporal variations of PMF factors resolved from the JST and LRK. HOA was observed throughout the year at JST in 2012 and contributes significantly to total OA, on average 20–24% (Table 1), while it was not observed at LRK in 2013. Seasonal average mass concentration of HOA varies from 0.5–2 µg m$^{-3}$ (Fig. 3c). Wider standard deviations in winter and fall suggest more variability in HOA mass in Atlanta during these seasons. LV-OOA, which was also observed throughout the year, contributes on average 30–43% of the total OA. Seasonal average concentration of LV-OOA is relatively constant between 1.3 µg m$^{-3}$, with less mass variability in summer and more variability in winter. PBL might have a role in the higher variability of HOA and LV-OOA at JST during winter. At LRK, LV-OOA was also observed throughout the year, accounting for a large proportion of total OA in winter, up to 66% (Table 1). Similar to JST, seasonal average concentration at LRK was 1–3 µg m$^{-3}$, with slightly more mass variability in winter and fall than in spring and summer.
BBOA and SV-OOA were both observed during winter and fall 2012 at JST. BBOA seasonal average concentration is about 1–2 µg m\(^{-3}\), accounting for average 15–19% of total OA. Standard deviations of mass concentrations indicate large variability of BBOA in winter, which narrows in fall (Fig. 7.3c). BBOA was observed only during winter 2013 at LRK. The average concentration of BBOA at LRK was consistently ~1 µg m\(^{-3}\) (Fig. 3b), but several episodes of high levels resulted in a large standard deviation (Figs. 7.3b,e). SV-OOA was resolved only at JST and only in the fall and winter (Fig. 3a), implying that it might be formed from local aging process or transported from nearby areas. Seasonal average concentration of SV-OOA was 1–2 µg m\(^{-3}\), contributing approximately 26 and 28% of the total OA in winter and fall, respectively. During spring and summer, SV-OOA concentrations were probably at or below the ACSM limits of detection.

IEPOX-OA concentrations at both sites were elevated throughout spring and summer of 2012 at JST and 2013 at LRK in accord with expected enhanced emission and photochemistry of isoprene (Fig. 3a-b). In Atlanta (JST), average concentration of IEPOX-OA was ~1 µg m\(^{-3}\) (32% of total OA) in spring and ~2 µg m\(^{-3}\) (37%) in summer (Table 2, Fig. 4c). Mass variability of IEPOX-OA in summer was large, primarily as a result of a sharp peak in early July, when levels were as high as ~4 µg m\(^{-3}\). In contrast to JST, IEPOX-OA was observed in spring, summer, and fall at LRK. Average IEPOX-OA concentrations was 1.35 µg m\(^{-3}\) in spring and 2.13 µg m\(^{-3}\) in summer, contributing 41% and 40% of total OA mass, respectively. Decrease of IEPOX-OA concentration in fall season is in accord with expected enhanced emission and photochemistry of isoprene. In accord with this explanation, IEPOX-OA was not observed during winter 2013 at LRK, suggesting that
isoprene emission was negligible. Standard deviations at LRK were large in both spring and summer and concentrations were similar to those observed at JST during summer.

91Fac OA was observed during spring and summer, and fall at JST and LRK in 2013, and through the fall season only at LRK. Seasonal average concentrations of 91Fac were $\leq 1\ \mu g \ m^{-3}$ (9% of total OA) at JST. However, at LRK, the seasonal average concentrations were 0.68 $\mu g \ m^{-3}$ (21%) in spring, 1.25 $\mu g \ m^{-3}$ (23%) in summer, and 0.25 $\mu g \ m^{-3}$ (9%) in fall. Further discussion about the possible source(s) of 91Fac is presented in section 4.2.5.

4 Discussion

4.13.4 IEPOX-OA Factor: Fragment Ion Contributions

The IEPOX-OA factor component has been observed in chamber experiments and field OA and sources datasets (Hu et al., 2015). Mass spectra generated by thermal decomposition of isomeric authentic 3-MeTHF and IEPOX standards directly atomized into the Aerodyne HR-ToF-AMS show major fragments at $m/z \ 82$ (mostly $C_5H_6O^+$), $m/z \ 53$ (mostly $C_4H_5^+$), and $75$ (mostly $C_3H_7O^+$), and 100 (mostly $C_5H_8O^+$) (Lin et al., 2012). The ion fragment at $m/z \ 100$ (mostly $C_5H_9O^+$) was also suggested as an ion marker for IEPOX-derived SOA (Lin et al., 2013b), however, field studies using ACSM (Budisulistiorini et al., 2013, Budisulistiorini et al., 2015) showed stronger signal at $m/z \ 100$ (possibly $C_5H_9O^+$).

Temporal variation of the $m/z \ 82$ fragment ion associated with LV-OOA, IEPOX-OA, and 91Fac (Fig. S275a-b) shows that the IEPOX-OA factor is the predominant contributor to $m/z \ 82$ at both LRK and JST in spring and summer. However, during fall the LV-OOA factor becomes a significant contributor at LRK (Fig. 5b).

In addition to the ion at $m/z \ 82$ fragment, the IEPOX-OA mass spectra show distinct fragment ions at $m/z \ 82$, $m/z \ 53$, and $m/z \ 75$ show weak and strong linear relationships with $m/z$.
and m/z 75, respectively and no correlation with m/z 100. (Fig. 95c). Presents scatter plots of the fractional contributions of ions at m/z 53 (f_{53}) and 75 (f_{75}) versus the contribution of the ion at m/z 82 (f_{82}) to IEPOX-OA mass spectra. f_{53} and f_{75} show a strong linear relationship ($r^2 = 0.9095$, slope = 0.4999 ± 0.0681) over different locations and seasons, while f_{53} and f_{82} are more weakly correlated ($r^2 = 0.4835$). Mass spectra generated by thermal decomposition of isomeric authentic 3-MeTHF and IEPOX standards directly atomized into the Aerodyne HR-ToF-AMS show major fragments at m/z 82 (mostly C_{5}H_{6}O^{+}), m/z 53 (mostly C_{4}H_{5}O^{+}), m/z 75 (mostly C_{3}H_{7}O_{2}^{+}), and 100 (mostly C_{5}H_{8}O_{2}^{+}) (Lin et al., 2012). While ions at m/z 53 and 75 were prominent in ACSM mass spectra acquired from the atomization of filter extracts of laboratory-generated IEPOX-derived SOA (Budisulistiorini et al., 2013) and in the IEPOX-OA factor resolved from field studies using the ACSM (Budisulistiorini et al., 2015), both sources gave a quite prominent ion at m/z 101 (C_{5}H_{9}O_{2}^{+}) rather than m/z 100. The scatterplots of f_{101} and f_{100} against f_{82} do not show a linear relationship ($r^2 <= 0.105$), perhaps as a consequence of the low intensity of m/z 101 these ions compared to the other ion fragments. Although parameterizations of IEPOX-OA factor based on its markers (Hu et al., 2015) was not done in this study, we offer this study presents some insights for the role of the m/z 82 fragment ion over different seasons in southeastern U.S. Fig. 5 suggests that observation of the m/z 75 fragment ion variation over different seasons indicates its potential could serve as an additional marker ion for IEPOX-OA detection. Here we have estimated from our field data, the intensity of the ion at m/z 75 is about half that of the ion at m/z 82 in IEPOX-OA mass spectra. This warrants future study to examine m/z 75 ion fragment detection from laboratory generated IEPOX-derived SOA using a higher-resolution aerosol mass spectrometer.
Insights into 91Fac OA Formation

Studies have reported significant time variations of an m/z 91 fragment ion (C$_3$H$_7$O$_3$)$^+$ measured by the Aerodyne AMS (e.g., Surratt et al., 2006, Robinson et al., 2011, Slowik et al., 2011, Chen et al., 2015). Surratt et al. (2006) found that this ion strongly correlated with OA mass during isoprene photooxidation under low-NO$_x$ and low-RH conditions in a chamber pre-seeded with ammonium sulfate, and proposed C$_3$H$_7$O$_3$ formula for this ion as a tracer for peroxide under low-NO$_x$ condition (Surratt et al., 2006). Observation of photooxidation of isoprene hydroxy hydroperoxide (ISOPOOH) in low-NO$_x$ condition showed formation of non-IEPOX low-volatility hydroperoxide compounds (St. Clair et al., 2015), leading to production of non-IEPOX SOA in chamber and field studies (Krechmer et al., 2015). Field measurements showed a PMF factor with intense signal at m/z 91 (91Fac) was resolved from OA measurements over densely forested areas where isoprene emissions were dominant and NO$_x$ level was negligible (Robinson et al., 2011, Budisulistiorini et al., 2015) as well as site influenced by monoterpene emissions (Slowik et al., 2011). In this study, we found that NO$_x$ does not influence 91Fac formation at LRK site (Fig. S28). On the other hand, a weak correlation ($r^2 = 0.2$) between m/z 91 ion of 91Fac and m/z 82 ion of IEPOX-OA factor might indicate that biogenic source(s) contributed to 91Fac formation in densely forested area like LRK site. High-volume PM$_{2.5}$ filter samples collected at LRK during 1 June – 17 July 2013 were analyzed offline for biogenic SOA tracers by ultra performance liquid chromatography/diode array detection-electrospray ionization-high-resolution quadrupole time-of-flight mass spectrometry (UPLC/DAD-ESI-HR-QTOFMS) (Budisulistiorini et al., 2015). In addition to monoterpene oxidation chemistry tracers (Surratt et al., 2008, Claeys et al., 2009, Yasmeen et al., 2010, Szmigielski et al., 2007) reported in Budisulistiorini et al. (2015), SOA tracers from isoprene...
ozonolysis chemistry (Safi Shalamzari et al., 2013, Riva et al., 2015) were also detected (Table 3). SOA tracers of isoprene ozonolysis were weakly to fairly correlated \( (r^2 = 0.2–0.5) \) with both IEPOX-OA and 91Fac, suggesting potential contribution of isoprene emission in the factors formation. Details of aerosol-phase tracers and electron ionization fragmentation pattern of non-IEPOX SOA produced from condensation of the low-volatility hydroperoxide compounds (St. Clair et al., 2015, Krechmer et al., 2015) are limited, thus peroxide contribution to formation of 91Fac could not be investigated in this study.

The moderate correlations with isoprene ozonolysis and photooxidation tracers suggest that 91Fac could be related to isoprene chemistry but not specifically related to the IEPOX pathway. However, the fair correlations of 91Fac with monoterpene SOA tracers suggest multiple sources could contribute to its formation. Laboratory studies found that relation of this AMS fragment ion to peroxide formation isoprene photooxidation (Surratt et al., 2006) and combined isoprene-, α-pinene-, and β-caryophyllene-derived SOA mass spectra (Boyd et al., 2015) produced an intense signal at \( m/z \) 91 associated with \( \text{C}_7\text{H}_7^+ \) has also been suggested. Due to limitation in unit mass resolution of ACSM measurements, we could not identify composition of \( m/z \) 91 fragment ion. Thus, contributions of \( \text{C}_7\text{H}_7^+ \) and \( \text{C}_7\text{H}_7\text{O}_3^+ \) could not be examined from this study. Additionally, a 91Fac factor was resolved from PMF analysis of atmospheric measurements over densely forested areas where isoprene emissions were dominant (Robinson et al., 2011, Budisulistiorini et al., 2015) SOA tracers from monoterpene chemistry were found to fairly correlate with 91Fac from Look Rock, USA (Budisulistiorini et al., 2015). However at LRK, isoprene was more abundant (~2 ppb) than monoterpenes (<1 ppb) during the 2013 SOAS campaign as measured by online high-resolution proton transfer reaction time-of-flight mass spectrometry (HR-PTR-TOFMS)
(Budisulistiorini et al., 2015). Thus, isoprene chemistry could be more influential in formation of 91Fac at LRK.

High-volume PM$_{2.5}$ filter samples at the LRK during 1 June—17 July 2013 were analyzed offline for biogenic SOA tracers by ultra performance liquid chromatography/diode array detection electrospray ionization high resolution quadrupole—time of flight—mass spectrometry (UPLC/DAD-ESI-HR-QTOFMS) (Budisulistiorini et al., 2015) (Budisulistiorini et al., 2015). SOA tracers from isoprene ozonolysis chemistry (Riva et al., 2015) and monoterpene oxidation chemistry were detected (Table 2) in addition to tracers of isoprene photooxidation. SOA tracers of isoprene ozonolysis were moderately correlated ($r^2 = 0.2–0.5$) with both IEPOX-OA and 91Fac, and several SOA tracers of isoprene ozonolysis correlated more strongly with 91Fac than monoterpene-derived SOA tracers ($r^2 = 0.1–0.4$).

Fig. 6 shows the correlation of m/z 91 of 91Fac at JST and LRK during spring and summer with NO$_x$ and the ion at m/z 82 of the IEPOX-OA factor. NO$_x$ and biogenic source(s) represented by m/z 82 ion of IEPOX-OA factor did not appear to influence formation of 91Fac during summer at JST. At LRK, 91Fac was not correlated with NO$_x$. However, a weak correlation with the m/z 82 ion of IEPOX-OA factor might indicate that biogenic source(s) contributed to 91Fac formation at LRK.

At the LRK site, isoprene mixing ratios were up to 12 ppb during the 2013 SOAS campaign as measured by online high resolution proton transfer reaction time-of-flight mass spectrometry (HR-PTR-TOFMS) (Budisulistiorini et al., 2015). The moderate correlations with isoprene ozonolysis and photooxidation tracers suggest that 91Fac could be related to isoprene chemistry but not specifically related to the IEPOX pathway. The abundance of 91fac warrants additional study to determine the source, since multiple sources might contribute to this factor. While there appears to be correlation with isoprene-derived SOA in
this study, 91Fac has been resolved from SOA produced in monoterpene-influenced sites (Slowik et al., 2011).

Conclusions

Seasonal characterization of NR-PM$_1$ collected in the southeastern U.S. revealed that OA is the most abundant species, accounting for 50–65% at LRK and 65–75% at JST. Sulfate is the most abundant inorganic species throughout the year, accounting for 20–30% and 10–20% at the rural and urban site, respectively. Nitrate and ammonium followed as the third and fourth most abundant inorganic species, respectively, and were dependent on the season and location. The highest average concentrations of OA, sulfate and ammonium were observed during summer season at LRK and during fall at JST.

Characterization of OA using PMF resolved a combined six factors at JST and LRK sites, with different factors being resolved depending on location, and season, and year. HOA and SV-OOA were resolved only at JST that represent urban OA. BBOA, LV-OOA, IEPOX-OA, and 91Fac were resolved from both sites during different seasons. HOA contributions to total OA mass were fairly consistent (15–25%) over four seasons, and its contribution peaked during winter. SV-OOA was observed only during colder seasons, having a consistent seasonal contribution of 27%. BBOA was only observed during winter and fall seasons, and on average contributed ~17% to the total OA mass, with the higher contribution of BBOA at LRK. The higher contribution of BBOA at LRK, that represent rural site, was likely due to a single, significant burning event.

Average IEPOX-OA contributions during warmer seasons were 40% and 35% at the rural and urban sites, respectively. While the IEPOX-OA resolved from PMF is characterized by the fragment ion at m/z 82, strong correlation of the fractional contributions of the ions m/z 82 and 75 fragment ions to IEPOX-OA mass spectra ($f_{75}/f_{82}$ ~0.5) suggests that both ions can
serve as markers for IEPOX-OA. Average 91Fac OA contribution was 9% and 22% at the urban and rural LRK site over spring and summer, respectively. Based on correlations with SOA tracer analysis performed offline, 91Fac showed an overall higher correlation with SOA markers of isoprene ozonolysis and photooxidation than with monoterpene oxidation. This might indicate that 91Fac at LRK could be influenced by isoprene chemistry, but might have different sources in other locations where isoprene is not in high abundance. The abundance of 91Fac at isoprene-dominated forested area such as LRK warrants further study to determine the source, since multiple biogenic sources or low-volatility hydroperoxide compounds might contribute to this factor.

Acknowledgements

This study was supported by the Electric Power Research Institute (EPRI). We thank Jerry Brown of Atmospheric Research and Analysis (ARA) as well as Bill Hicks of the Tennessee Valley Authority (TVA) for their assistance in collecting the collocated monitoring data at the JST and LRK sites, respectively. S. H. Budisulistiorini was supported in part by a Fulbright Presidential Fellowship (2010–2013) for attending the University of North Carolina at Chapel Hill, the UNC Graduate School Off-Campus Dissertation Research Fellowship, and EPRI.

References


Table 1. Seasonal classification period of measurements at JST and LRK

<table>
<thead>
<tr>
<th></th>
<th>JST</th>
<th>LRK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter</td>
<td>22/12/2011 – 19/03/2012</td>
<td>18/01/2013 – 19/03/2013</td>
</tr>
<tr>
<td>Spring</td>
<td>20/03/2012 – 19/06/2012</td>
<td>20/03/2013 – 31/05/2013</td>
</tr>
<tr>
<td>Summer</td>
<td>20/06/2012 – 21/09/2012</td>
<td>01/06/2013 – 21/09/2013*</td>
</tr>
<tr>
<td>Fall</td>
<td>22/19/2012 – 20/12/2012</td>
<td>22/09/2013 – 20/12/2013</td>
</tr>
</tbody>
</table>

*Measurements in summer at Look Rock coincided with 2013 SOAS campaign from 1 June to 17 of July 2013. Thus, summer season for LRK was classified to include period of SOAS.
Table 2. Seasonal averaged mass concentrations of non-refractory PM$_1$ (NR-PM$_1$) in µg m$^{-3}$, percent contributions of organic and inorganic species measured by the Aerodyne ACSM and PMF factors resolved from Atlanta, GA (JST site) and Look Rock, TN (LRK site) during 2012 and 2013.

<table>
<thead>
<tr>
<th></th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Fall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>JST</td>
<td>LRK</td>
<td>JST</td>
<td>LRK</td>
</tr>
<tr>
<td>NRPM$_1$</td>
<td>10.50±7.32</td>
<td>4.77±3.32</td>
<td>6.19±2.85</td>
<td>5.59±3.47</td>
</tr>
<tr>
<td>OA</td>
<td>69.0%</td>
<td>50.2%</td>
<td>75.9%</td>
<td>57.8%</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>13.4%</td>
<td>30.6%</td>
<td>12.0%</td>
<td>26.9%</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>9.3%</td>
<td>9.2%</td>
<td>5.6%</td>
<td>6.1%</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>7.9%</td>
<td>9.9%</td>
<td>6.3%</td>
<td>9.0%</td>
</tr>
<tr>
<td>Cl</td>
<td>9.3%</td>
<td>0.1%</td>
<td>0.2%</td>
<td>0.1%</td>
</tr>
</tbody>
</table>

**OA speciation**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th>HOA</th>
<th></th>
<th></th>
<th></th>
<th>HOA</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>JST</td>
<td>LRK</td>
<td>20%</td>
<td>JST</td>
<td>LRK</td>
<td>18%</td>
<td>JST</td>
<td>LRK</td>
</tr>
<tr>
<td>BBOA</td>
<td>19%</td>
<td>n.a.</td>
<td>33%</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>15%</td>
<td>n.a.</td>
</tr>
<tr>
<td>SV-OOA</td>
<td>26%</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>28%</td>
<td>n.a.</td>
</tr>
<tr>
<td>LVOOA</td>
<td>30%</td>
<td>66%</td>
<td>43%</td>
<td>37%</td>
<td>44%</td>
<td>36%</td>
<td>37%</td>
<td>63%</td>
</tr>
<tr>
<td>91Fac</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>21%</td>
<td>n.a.</td>
<td>22%</td>
<td>n.a.</td>
<td>9%</td>
</tr>
<tr>
<td>IEPOX-OA</td>
<td>n.a.</td>
<td>n.a.</td>
<td>37%</td>
<td>41%</td>
<td>38%</td>
<td>40%</td>
<td>n.a.</td>
<td>27%</td>
</tr>
</tbody>
</table>

n.a. is not available or resolved from PMF analysis. PMF analysis yielded some residuals of unresolved OA mass that make up the remaining percentage of OA factors.
Table 3. Correlations of PMF factors resolved from OA measurements at LRK, TN against SOA tracers from monoterpene chemistry and isoprene ozonolysis quantified during 2013 SOAS. Some of the monoterpene SOA tracers have previously published in Budisulistiorini et al. (2015).  

<table>
<thead>
<tr>
<th>Monoterpene SOA tracers</th>
<th>IEPOX-OA</th>
<th>LV-OOA</th>
<th>91Fac</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{18}\text{O}_{5}\text{S}$</td>
<td>0.28</td>
<td>0.26</td>
<td>0.39</td>
<td>(1)</td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{16}\text{O}_{7}\text{S}$</td>
<td>0.42</td>
<td>0.26</td>
<td>0.37</td>
<td>(1)</td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{17}\text{NO}_{7}\text{S}$</td>
<td>0.11</td>
<td>0.15</td>
<td>0.26</td>
<td>(1)</td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{18}\text{O}_{5}\text{S}$</td>
<td>0.32</td>
<td>0.36</td>
<td>0.41</td>
<td>(1)</td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{16}\text{O}_{7}\text{S}$</td>
<td>0.12</td>
<td>0.21</td>
<td>0.19</td>
<td>(1)</td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{17}\text{NO}_{7}\text{S}$</td>
<td>0.15</td>
<td>0.21</td>
<td>0.25</td>
<td>(1)</td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{18}\text{O}_{5}\text{S}$</td>
<td>0.10</td>
<td>0.17</td>
<td>0.20</td>
<td>(1)</td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{16}\text{O}_{7}\text{S}$</td>
<td>0.21</td>
<td>0.32</td>
<td>0.27</td>
<td>(1)</td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{18}\text{O}_{5}\text{S}$</td>
<td>0.15</td>
<td>0.27</td>
<td>0.14</td>
<td>(1)</td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{16}\text{O}_{7}\text{S}$</td>
<td>0.35</td>
<td>0.42</td>
<td>0.42</td>
<td>(1)</td>
</tr>
</tbody>
</table>

Isoprene ozonolysis tracers

| $\text{C}_{4}\text{H}_{8}\text{O}_{6}\text{S}$ | 0.46     | 0.40   | 0.51  | (5,6) |
| $\text{C}_{5}\text{H}_{12}\text{O}_{6}\text{S}$ | 0.39     | 0.19   | 0.35  | (5,6) |
| $\text{C}_{5}\text{H}_{10}\text{O}_{5}\text{S}$ | 0.19     | 0.19   | 0.22  | (5,6) |
| $\text{C}_{6}\text{H}_{12}\text{O}_{7}\text{S}$ | 0.33     | 0.38   | 0.41  | (5,6) |
| $\text{C}_{7}\text{H}_{10}\text{O}_{4}\text{S}$ | 0.00     | 0.07   | 0.03  | (5,6) |
| $\text{C}_{8}\text{H}_{10}\text{O}_{6}\text{S}$ | 0.24     | 0.33   | 0.48  | (5,6) |
| $\text{C}_{9}\text{H}_{14}\text{O}_{6}\text{S}$ | 0.21     | 0.30   | 0.38  | (5,6) |
| $\text{C}_{9}\text{H}_{16}\text{O}_{7}\text{S}$ | 0.38     | 0.50   | 0.46  | (5,6) |
| $\text{C}_{10}\text{H}_{20}\text{O}_{9}\text{S}$ | 0.36     | 0.29   | 0.39  | (5,6) |

* Budisulistiorini et al. (2015). Only night time samples were used in PMF factor correlation with isoprene ozonolysis tracers. References: (1) Surratt et al. (2008); (2) Claeys et al. (2009); (3) Yasmeen et al. (2010); (4) Szmigielski et al. (2007); (5) Safi Shalamzari et al. (2013); (6) Riva et al.
Figure 1. Annual temporal variations of OA and inorganic species measured at the (a) JST site in 2012; and (b) LRK site in 2013. Included in the plots are pH and liquid water content (LWC) estimated by ISORROPIA-II.
**Figure 2.** Seasonal average of OA, inorganic species and pH from JST (solid squares) and LRK (open triangles). Error bars show ± 1-standard deviation. Seasons are classified into winter (wtr), spring (spr), summer (smr), and fall.
Figure 3. Mass spectra of PMF factors resolved from (a) winter, (b) spring, (c) summer, and (d) fall OA measurements at JST in 2012.
Figure 4. Mass spectra of PMF factors resolved from (a) winter, (b) spring, (c) summer, and (d) fall OA measurements at LRK in 2013.
Figure 5. Annual temporal variation of PMF factors resolved from OA measurements at the JST site during 2012.
Figure 6. Annual temporal variation of PMF factors resolved from OA measurements at the LRK site during 2013. Measurements in the summer coincided with Southern Oxidant Aerosol Study (SOAS) campaign that results have been published in Budisulistiorini et al. (2015).
Figure 7. Seasonal average mass concentration of PMF factors resolved from JST (solid squares) and LRK (open triangles). Error bars are shown as ± 1-standard deviation.
Figure 8. Diurnal variations of (a) OA and inorganic species measured by ACSM and (b) OA factors resolved by PMF analysis from winter, spring, summer, and fall measurements at the JST site (solid lines) and LRK site (dash lines).
Figure 9. Scatterplots of the m/z 53 (possibly C_4H_5O^+), m/z 75 (possibly C_3H_7O_2^+), m/z 100 (possibly C_5H_8O_2^+) and m/z 101 (possibly C_5H_9O_2^+) normalized fragment ions from the IEPOX-OA mass spectra versus the m/z 82 normalized fragment ion from the same mass spectra over different seasons at the JST and LRK sites. ACSM measures unit mass resolution (UMR), thus the proposed formulas are based on previous study using HR-ToF-AMS (Lin et al., 2012). The asterix marker is the respective ion fragments of IEPOX-OA mass spectra resolved from OA measurements during summer 2011 at the JST site (Budisulistiorini et al., 2013).