Referee #3

While this manuscript fits the scope of the journal, there are a number of major comments that the authors need to address before this manuscript can be accepted:

1. There are a number of papers with high res seasonal OA data from Atlanta, in multiple sites at multiple seasons. In fact, the same JST site as discussed in this paper. (Xu et al PNAS 2015, ACP 2015). Given the large number of papers published about the OA in the SE US (including Budisulistiorini et al. EST 2013, Xu et al. PNAS 2015, Xu et al. ACP 2015), this manuscript fails to situate their results in the context of what we currently know about organic aerosol in the SE US. Specifically, Xu et al. (PNAS 2015 and ACP 2015) presented high res data from multiple seasons from Jefferson Street already. What is new in this work in terms of OA characterization at JST in Atlanta? If their results are all consistent with Xu et al., please say so. If not, please discuss the differences.

In this study, we performed measurements of OA at the JST site spanning over four seasons, i.e., winter, spring, summer, and fall, of the same year 2012. Budisulistiorini et al. (2013) presents identification of IEPOX-derived SOA for the first time by PMF analysis of OA measured in summer 2011 at JST site supported by laboratory experiments. Xu et al. (2015, ACP) and Xu et al. (2015, PNAS) present OA measurement at JST in May and November 2012, for one month each. What is new about our work is we provide continuous OA measurements over the entire year at JST in 2012 as well as at LRK in 2013. The latter site has not had AMS nor ACSM measurements made before over such a time scale. In addition we made filter measurements to support our PMF analyses, which has not been done in Xu et al. (2015). We have more directly pointed out where there are consistencies between our results an results from the Xu et al. (2015) studies.

2. Published high res data suggest that the m/z 91 is C7H7, not C3H7O3 as proposed by the authors. The authors acknowledged that ACSM cannot differentiate between these two, but HR-ToF-AMS can. Therefore, if the authors believe that their so called 91Fac is different from the LO-OOA factor (high in m/z 91, C7H7) proposed by Xu et al. (PNAS 2015), they need to justify this better. After all, their data and Xu et al are from the same site (JST) obtained around the same time period. Their revised manuscript has not done this sufficiently.

We would like to clarify that based on the latest version of manuscript we have removed 91Fac identification from JST OA. Previous referee recommendations on this issue were addressed in the last revision of our manusript and our re-analysis suggest that the JST 91Fac shows indication of splitting factor with LV-OOA (or MO-OOA). The latter is based on noisy temporal variation and similarities of mass spectra. We have already revised the text and proposed a 3-factor solution (i.e., HOA, LV-OOA, and IEPOX-OA) as the best factor solution. Therefore, we do not find the contradiction between our findings and Xu et al. (2015).

Regarding the 91Fac that is resolved from LRK site, we propose biogenic emissions as its source based on SOA tracers quantified from filter samples. Unfortunately, we did not have a high-resolution AMS to identify the elemental composition of the fragment ion at *m/z* 91. Thus, in the text we do not suggest that *m/z* 91 is $C_3H_7O_3^+$ nor $C_7H_7^+$. Based on comparison between 91Fac from PMF analysis and SOA tracers from filter samples, we do tentatively propose that the source of 91Fac is likely biogenic. We propose that the low-NO_x conditions at LRK lead to SOA formation through a non-IEPOX route that would form 91Fac based on recent chamber experiments at UNC using authentic ISOPOOH + OH that shows *m/z* 91 is $C_7H_7^+$ from HR-ToF-AMS analysis of aerosol filters collected from these experiments (Riva et al., in preparation). However, we do not mention these results in this manuscript since we have not yet published these results. We are happy to show the reviewer and Editor these results, but for now we will not as the wording we use in the text make only a proposal that the 91Fac is derived from biogenic oxidation under low-NO_x conditions due to correlation with our biogenic SOA tracers measured from filters at this site.

3. I am not convinced that the 91Fac is related to isoprene SOA. I think that the 91Fac is probably just the SVOOA factor with some interference from m/z 44. The reason why I think that is the case is that in Xu et al. (PNAS 2015 and ACP 2015), the authors resolved SVOOA all the year round using a HR-Tof-AMS at the JST site. However, the authors only resolved SVOOA in winter and fall in JST in this manuscript. I strongly urge the authors to go over their PMF analysis again.

As we have explained above, we have looked into our PMF analyses for JST OA again in the last revision and removed 91Fac from JST OA analysis for spring and summer 2012. We only resolved SV-OOA (or LO-OOA) in winter and fall because the spring and summer show splitting factor with LV-OOA (or MO-OOA) and not because of small interference by *m/z* 44. Moreover, temporal variations of the splitting factor are very noisy as pointed out by the previous referee. The noisy time series is likely due to lower resolution of our ACSM instrument, compared to the high-resolution AMS. Therefore, we concluded to propose 3-factor solution (i.e., HOA, LV-OOA, and IEPOX-OA) as the best solution for spring and summer at JST in 2012 based on our measurements.

4. I see a number of other problematic details in their PMF analysis. For example, in Fig. 6, the time series of 91Fac drops suddenly from summer to fall. This suggests that their season dividing is problematic, and this will affect the conclusions drawn in this manuscript. It is possible that if the authors include the first day in fall to the summer period, the 91Fac concentration will change a lot. The authors need to discuss how the seasonal dividing will affect their conclusions. Also, the HOA diurnal trend at the JST site shown in Fig. 8b seems unlike what has been published before. Specifically, I find that steep and huge drop between 0800 and 2000 pretty unbelievable even though the authors have attributed the diurnal trend to urban OA associated with morning traffic. Yes, a drop would be expected but not something this steep. The diurnal trend of the HOA factor at the JST has been published previously (Xu et al. ACP 2015), and such a steep drop was not observed. This is another sign that the PMF analysis in this manuscript may be problematic. Again, I strongly urge the authors to go over their PMF analysis again.

The seasons are divided based on direction of Earth's angle in relation to the sun as provided in the Old Farmer Almanac website, which is also used in public calendar. Regarding the drop of 91Fac from summer to fall in Fig. 6 (now Fig. 7), it is consistent with decrease of OA as presented in Figure 1b. Concentration of OA decreases pretty dramatically, from ~8 ug/m3 to ~1 ug/m3, within one day, September 21, 2013, and it is reflected in PMF OA analysis. The drop might be due to change in meteorology as we recorded temperature decreases drastically from ~25C to ~10C within one day. Concentration of OA and PMF factors increase the following days (fall season) but do not get to the same level as those during summer season.

Without dividing into seasons, yearlong PMF analysis resulted in splitting factors. This is because factor with small mass contribution and seasonal specific source would be averaged throughout the year, and loosing its distinctive feature. For example, the IEPOX-OA factor in the yearlong PMF analysis is enhanced during burning event in winter, which is unlikely due to limited emission of isoprene during that time period. We spent a considerable amount of time consulting directly with Aerodyne about these issues, and we are more convinced that splitting the PMF analysis by seasons yields the best results for reasons as described above.

HOA diurnal trend in fall season at JST (now Fig. 8) is consistent with Xu et al. (2015, ACP) who also reported a huge drop between 08:00 to 20:00 for JST-Nov period (Fig. 5f, grey line). The diurnal trends from this paper and Xu et al. (2015) are attributed to morning and evening rush hour peaks. Therefore, there is no conflicting result with regard to HOA diurnal trend between this study and Xu et al. (2015, ACP).

5. I strongly suggest that the authors specifically discuss what new insights this manuscript can provide to the scientific community. As it currently stands, I fail to see any new scientific insights, whether it is from biogenic-anthropogenic interactions in SE USA or seasonal OA trends, provided by this manuscript that has not already been discussed in published literature.

What is new from this study is that we present continuous one-year ambient PM_1 measurements and OA characterization at JST site in 2012 and LRK site in 2013. Budisulistiorini et al. (2013) reported OA characterization during summer and fall 2011 at JST site, but it mainly focused on identification of IEPOX-OA factor based on online and offline measurements. Xu et al. (2015, ACP) is limited to one-month measurements circling between different sites for one-year. Xu et al. (2015) suggested that the PM_1 and OA characterization is spatially homogeneous, based on comparison between rotating instrument (AMS) and stationary instrument (ACSM). However, the measurements did not cover a whole 12 months. Moreover, the spatial analysis is limited to sites located in Georgia, which the furthest site is about 100 km from the stationary site. The spatial analysis in Xu et al. (2015) did not include Centerville, Alabama site, hence it is possible that OA characterization may not be homogeneous between Georgia and Alabama. In this study, we present wider time span (3-month of each season at each site) and area coverage (Georgia and Tennessee which is about 190 km apart) for PM_1 and OA characterization. Therefore, this study provides new scientific insights to the biogenic-anthropogenic interactions in the southeastern US and/or seasonal OA trends.

Other more detailed comments:

6. Page 5, lines 8-12: "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." This does not accurately reflect the state of the current literature. Xu et al. (ACP 2015) has comprehensively characterized the OA in multiple seasons at multiple sites in Atlanta using high resolution mass spectrometry.

We revised the sentences as follow:

"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 characterization of ambient PM_1 by high-resolution time-of-flight AMS (HR-ToF-AMS) from multiple sites in Georgia, including Atlanta, but they were limited by one-month measurement periods at each site (Xu et al., 2015a) ."

7. Page 5, line 15: "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)" Xu et al. (ACP 2015) needs to be cited here as well.

We have added this citation.

8. Page 6, line 5-6: "Because previous studies on detailed OA composition in the southeastern U.S. are limited by low-time resolution…" This does not accurately reflect the state of the current literature, please revise. See comments 1 and 6.

We have revised the sentence as follows:

"We present 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."

9. Page 12, lines 8-9: "The lack of correlations between OA and pH as well as LWC indicate that pH and LWC might not limiting factors in OA production in this region." Xu et al. (ACP 2015) first demonstrated that pH and LWC are not limiting factors for OA production in the SE US. It would be appropriate to cite it here.

We have revised the sentence as follows:

"The lack of correlation between OA and pH as well as LWC indicates that pH and LWC might not limiting factors in OA production in this region, consistent with previous studies in Georgia and Alabama (Xu et al., 2015a) and Tennessee (Budisulistiorini et al., 2015)."

10. Page 14, lines 12-14: "Variability in organic-to-sulfate ratio could indicate different photochemical conditions that could affect concentrations of OA and sulfate (Hildebrandt et al., 2010)" Do the authors mean aging? If that is the case, the authors should explicitly state this, instead of making the readers infer this.

We have removed this statement because it is based on OA:SO_4 ratio from field measurements and not supported by laboratory studies.

11. Page 16, lines 9-10: "Diurnal patterns of IEPOX-OA are different at JST and LRK." Why are the diurnal trends different? This needs to be addressed.

We have discussed that in the following sentences. We clarified the discussion as follows:

"Diurnal patterns of IEPOX-OA are different at JST and LRK. At LRK, IEPOX-OA has insignificant diurnal variability, which is likely influenced by small variability of sulfate as previously observed (Tanner et al., 2005). However, a small increase in the afternoon and constant concentration until the evening suggests that this factor is driven by photooxidation of isoprene (Budisulistiorini et al., 2013). 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. This pattern is different from previous observations at JST during summer 2011 (Budisulistiorini et al., 2013) but quite similar to isoprene-OA from May 2012 reported by Xu et al. (2015a), suggesting influence of year-to-year changes in meteorology, such as precipitation and solar radiation (Table S1)."

12. Page 16, lines 12-14: "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)." Why are these observations different from the previous study given that the same sampling time period and site?

We have answered this in the previous question (#11).

13. Page 17 lines 7-8: "Ratios of LV-OOA:sulfate at both sites were on average >1, suggesting the LV-OOA was aged." How did the authors come to this conclusion? If there is a previous study discussing this, the authors need to cite it to support their conclusions.

We have removed this statement because it is based on OA:SO_4 ratio from field measurements and not supported by laboratory studies.

14. Page 17 lines 13-14: "average ratio of 91Fac:sulfate of <1 (Fig. S25) suggest that 91Fac was a less oxidized factor." Similar comment as comment 13.

We have removed this statement because it is based on OA:SO_4 ratio from field measurements and not supported by laboratory studies.

15. Section 3.3: "Seasonal changes and contributions of OA sources" The authors should discuss their results in the context of those published by Xu et al. (ACP 2015) given the similarities of the work.

We added Table S4 that list mass concentration of species measured in Atlanta from this study and those measured by Xu et al. (2015) and Budisulistiorini et al. (2013).

16. Page 21, lines 7-8: "However, during the fall the LV-OOA factor becomes a significant contributor at LRK." Why is this the case? Some explanations should be provided.

We have added an explanation as follows:

"During fall the LV-OOA factor becomes a significant contributor to *m/z* 82 at LRK, which might be due to influence of aged IEPOX-OA. Further studies, however, will be needed to examine effects of atmospheric oxidation in IEPOX-OA and LV-OOA mass spectra."

17. Page 22, lines 16-19: "On the other hand, a weak correlation (r2 = 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." I find this sentence confusing. Is the

author saying that the observed weak correlation indicates biogenic sources?

We have revised the sentences as follows:

"In this study, we found that NO_x is not correlated (r^2 ~0) with *m/z* 91 of 91Fac during spring and summer, suggesting that at LRK site the factor is not influenced by NO_x (Fig. S27). Correlation values of 0.14 and 0.2 were found between *m/z* 91 ion of 91Fac and *m/z* 82 ion of IEPOX-OA factor during spring and summer, respectively. Since IEPOX-OA is associated with isoprene-derived SOA, the weak correlations indicate that biogenic source(s)—not necessarily isoprene—might contribute to 91Fac formation in densely forested areas like at the LRK site."

18. Page 23, lines 2-3: " SOA tracers of isoprene ozonolysis were weakly to fairly correlated (r2 = 0.2–0.5) with both IEPOX-OA and 91Fac" What is the correlation between the 91Fac and other tracers they detect?

We have clarified this particular discussion as follows:

"Correlations between 91Fac and SOA tracers from isoprene ozonolysis and monoterpene chemistry are on average 0.4 and 0.3, respectively. These suggest higher potential contribution of isoprene chemistry through a non-IEPOX pathway over monoterpene chemistry in 91Fac formation. Photooxidation of isoprene hydroxy hydroperoxides (ISOPOOH) under low-NO_x conditions was recently shown to yield the formation of low-volatility hydroperoxide compounds (St. Clair et al., 2015), leading to the production of non-IEPOX SOA in chamber and field studies (Krechmer et al., 2015). Further investigations of peroxide contributions to formation of 91Fac could not be performed in this study because the details of aerosol-phase tracers and electron ionization fragmentation patterns of non-IEPOX SOA produced from condensation of the low-volatility hydroperoxide compounds are not yet known (St. Clair et al., 2015, Krechmer et al., 2015). This should be a focus of future work."

19. Page 23, lines 19-23: "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." I don't agree with this conclusion. Higher isoprene concentrations does not mean higher influence on SOA. After all, monoterpenes have higher SOA yields than isoprene.

We agree with referee's suggestion and have removed this from the text.

Editor

General Comments

The PMF analysis, uncertainty, and sensitivity to different choices needs to be more thoroughly addressed. Although the discussion relating to the PMF analysis has been improved from the initial version, I think that additional information is still needed. For instance, the very different Q/Qexp for the two different sites needs to be addressed. This does not necessarily need to be in the manuscript, but should at least be included in the supplement. In general, it may be useful to move the discussion on the PMF analysis from the captions of the supplement figures to a text section within the supplement. This is the author's choice, but I think it would be easier for the reader to evaluate the results if the discussion was more continuous.

We have added more discussion of PMF analysis, including the different Q/Qexp for the different sites, into the SI section as well as removed the discussion of PMF analysis from the captions of the SI figures to the text section of SI.

To address the different Q/Qexp at the two sites, we have add the following text on Pages 9 – 10, Lines 19-24 and Lines 1-2, respectively:

"Q/Qexp from PMF analysis of JST data for all four seasons is 2.2–2.9, which indicate that the errors are somewhat underestimated (Ulbrich et al., 2009). This could be due to some missing data points and the lack of distinct time series during nighttime due to stable atmosphere and limitation of ACSM measurements (not high-resolution), such as observed by Guha et al. (2015). Q/Qexp from PMF analysis of LRK data for all four seasons is between 0.15–0.28, suggesting that the errors are overestimated (Ulbrich et al., 2009). However, the error values are deemed appropriate since Q/Qexp is consistently less than unity, regardless of the number of factor and the datasets."

I think that the PMF interpretation would also benefit from a discussion about how the seasonal splits were determined. In this discussion, please address how the seasonal split impacts the derived factors. For instance, the sharp drop in LV-OOA at JST (Fig. 5) between winter and spring and the sensitivity to the seasonal split should be addressed. It would also be worth discussing why SV-OOA at JST is increasing up to the end of winter and then suddenly is no longer present. Likewise the large spike in the IEPOX-OA factor at the beginning of summer should be discussed. For the LRK, 91Fac also shows a similar discontinuity. Currently, these abrupt changes lead the reader to question some of the PMF results (as pointed out by Referee #3); addressing the sensitivity of the PMF results to the seasonal split and/or discussing chemical/meteorological changes that could explain the abrupt shifts would results would increase the reader's confidence in the PMF results.

Below is information that we have added about classification of seasonal splits:

"Analysis of data obtained from measurements at JST and LRK was classified into seasons (Table 1), which are based on angle of Earth to the sun and angle of the sunlight. Information about classification of seasons is available through Old Farmer's Almanac website (http://www.almanac.com/content/reason-seasons). This classification was able to capture changes in meteorology, in particular ambient temperature, as illustrated in Figs. 1 and 2. The period with the coldest temperatures is classified as the winter season, and when the temperature rises, the period is classified as the spring season. Summer season is signified by constant high temperature at the JST and LRK sites. When temperature decreases after summer, this period is categorized as the fall season."

About the PMF analysis, we previously analyzed the yearlong datasets by PMF prior to classifying them into seasonal data. The yearlong data resulted in splitting components that were difficult to confidently identify. Therefore, based on consultations with Dr. Manjula Canagaratna, we decided to divide the data based on season. We have added the following discussion into PMF analysis method section:

"PMF analysis on yearlong data collected from JST and LRK yielded similar factor solutions as those obtained from seasonal data, but showed additional factor splitting that made solid identification of unique factors difficult. Therefore, we present results from PMF analysis performed separately for winter, spring, summer and fall seasons for the JST and LRK sites."

Page 15 line 5-6: I think that there are numerous other factors (boundary layer dynamics in particular) that could also result in this trend. Please support this statement with chemical information from the measurements and/or add a discussion regarding other possible factors.

We added information into the statement.

"The diurnal profile of SV-OOA showed an increase in the evening and decrease in the morning, similar to the BBOA and HOA factor profiles. Moreover, it tracked well with the diurnal profile of NO_3^-. This suggests possible influence of nitrate-radical chemistry on nighttime SOA formation during winter (Xu et al., 2015b, Rollins et al., 2012) ."

Technical Comments

Pg 2 Line 23: Please fix the wording.

We have revised the wording as follows:

"An ion fragment at *m/z* 75 is well correlated with the *m/z* 82 fragment ion associated with the aerosol mass spectrum of IEPOX-derived secondary organic aerosol (SOA)."

Pg 6 lines 2-4: "Moreover, OC at LRK is the primary component of SOA …" I do not understand what this is trying to say. Please fix.

We have revised the wording as follows:

"SOA is the predominant component of $PM_{2.5}$ mass during summer and early fall, but POA is more dominant in the late fall (Ke et al., 2007), suggesting that the LRK site is influenced by both biogenic and anthropogenic emissions."

Pg 8 line 10 "…is about 10-20% from density" I believe you are missing the word *different.* Also, where does the 20% come from? These average differences look to be at most 13% different. If you are not referring to differences between the averages, please reword to make this apparent.

We have revised the wording as follows:

"The estimated dry aerosol densities at both the JST and LRK sites are 1.55 g cm^{-3} on average (Table S1), which is about 13% different from the density of 1.75 at JST (Budisulistiorini et al., 2014) and 1.52 g cm^{-3} at LRK (Budisulistiorini et al., 2015) during summer."

Page 10 Lines 2-4: I don't find this particularly surprising since numerous other results have found similar results. Please place your results in context of the literature or explain how this case is different.

We have added some references and revised the wording as follows:

"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 (Tanner et al., 2015, Xu et al., 2015a)."

Page 21 line 4: This should be *m/z* 101.

We have fixed the error.

Page 23 line 11: Please point the reader to where they can find the "fair correlations" listed.

We have added more information and fixed the sentence as follows:

"Correlations between 91Fac and SOA tracers from isoprene ozonolysis and monoterpene chemistry are on average 0.4 and 0.3 (Table 3), respectively."

Page 24 line 14-15: I find the wording regarding a "consistent seasonal contribution" confusing since it was only observed in two season. Please re-phrase.

We deleted the word "seasonal" in this phrase. It should be clear from the former phrase that SV-OOA was observed only during colder seasons. Thus, the contribution is related to those colder seasons.

Page 24 line 15-17: There is only one number referred to here so I don't know what "with the higher contribution of BBOA at LRK" is referring to.

We have added the following information and fixed the sentence as follows:

"BBOA was observed during winter and fall seasons at JST and only during winter at LRK, with highest contribution of 33% of total OA observed during winter at the LRK site and on average 17% of total OA at the JST site."

Conclusions – Be clear about what the % is referring to. There are cases where the discussion is of a percentage of total aerosol and others where it is a percentage of OA. Please clarify.

We have clarified whether the % is for total OA or total NR-PM_1 in the conclusions section.

Table 2: Please include an entry in the table with the residual.

We have added the residuals into Table 2.

Fig.1: These graphs are very difficult to read. Please reduce the y-axis for concentration (off-scale values can be noted with something like an asterisk) so that the typical variability can be better seen. pH and LWC should be in different panels from the concentrations.

We have separated JST and LRK figures, and placed pH and LWC in different panels from concentrations. In addition, we have added RH and temperature data.

Fig 3&4: Please consider a multiplicative factor for intensities of ions at m/z > 50. Currently, differences between the various factors at m/z > 50 are difficult to distinguish and it is important that the reader be able to do this, particularly for 91fac. This is particularly true in Fig 4 since the 91Fac, IEPOX-OA, and LV-OOA factors are all quite similar at low m/z.

We have now multiplied the signal for *m/z* >50 for Fig 3 and 4 (now 4 and 6).

Fig. 8: Please add a title to the panels identifying the seasons.

We have added names of seasons on Fig 8 (now 9).

Supplement: Please proofread the figures and captions. There are several times where the incorrect panel is referenced. Additionally, please ensure that all axis labels are readable.

We have moved the description from figure captions and fixed the figures as suggested by the Editor.

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-~~up to 76%) and ~~inorganic~~ sulfate (~~12-~~up to 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 (LV-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-~~up to 66% of total OA mass. HOA was ~~also~~ observed during the entire year only at the urban site (~~15-24~~on average 21% 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 ~~showed to correlate~~is well correlated 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 significant (~~21–23%)~~on average 22% of OA mass) at the rural site only 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~~plays 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~~its sources, formation, and aging mechanisms, as well as ~~their~~ atmospheric ~~lifetimes~~lifetime. 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~~has 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 data are 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). 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 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). 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.

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~~characterization of ambient NR-PM$_1$ by high-resolution time-of-flight AMS (HR-ToF-AMS) from multiple sites in Georgia, including Atlanta, but was limited by one-month measurement periods at each site (Xu et al., 2015a). Non-fossil carbon derived from modern sources (e.g., biogenic) ~~accounts~~is reported to account 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~~was recently observed to contribute substantially to SOA in downtown Atlanta during summer ~~(Budisulistiorini et al., 2013, Xu et al., 2015).~~(Budisulistiorini et al., 2013, Xu et al., 2015a, Xu et al., 2015b). 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 al., 2014) conditions, in the presence of acidic sulfate aerosol (Budisulistiorini et al., 2013).

Biogenic hydrocarbons and their oxidation products are major contributors to ambient fine aerosol in rural areas where anthropogenic sources are low (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~~less influential in determining concentrations of long-lived species (Tanner et al., 2005). ~~Moreover, OC at LRK~~ SOA is ~~the primary~~predominant component of ~~SOA in summer, while POA from wood burning can contribute significantly~~$PM_{2.5}$ mass during summer and early fall but POA is more dominant in the late fall (Ke et al., 2007)~~.~~, suggesting that LRK site is influenced by biogenic and anthropogenic emissions.

~~Because previous studies on detailed OA composition in the southeastern U.S. are limited by low time resolution, we undertook~~We present 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 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).~~ Analysis of data obtained from measurements at JST and LRK was classified by season (Table 1), which was able to capture changes in meteorology, in particular ambient temperature, at JST in 2012 and LRK in 2013 as illustrated in Figs. 1 and 2. The period with the coldest temperatures is classified as the winter season, and when the temperature rises, the period is classified as the spring season. Summer season is signified by constant high temperature at the JST and LRK sites. When temperature decreases after summer, this period is categorized as the fall season.

Organic and inorganic species characterizations during 2013 Southern Oxidant Aerosol Study (SOAS) (Budisulistiorini et al., 2015) were included in analysis of the summer season at LRK site ~~of~~in 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) from 1999–2013 at JST (Hidy et al., 2014).~~) (Edgerton et al., 2006). 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 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) 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). 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 S1), which is about ~~10–20% from~~13% less than the density of 1.75 at JST (Budisulistiorini et al., 2014) and similar to the density of 1.52 g cm^{-3} at LRK (Budisulistiorini et al., 2015) during summer. 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 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~~to all seasonal datasets.

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~~interference from naphthalene calibrant at *m/z* 128~~ signal~~.

PMF analysis ~~was~~of yearlong data collected from JST and LRK yielded similar factor solutions as those obtained from seasonal data, but showed additional factor splitting that made solid identification of unique factors difficult. Therefore, we present results from PMF analysis performed separately for winter, spring, summer and fall seasons ~~at both~~for 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~~seed parameter varied from 0 to 100, in steps of 5), FPEAK parameters, and 100 bootstrapping runs. PMF analysis of each season ~~are~~is detailed in Figures S1–S24 and correlations of selected PMF factors with external tracers and reference mass spectra are provided in Tables S2-S3. Q/Q_{exp} from PMF analysis of JST data for all four seasons is 2.2–2.9 indicate that the errors are somewhat underestimated (Ulbrich et al., 2009). This could be due to some missing data points and the lack of distinct time series during nighttime due to atmospheric stability and limitation of ACSM measurements (not high-resolution), such as observed by Guha et al. (2015). Q/Q_{exp} from PMF analysis of LRK data for all four seasons is between 0.15–0.28, suggesting that the errors are overestimated (Ulbrich et al., 2009). However, the error values are deemed appropriate since Q/Q_{exp} is consistently less than unity, regardless of the number of factors and the datasets.

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 μmol 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^+, μg m^{-3}) and aerosol liquid water content (LWC, mol L^{-1}). Calculation of aerosol pH follows that of Eq. 1 in Budisulistiorini et al. (2015).

3 Results

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~~),~~) (Table 2). 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 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 LRK site (8.4 μg m^{-3}). ~~Interestingly, these~~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~~.~~ (Tanner et al., 2015, Xu et al., 2015a).

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 (Fig. 2) (Guenther et al., 2006). A different pattern was observed at the urban site~~,~~ (Fig. 1), where average OA loadings were highest during the fall (8.2 μg m^{-3}) ~~and~~followed by winter (7.2 μg m^{-3}~~) seasons,~~), suggesting contributions from biomass burning-related OA and non-biogenic sources. High concentration of OA in fall is slightly lower than ACSM measurement in fall 2011 (Budisulistiorini et al., 2013), but consistent with HR-ToF-AMS measurements in November 2012 (Xu et al., 2015a) (Table S4), suggesting the role of meteorology. Average OA contributions to NR-PM$_1$ were higher in spring and summer at JST and LRK, suggesting that biogenic SOA plays a 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}~~), when OA concentrations also reached a maximum (Fig. 2~~) (Fig. 3). This suggests that sulfate may contribute to enhanced SOA formation in this region (Lin et al., 2013a, Xu et al., ~~2015~~2015b, Budisulistiorini et al., 2015). Changes in sulfate concentration at LRK were~~ suggested to be~~ mainly affected by changes in SO$_2$ emissions from electrical-generating units in the region (Tanner et al., 2015). At JST, sulfate measurements are lower but still within a standard deviation of those measured by HR-ToF-AMS in May and July 2012 in Atlanta (Xu et al., 2015a). SO$_2$ emissions from coal-fired power plants nearby Atlanta contributed to spatial variability of sulfate concentration (Peltier et al., 2007). The average contribution of sulfate to NR-PM$_1$ 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. The average ammonium and nitrate contribution to seasonal average NR-PM$_1$ loadings is small compared ~~to those ~~of OA and sulfate (Table 2). Both ammonium and nitrate showed similar trends at the 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 PM$_1$. 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. 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-PM$_1$, in accord with observations in other major urban areas ~~(Sun et al., 2011b, Petit et al., 2015)~~ (Sun et al., 2011, Petit et al., 2015).

The lowest seasonal average pH was observed in summer (1.45) for JST (Fig. 3) and in fall (1.53) for LRK (Fig. ~~2~~3). 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). 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) was not available in this study. 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, Guo et al. (2015) suggested that pH prediction using ISORROPIA-II based on inorganic ions alone gave a reasonable estimate. The lack of ~~correlations~~correlation between OA and pH as well as LWC indicate that pH and LWC might not limiting factors in OA production in this region~~.~~, consistent with previous studies in Georgia and Alabama (Xu et al., 2015a) and Tennessee (Budisulistiorini et al., 2015). 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 OA Characterizations

The mass spectra and time series of OA factors resolved from PMF analysis at ~~both~~ JST in 2012 ~~and LRK in 2013~~ are ~~depicted~~provided in Figs. ~~3~~4 and ~~4~~5, respectively~~.~~, and LRK in 2013 are in Figs. 6 and 7, respectively. More PMF factors were resolved from JST OA than from LRK OA, which could be due to ~~more~~a larger number of OA ~~sources~~source types in urban ~~area~~areas. Each factor ~~has~~had a distinctive time trend throughout 2012 (Fig. 5) at JST and 2013 at LRK (Fig. ~~6~~7). OA measured at JST in 2012 and LRK in 2013 ~~mainly~~was composed primarily 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~~8). 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 for ~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 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.

3.2.1 Winter

PMF analysis of winter OA yielded a four-factor solution at JST (~~Fig. 3a~~Figs. 4a and 5a) and a two-factor solution at LRK (~~Fig. 4a~~Figs. 6a and 7a). HOA, BBOA, 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. Increasing the number of factors in PMF analysis of LRK data resulted in splitting factors that share similarities with BBOA factor. Thus, we selected a two-factor solution (*p* = 2) for LRK in winter.

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_y) (Table S2). Moreover, its diurnal variation (Fig. ~~8~~9) 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~~JST (Fig. ~~8~~9), which could be related to residential and non-residential wood burning as well as PBL dynamics. BBOA at the LRK site also showed a large nighttime peak with a gradual decrease during the day~~.~~ (Fig. 10). 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 0.4–0.5 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). BBOA mass spectra from JST and LRK were highly correlated (r^2 ~0.7), indicating similarity of the sources. ~~Comparisons~~Comparison of the BBOA mass spectra with reference mass spectra showed correlation with other OOA factors (Tables ~~S1~~S2 and ~~S2~~S3), a known caveat in resolution of BBOA based on unit mass resolution (UMR) data such as ~~that~~those from ACSM measurements (Wood et al., 2010). The similarity of BBOA and OOA ~~factors~~factor mass spectra could indicate ~~aged~~aging of the 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 an 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) and is the most abundant OA type at both JST and LRK (Table 2). Maxima around midnight at JST (Fig. 9) and in the mid-afternoon at LRK (Fig. ~~8~~10) 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~~.~~, such as sulfate (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 organic-to-sulfate ratio could indicate different photochemical conditions that could affect concentrations of OA and sulfate (Hildebrandt et al., 2010). Large variability of LV-OOA:sulfate ratio (Fig. S25) 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).~~. Weak correlation ($r^2 < 0.2$) between LV-OOA and sulfate might be due to a complex oxidation process, as previously observed in urban ambient aerosol (Sun et al. 2011a). On the other hand, the mass spectral comparison of LV-OOA from both sites were strongly correlated (r^2 ~1, Fig. ~~S26~~S25), 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~~at JST, showed an f_{44} smaller than that of LV-OOA (Fig. 4a) 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 ~0.4) with nitrate (~~Fig. 8,~~ Table S2) 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~~prominent 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. 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. Moreover, it tracked well with diurnal profile of NO_3^-. This ~~variability~~ suggests ~~an~~a possible influence of nitrate-radical chemistry on nighttime SOA formation ~~(Xu et al., 2015)~~during winter (Xu et al., 2015b, Rollins et al., 2012).

3.2.2 Spring

PMF analysis of spring OA resulted in a three-factor solution (i.e., HOA, LV-OOA, and IEPOX-OA) for the JST site (~~Fig. 3b~~Figs. 4b and 5b) and a three-factor solution (i.e., LV-OOA, 91Fac, and IEPOX-OA) for the LRK site (~~Fig. 4b).~~Figs. 6b and 7b). Increasing the number of factors in PMF analysis of JST resulted in splitting components, and thus, SV-OOA was not resolved in spring. The lack of the SV-OOA factor might result from evaporation of semi-volatile species in warmer periods and/or the inability of the ACSM to pick up on the variability of a factor with low concentration. Similarly, a splitting component was observed in PMF analysis of LRK data p = 4. Thus, BBOA and/or HOA were not resolved from LRK in spring.

The average concentration of HOA in Atlanta was ~~significantly~~ lower in spring (0.7 µg m^{-3}) than in winter (1.7 µg m^{-3}), ~~but~~which could be influenced by dilution — from rise of PBL — and evaporation of POA during warmer conditions (Robinson et al., 2007). Although its concentration decreases, the diurnal pattern of HOA was ~~similar~~consistent from winter to spring (Fig. ~~8~~9) and~~ temporal~~ correlation with primary species was strong (r^2 ~0.6, Table ~~S1).~~ S2).

Average LV-OOA concentration at JST also was the lowest in spring (1.4 µg m^{-3}), which might be attributed to warming temperatures that elevate the PBL and enhance atmospheric mixing. Diurnal variation of ~~rural~~LRK LV-OOA (Fig. 10) showed a small diurnal maximum in the afternoon, whereas no variation was observed for JST LV-OOA (Fig. ~~8~~9). LRK LV-OOA showed moderate correlation with sulfate (r^2 > 0.4, Table S3~~).~~), suggesting influence of sulfate at this site during spring (Tanner et al., 2015). Although no correlation was found for JST LV-OOA versus sulfate, comparison of mass spectra revealed the same strong correlation (r^2 ~1, Fig. ~~S26~~S25) between JST and LRK LV-OOA factors observed in winter, suggesting possible similar sources over a regional scale.

~~91Fac was resolved at the LRK site and accounted 0.7–1.2 µg m^{-3}. 91Fac has been attributed to various sources: monoterpene derived SOA (Budisulistiorini et al., 2015) and biogenic SOA (Chen et al., 2015). 91Fac had also been attributed to aged BBOA (Robinson et al., 2011), however, a recent field study identified ions at at *m/z* 18, 29, and 44 as markers for aged BBOA but not *m/z* 91 ion (Bougiatioti et al., 2014). Since BBOA was not resolved from OA measurements 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.~~

The IEPOX-OA factor, attributed to IEPOX heterogeneous chemistry (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 OA component at LRK (Table 2). 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. Diurnal patterns of IEPOX-OA are different at JST and LRK. At LRK, IEPOX-OA ~~increased~~has insignificant diurnal variability, which is likely influenced by small variability of sulfate as previously observed at this site (Tanner et al., 2005). However, a small increase in the afternoon and ~~remained high~~constant concentration until the evening~~, suggesting~~ suggests that this factor is driven by photooxidation of isoprene~~.~~ (Budisulistiorini et al., 2013). 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~~. This diurnal pattern is different from previous observations at JST during summer 2011 (Budisulistiorini et al., 2013)~~.~~, but quite similar to isoprene-OA from May 2012 reported by Xu et al. (2015a), suggesting influence of year-to-year changes in meteorology, such as precipitation and solar radiation (Table S1). Nevertheless, the mass spectra of IEPOX-OA at JST and LRK are tightly correlated (r^2 ~1), indicative of similar composition.

91Fac was resolved only at the LRK site and accounted for 0.7–1.2 μg m^{-3}. 91Fac has been attributed to various sources: monoterpenes-derived SOA (Budisulistiorini et al., 2015, Boyd et al., 2015), biogenic SOA (Chen et al., 2015), and 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). Since BBOA was not resolved from OA measurements in spring, aging of BBOA seems unlikely to be the source of 91Fac in this study, although it cannot be conclusively ruled out. The lack of 91Fac at the JST site suggests that its sources may be limited to emissions and chemical processes in forested and/or rural areas. 91Fac will be further discussed in section 4.2.

3.2.3 Summer

PMF analysis of summer OA resolved the same factors as spring at both sites: HOA, LV-OOA, and IEPOX-OA factors at JST (~~Fig. 3c~~Figs. 4c and 5c), and LV-OOA, 91Fac, and IEPOX-OA factors at LRK (~~Fig. 4c~~Figs. 6c and 7c). Average HOA mass concentration at JST increased in summer to ~1.1 μg m^{-3} (Fig. ~~7~~8). Temporal variation of HOA was well correlated

(r^2 ~0.6) with BC, CO, and NO_x (Table S2) and the diurnal pattern was similar to that of spring (Fig. ~~8~~9). Similar to spring, SV-OOA was not resolved in summer, which could be attributed to rapid evaporation of semi-volatile species under high ambient temperatures (Table S1).

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. 7,~~ Table 2). The time series of LV-OOA was weakly correlated with sulfate (r^2 ~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~~LRK LV-OOA showed a local maximum in mid-afternoon ~~tracking~~(Fig. 10) and have a moderate correlation (r^2 ~0.4) with the sulfate ~~diurnal profile (Fig. 8). At JST, LV-OOA and~~ (Table S3), suggesting that sulfate ~~increased slightly during mid-morning, and while LV-OOA remained high, sulfate decreased in the evening.~~ plays a role to LV-OOA in summer at LRK. Comparison of JST and LRK LV-OOA mass spectra revealed a strong correlation (r^2 = 0.94~~). Ratios of LV-OOA:sulfate at both~~), possibly suggesting similar sources between two 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 concentration of the 91Fac OA at LRK was higher in summer than spring~~.~~, which indicates the role of meteorology — increasing temperature from ~13°C in spring to ~21°C in summer (Table S1). The relative contribution of 91Fac to total OA increased at LRK (Table 2) and its diurnal profile showed a local maximum around noon. A moderate correlation of 91Fac with nitrate (r^2 ~0.5~~) was observed (Tables S2) and average ratio of 91Fac:sulfate of <1 (Fig. S25) suggest that 91Fac was a less oxidized factor. Variability of~~

~~LRK 91Fac was large suggesting that it was gradually aged in both spring and summer seasons.~~, Table S3) suggests that the factor is moderately oxidized.

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. Concentrations of IEPOX-OA at both sites are comparable (Fig. ~~7~~8), suggesting that in summer this factor may become spatially homogeneous in the southeastern U.S. Since measurements at JST and LRK were conducted ~~at~~during 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 ~0.4) at JST, ~~whereas~~and at LRK~~,~~ stronger correlations (r^2 >0.5) with ~~inorganics (i.e.,~~ sulfate~~,~~ and nitrate ~~and ammonium)~~ were observed, suggesting that this factor is moderately oxidized.

3.2.4 Fall

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~~) (Figs. 3d and 4d, respectively). The concentration of HOA increased to a level comparable to that in winter (Fig. 7). The correlations of the time series of HOA with BC, CO, and NO$_x$ (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. 8).~~). Increasing the number of factors in PMF analysis of JST fall data resulted in factor splitting, and thus, the IEPOX-OA factor was not resolved from this data set. Similarly, we could not resolve the BBOA factor from LRK fall data because the analysis resulted in splitting components.

The concentration of JST HOA increased to a level comparable to that in winter (Fig. 5), which might be influenced by meteorology — low ambient temperature and less solar radiation — in fall and winter. The correlation of the time series of HOA with BC, CO, and NO_x ($r^2 > 0.7$) was similar to spring and summer and slightly stronger than in winter (Table S2) and the diurnal profile appears similar to that in winter (Fig. 9). The presence of the HOA factor throughout the year at JST is expected due to traffic emissions in urban areas (Xu et al., 2015a).

At JST, the BBOA factor was resolved again from OA ~~in fall~~ with average concentration and fractional contribution to total OA less than ~~from~~observed in 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.~~The lack of the BBOA factor at LRK could be attributed to the inability of the ACSM to capture a factor with low concentration. In winter, the ACSM could capture the strong signal of BBOA due to some periods of intense burning which would not be expected in fall.

SV-OOA was also resolved from JST OA with slightly higher average concentration and fractional contribution than that observed in winter. The diurnal profile of fall SV-OOA was similar to that in winter, suggesting similar sources and role of PBL. The return of SV-OOA might be influenced by decreases in temperature from ~26°C in summer to ~15°C in fall (Table S1), resulting in less evaporation of semi-volatile species.

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. ~~7~~8). 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 2). JST LV-OOA did not show diurnal variation, whereas Xu et al. (2015a) observed a small diurnal variation by HR-ToF-AMS. The mass resolution of the ACSM instrument is not as high as the HR-ToF-AMS, thus, it might not be able to capture the diurnal variability. LRK LV-OOA increased in mid-morning and reached a maximum around mid-afternoon. Temporal variation of LV-OOA was weakly correlated (r^2 ~0.2) with inorganics at JST, but moderately correlated (r^2 = 0.4–0.5) at LRK. Strong correlation of LV-OOA mass spectra (r^2 ~1, slope = 0.8–1.1, Fig. ~~S26~~S25) 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. 7, Table 2). 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.~~

The concentration of 91Fac at LRK dropped significantly in fall. The drop coincided with decrease of total OA concentration and ambient temperature — from around 20°C to around 10°C (Fig. 2). Temperature has been shown to have a negative effect on SOA formation from monoterpenes (Emanuelsson et al., 2013), but isoprene SOA is shown to be dependent on temperature (Worton et al., 2013). Similar to 91Fac, IEPOX-OA concentration at LRK also decreased in fall, suggesting that their sources could be similar. The lack of the

IEPOX-OA factor at JST is likely due to reduced isoprene emissions, leading to low SOA formation consistent to previous studies (Budisulistiorini et al., 2013, Xu et al., 2015a).

3.3 Seasonal Changes and Contribution of OA Sources

HOA was observed throughout the year at JST in 2012 and contributes significantly to total OA~~, –~~ (on average ~~20–24%,~~21%), while it was not observed at LRK in 2013. 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. At LRK, LV-OOA was also observed throughout the year, accounting for a large proportion of total OA in winter, up to 66%. Results from JST and LRK sites suggest that LV-OOA is annually and spatially homogeneous, consistent with previous observations in this region (Xu et al., 2015a).

BBOA ~~and SV-OOA were both~~was observed during winter and fall 2012 at JST~~.~~ ~~BBOA~~ and accounted on average ~~15–19~~17% of total OA. Standard deviations of mass concentrations indicate large variability of BBOA in winter~~, which narrows in fall (Fig. 7).~~ (Fig. 8), which could be related to increases of biomass burning in urban areas during colder seasons. BBOA was observed only during winter 2013 at LRK. The average concentration of BBOA at LRK was consistently ~1 μg m^{-3}, but several episodes of high levels resulted in a large standard deviation (Figs. ~~7).~~ 8). The LRK site is located quite far from residential areas, thus emissions from residential burning activities might not be well captured by the ACSM during the fall season.

SV-OOA was resolved only at JST and only in the fall and winter, implying that it might be formed from local aging process or transported from nearby areas. SV-OOA contributed ~~approximately 26 and 28~~on average 27% 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 due to higher ambient temperatures that likely promote evaporation of semi-volatile species.

IEPOX-OA concentrations were elevated ~~throughout~~from spring ~~and~~to summer of 2012 at JST and 2013 at LRK in accord with expected enhanced emission and photochemistry of isoprene. In Atlanta (JST), ~~average~~ concentration of IEPOX-OA was ~~$\sim$1 μg m^{-3} (32~~on average 38% of total OA~~) in~~ over spring and ~~$\sim$2 μg m^{-3} (37%) in~~ summer. Mass variability of JST 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~~At LRK, IEPOX-OA was observed in spring, summer, and fall ~~at LRK. Average IEPOX-OA~~seasons with average concentrations ~~was~~of 1.~~35~~4 μg m^{-3}, 2.1 μg m^{-3}, and 0.8 μg m^{-3} in spring ~~and 2.13 μg m^{-3} in,~~ summer, and fall, respectively, contributing ~~41% and 40~~on average 36% of total OA mass~~, respectively. Decrease~~. The drastic decrease of IEPOX-OA concentration ~~in fall season~~from summer to fall at LRK (Fig. 7) could be attributed to the drop of ambient temperature that might affect SOA formation (Worton et al., 2013). Also, significant IEPOX-OA drop is consistent with loss of tree foliage as a major source of isoprene emission~~. Additionally,~~, which is supported by missing of IEPOX-OA ~~was not observed~~ during winter ~~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~~factor was observed during spring, summer, and fall at LRK in 2013. Seasonal average concentrations of 91Fac were 0.68 μg m^{-3} (21%) in spring, 1.25 μg m^{-3} (23%) in summer, and 0.25 μg m^{-3} (9%) in fall. Further discussion about the possible source(s) of 91Fac is presented in section 4.2. Decrease of 91Fac factor from summer to fall

(Fig. 7) coincided with decrease total OA and IEPOX-OA factor, possibly suggesting a similar biogenic source.

4 Discussion

4.1 IEPOX-OA Factor: Fragment Ion Contributions

The IEPOX-OA component has been observed in chamber experiments and field OA (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 $C_3H_7O_2^+$), (Lin et al., 2012). The ion fragment at *m/z* 100 (mostly $C_5H_8O_2^+$) 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~~101 (possibly $C_5H_9O_2^+$). Temporal variation of the *m/z* 82 fragment ion associated with LV-OOA, IEPOX-OA, and 91Fac (Fig. ~~S27~~S26) 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~~During fall the LV-OOA factor becomes a significant contributor to *m/z* 82 at LRK, which might be due to influence of aged IEPOX-OA. Further studies, however, will be needed to examine effects of atmospheric oxidation in IEPOX-OA and LV-OOA mass spectra. The IEPOX-OA mass spectra fragment ions at *m/z* 82 show weak and strong linear relationships with *m/z* 53 and *m/z* 75, respectively and no correlation with *m/z* 100 (Fig. 9). Fractional contribution of ions at 75 (f_{75}) versus the contribution of the ion at *m/z* 82 (f_{82}) to IEPOX-OA mass spectra show a strong linear relationship ($r^2 = 0.95$, slope = 0.49±0.06) over different locations and seasons, while f_{53} and f_{82} were moderately correlated ($r^2 = 0.48$). 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) gave a quite prominent ion at *m/z* 101 rather than *m/z* 100. The scatterplots of f_{101} and f_{100} against f_{82} do not show a linear relationship ($r^2 < 0.1$), perhaps as a consequence of the low intensity of 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, this study presents some insights of role of the *m/z* 82 fragment ion over different seasons in southeastern U.S. Observation of the *m/z* 75 fragment ion variation over different seasons indicates its potential as a 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.

4.2 Insights into 91Fac OA Formation

~~Studies~~Laboratory and field studies have reported significant signal of an *m/z* 91 fragment ion 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 using ToF-AMS, and proposed $C_3H_7O_3^+$ formula for this ion as a tracer for peroxide under low-NO$_x$ condition. ~~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~~is not ~~influence 91Fac formation~~ correlated (r^2 ~0) with *m/z* 91 of 91Fac during spring and summer, suggesting that at LRK site the factor is not influenced by NO_x (Fig. ~~S28). On the other hand, a weak correlation (r^2 =~~S27). Correlation values of 0.14 and 0.2~~)~~ were found between *m/z* 91 ion of 91Fac and *m/z* 82 ion of IEPOX-OA factor ~~might~~ during spring and summer, respectively. Since IEPOX-OA is associated with isoprene-derived SOA, the weak correlations indicate that biogenic source(s) ~~contributed~~ — not necessarily isoprene — might contribute to 91Fac formation in densely forested ~~area~~areas like at the 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). Correlations between 91Fac and SOA tracers from isoprene ozonolysis and monoterpene chemistry are on average 0.4 and 0.3 (Table 3), respectively. These suggest higher potential contributions of isoprene chemistry through a non-IEPOX pathway over monoterpene chemistry in 91Fac formation. Photooxidation of isoprene hydroxy hydroperoxide (ISOPOOH) under low-NO_x conditions was recently shown to yield the formation of low-volatility hydroperoxide compounds (St. Clair et al., 2015), leading to the production of non-IEPOX SOA in chamber and field studies (Krechmer et al., 2015). ~~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~~Further investigations of peroxide contributions to formation of 91Fac could not be performed in this study because the 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 yet known (St. Clair et al., 2015, Krechmer et al., 2015). This should be ~~investigated in this study.~~

a focus of future work. 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~~weak correlations of 91Fac with monoterpene SOA tracers ~~suggest~~ (r^2 = 0.3, Table 3) might indicate that multiple sources could contribute to ~~its~~the formation of 91Fac. Laboratory studies found that combined isoprene-, α-pinene-, and β-caryophyllene-derived SOA mass (Chen et al., 2015) as well as β-pinene+NO_3 SOA mass spectra (Boyd et al., 2015) produced an intense signal at *m/z* 91 associated with $C_7H_7^+$. Due to limitation in unit mass resolution of ACSM measurements, we could not identify composition of *m/z* 91 fragment ion. Thus, contributions of $C_7H_7^+$ and $C_3H_7O_3^+$ 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.~~

5 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% of total NR-PM$_1$ at LRK and 65–

75% of total NR-PM$_1$ at JST. Sulfate is the most abundant inorganic species throughout the year, accounting for 20–30% and 10–20% of total NR-PM$_1$ 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, season, and year. HOA and SV-OOA were resolved only at JST that represent urban OA. BBOA, LV-OOA, and IEPOX-OA~~, and 91Fac~~ were resolved from both sites during different seasons~~.~~, while 91Fac was resolved only from LRK site during warmer seasons. HOA contributions to total OA mass were fairly consistent ~~(15–25%)~~(~21% of total OA) over four seasons, and its contribution peaked during winter. SV-OOA was observed only during colder seasons, having a consistent ~~seasonal~~ contribution of 27~~%.~~% of total OA. BBOA was ~~only~~ observed during winter and fall seasons~~, and on average contributed ~17% to the total OA mass~~ at JST and only during winter at LRK, with ~~the higher~~highest contribution of ~~BBOA at LRK.~~33% of total OA observed during winter at LRK site and on average 17% of total OA at JST site. The higher contribution of BBOA at LRK was likely due to a single, significant burning event, whereas contribution at JST is more consistent between winter and fall.

Average IEPOX-OA contributions during warmer seasons were ~~40~~~38% and ~~35%~~~41% of total OA at ~~the rural~~JST and ~~urban~~LRK 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 ~22% of total OA at LRK site over spring and summer. 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.

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Table 1. Seasonal classification ~~period~~ of measurements at JST and LRK is based on direction of angle of the Earth to the sun and the angle of the sunlight as it hits the Earth.

	JST	LRK
Winter	22/12/2011 – 19/03/2012	18/01/2013 – 19/03/2013
Spring	20/03/2012 – 19/06/2012	20/03/2013 – 31/05/2013
Summer	20/06/2012 – 21/09/2012	01/06/2013 – 21/09/2013*
Fall	22/~~19~~09/2012 – 20/12/2012	22/09/2013 – 20/12/2013

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

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Table 2. Seasonal averaged mass concentrations of non-refractory PM_1 ($NR\text{-}PM_1$) 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.

	Winter		**Spring**		**Summer**		**Fall**	
	JST	LRK	JST	LRK	JST	LRK	JST	LRK
$NRPM_1$	10.50±7.32	4.77±3.32	6.19±2.85	5.59±3.47	8.78±4.46	8.39±4.44	12.47±6.72	4.55±2.55
OA	69.0%	50.2%	75.9%	57.8%	70.0%	63.4%	65.9%	62.1%
SO_4^{2-}	13.4%	30.6%	12.0%	26.9%	17.4%	24.5%	15.8%	21.6%
NO_3^-	9.3%	9.2%	5.6%	6.1%	4.5%	3.8%	9.3%	7.2%
NH_4^+	7.9%	9.9%	6.3%	9.0%	7.9%	8.2%	8.6%	9.1%
Cl^-	0.3%	0.1%	0.2%	0.1%	0.1%	0.1%	0.3%	0.0%
				OA speciation				
HOA	24%	*n.a.*	20%	*n.a.*	18%	*n.a.*	20%	*n.a.*
BBOA	19%	33%	*n.a.*	*n.a.*	*n.a.*	*n.a.*	15%	*n.a.*
SV-OOA	26%	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	28%	*n.a.*
LVOOA	30%	66%	43%	37%	44%	36%	37%	63%
91Fac	*n.a.*	*n.a.*	n.a.	21%	n.a.	23%	*n.a.*	9%
IEPOX-OA	*n.a.*	*n.a.*	37%	41%	38%	40%	*n.a.*	27%
Residuals	1%	1%	0%	1%	0%	1%	0%	1%

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.

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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~~been published in Budisulistiorini et al. (2015)

	IEPOX-OA	LV-OOA	91Fac	Ref.
Monoterpene SOA tracers				
$C_{10}H_{18}O_5S$	0.28	0.26	0.39	(1)
$C_{10}H_{16}O_7S^a$	0.42	0.26	0.37	(1)
$C_{10}H_{17}NO_7S$	0.00	0.00	0.01	(1)
$C_9H_{15}NO_8S^a$	0.12	0.22	0.22	(1)
$C_{10}H_{17}NO_{10}S$	0.11	0.15	0.26	(1)
$C_8H_{12}O_4$ (Terpenylic acid)^a	0.32	0.36	0.41	(2)
$C_9H_{14}O_4$ (Pinic acid)	0.12	0.21	0.19	
$C_{10}H_{16}O_4$ (Hydroxy pinonic acid)	0.15	0.21	0.25	
$C_{10}H_{16}O_3$ (Pinonic acid)	0.10	0.17	0.20	
$C_7H_{10}O_4$ (Terebic acid)	0.21	0.32	0.27	(3)
$C_8H_{12}O_6$ (MBTCA)	0.15	0.27	0.14	(4)
$C_{10}H_{16}O_6$ (DTAA)	0.35	0.42	0.42	(2)
***Isoprene ozonolysis tracers**^{b}*				
$C_4H_8O_6S$	0.46	0.40	0.51	(5,6)
$C_5H_{12}O_6S$	0.39	0.19	0.35	(5,6)
$C_5H_{10}O_5S$	0.19	0.19	0.22	(6)
$C_5H_{10}O_6S$	0.33	0.38	0.41	(6)
$C_8H_{10}O_4S$	0.00	0.07	0.03	(6)
$C_6H_{12}O_7S$	0.24	0.33	0.48	(6)
$C_9H_{14}O_6S$	0.21	0.30	0.38	(6)
$C_9H_{16}O_7S$	0.38	0.50	0.46	(6)
$C_{10}H_{20}O_9S$	0.36	0.29	0.39	(6)

~~^{a}Budisulistiorini~~^{a}Published in Budisulistiorini et al. (2015). ^{b}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~~. (2015)~~. (2015)

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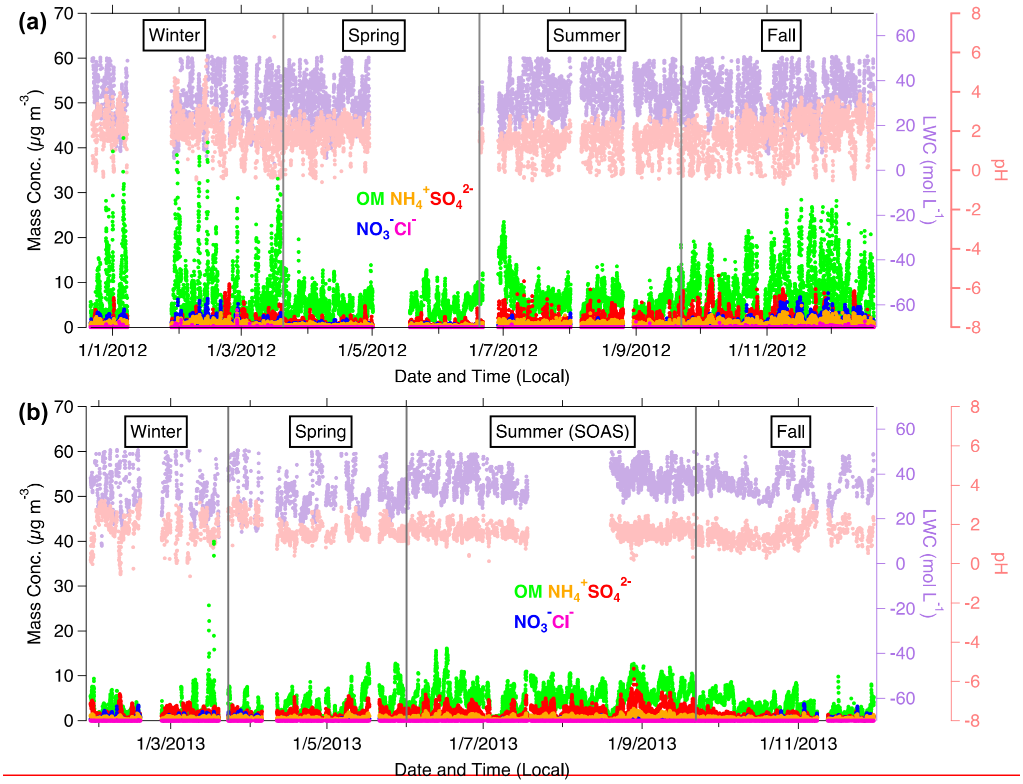
(a)
Winter
Spring
Summer
Fall
Mass Conc. (μg m^{-3})
LWC (mol L^{-1})
pH
OM NH$_4^+$ SO$_4^{2-}$
NO$_3^-$ Cl$^-$
0
10
20
30
40
50
60
70
-60
-40
-20
0
20
40
60
-8
-6
-4
-2
0
2
4
6
8
1/1/2012
1/3/2012
1/5/2012
1/7/2012
1/9/2012
1/11/2012
Date and Time (Local)
(b)
Winter
Spring
Summer (SOAS)
Fall
Mass Conc. (μg m^{-3})
LWC (mol L^{-1})
pH
OM NH$_4^+$ SO$_4^{2-}$
NO$_3^-$ Cl$^-$
1/3/2013
1/5/2013
1/7/2013
1/9/2013
1/11/2013
Date and Time (Local)

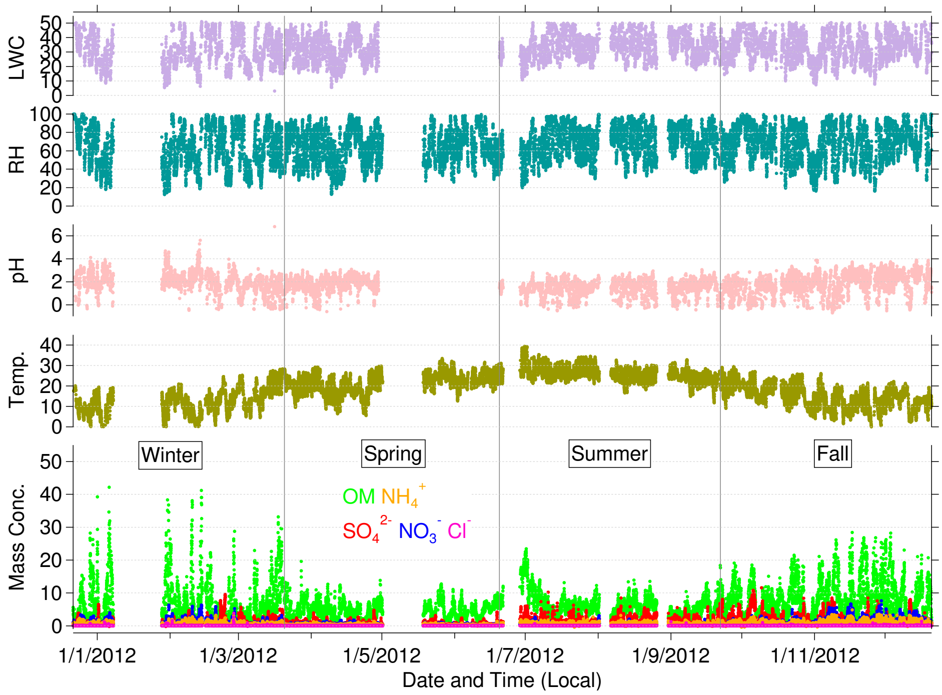
LWC
0
10
20
30
40
50
RH
0
20
40
60
80
100
pH
0
2
4
6
Temp.
0
10
20
30
40
Mass Conc.
0
10
20
30
40
50
Winter
Spring
Summer
Fall
OM NH$_4^+$
SO$_4^{2-}$ NO$_3^-$ Cl$^-$
1/1/2012
1/3/2012
1/5/2012
1/7/2012
1/9/2012
1/11/2012
Date and Time (Local)

Figure 1. Annual temporal variations of OA and inorganic species (µg m^{-3}) measured at the ~~(a)~~ Jefferson street (JST) site, Atlanta, Georgia in 2012~~; and (b) LRK site in 2013.~~ . Included in the plots are ambient temperature (°C) and relative humidity (RH, in %) measured by SEARCH network, as well as pH and liquid water content (LWC, in mol L^{-1}) estimated by ISORROPIA-II.

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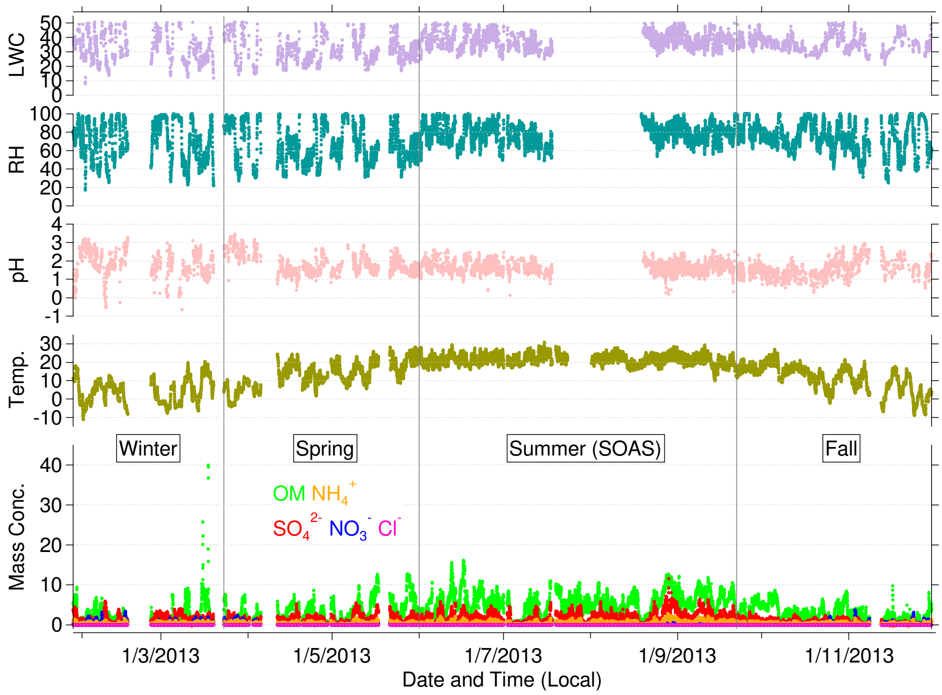


Figure 2. Annual temporal variations of OA and inorganic species (µg m^{-3}) measured at the Look Rock (LRK) site, Great Smoky Mountains, Tennessee in 2013. Included in the plots are ambient temperature and RH (%) measured by Tennessee Valley Authority (TVA), as well as pH and LWC (mol L^{-1}) estimated by ISORROPIA-II.

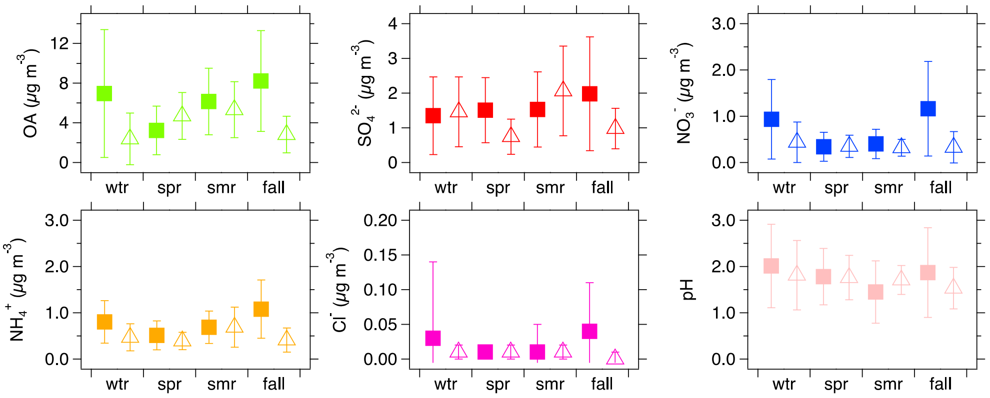
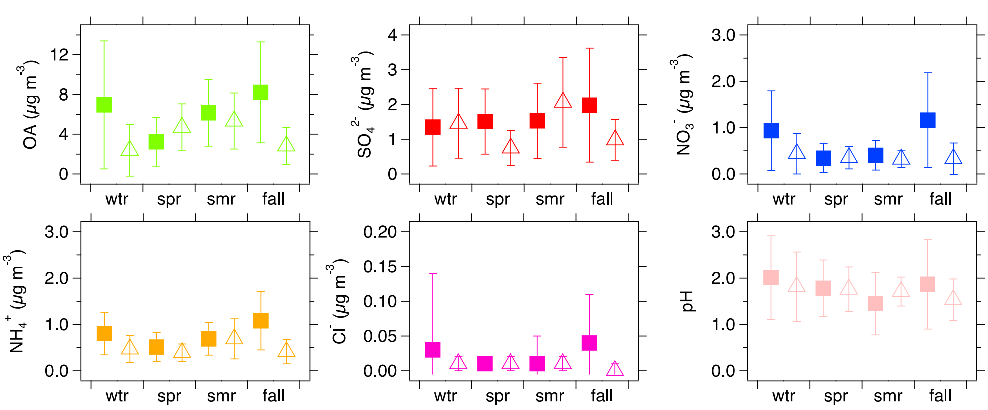

OA (μg m^{-3})
0
4
8
12
SO_4^{2-} (μg m^{-3})
0
1
2
3
4
NO_3^- (μg m^{-3})
0.0
1.0
2.0
3.0
NH_4^+ (μg m^{-3})
0.0
1.0
2.0
3.0
Cl^- (μg m^{-3})
0.00
0.05
0.10
0.15
0.20
pH
0.0
1.0
2.0
3.0
wtr
spr
smr
fall

Figure 3.



Seasonal averages~~**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.

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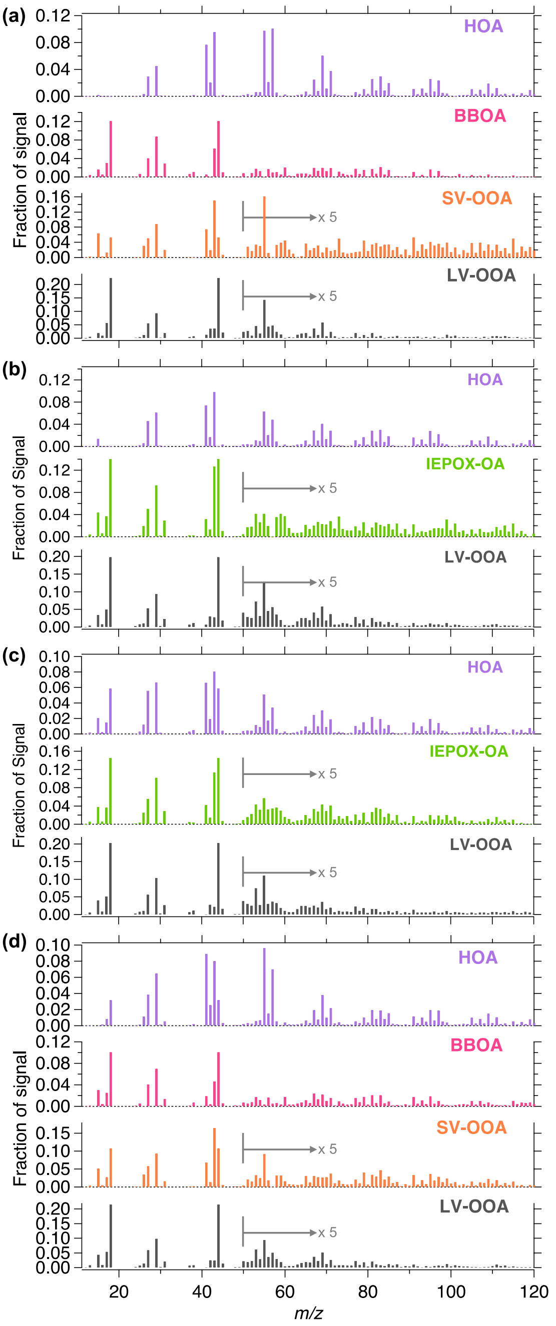
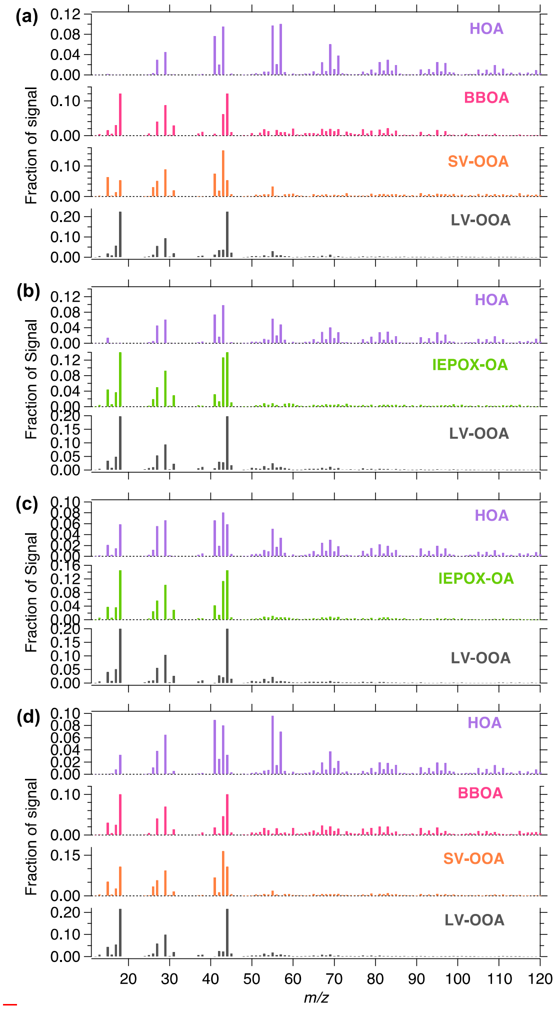

(a)
HOA
BBOA
SV-OOA
LV-OOA
Fraction of signal
(b)
HOA
IEPOX-OA
LV-OOA
Fraction of Signal
(c)
HOA
IEPOX-OA
LV-OOA
Fraction of Signal
(d)
HOA
BBOA
SV-OOA
LV-OOA
Fraction of signal
x 5
0.00
0.04
0.08
0.12
0.16
0.05
0.10
0.15
0.20
20
40
60
80
100
120
m/z



~~**Figure 3.**~~ ~~Mass spectra of PMF factors resolved from (a) winter, (b) spring, (c) summer, and (d) fall OA measurements at JST in 2012.~~

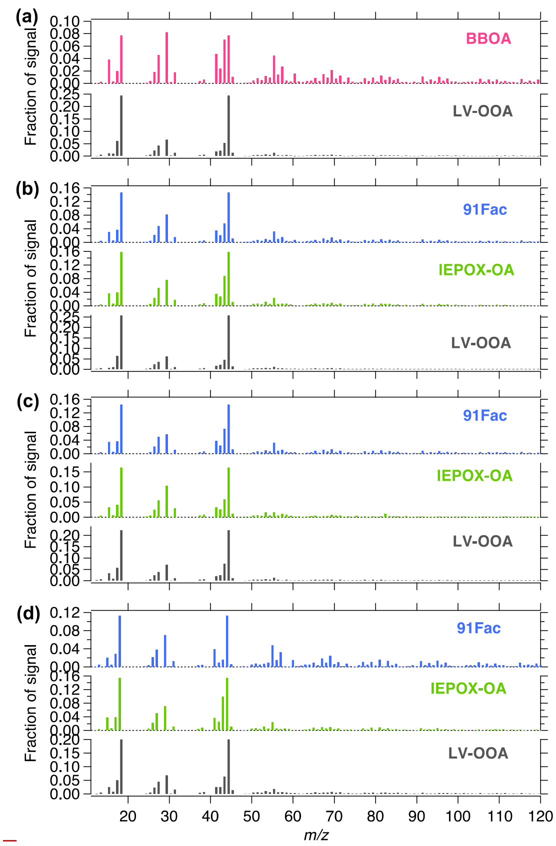
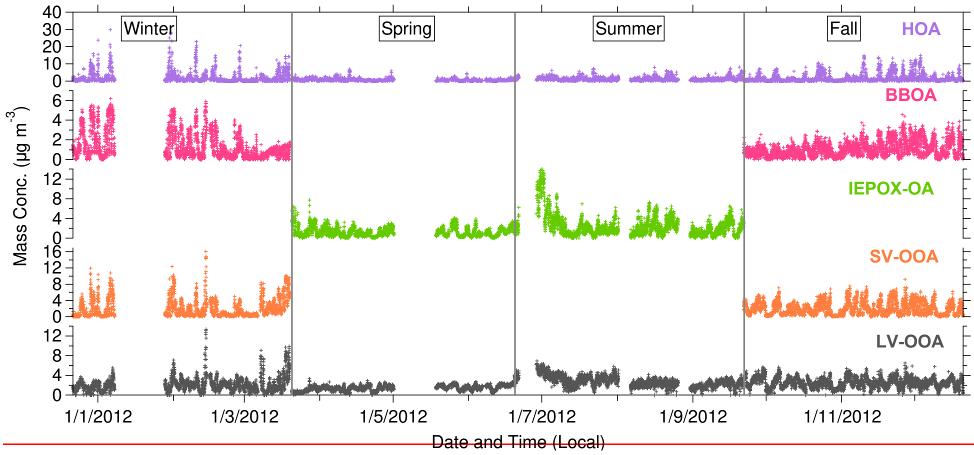


Figure 4. Mass spectra of PMF factors resolved from (a) winter, (b) spring, (c) summer, and (d) fall OA ~~measurements~~measured at ~~LRK~~JST in ~~2013~~2012.


Winter
Spring
Summer
Fall
HOA
BBOA
IEPOX-OA
SV-OOA
LV-OOA
Mass Conc. (µg m-3)
40
30
20
10
0
6
4
2
0
12
8
4
0
16
12
8
4
0
12
8
4
0
1/1/2012
1/3/2012
1/5/2012
1/7/2012
1/9/2012
1/11/2012
Date and Time (Local)

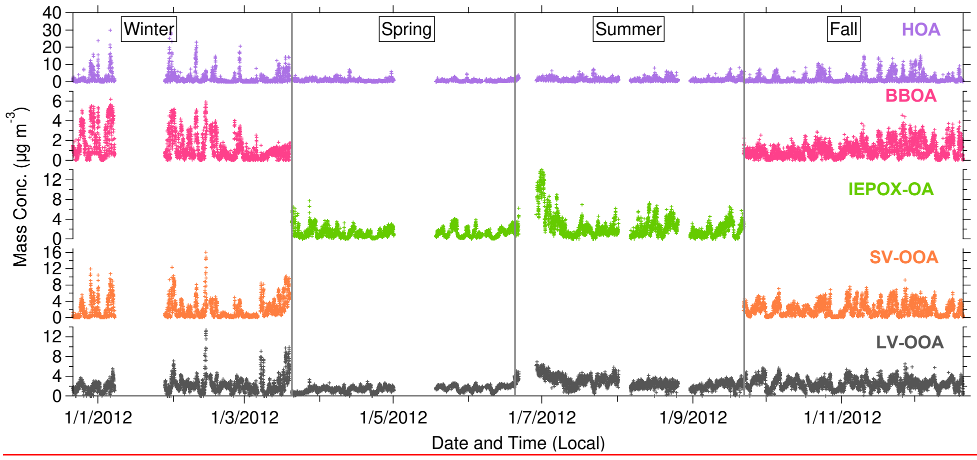
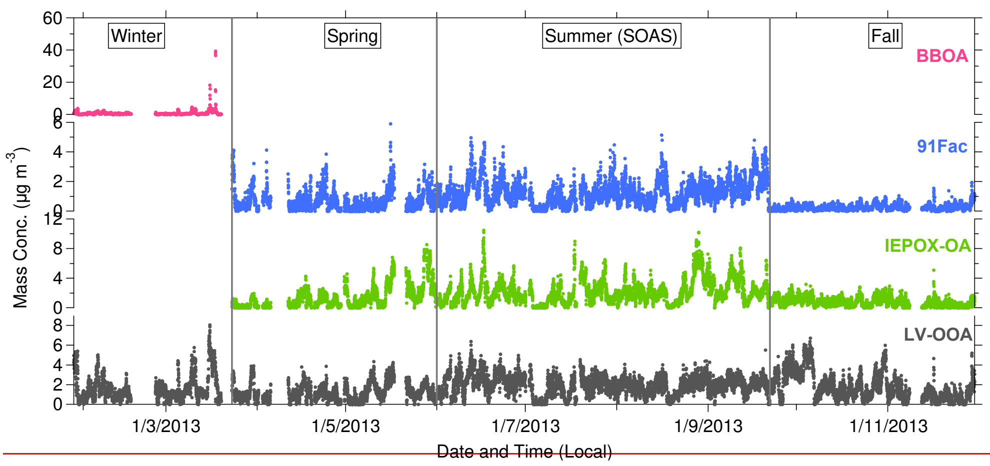


Figure 5. Annual temporal variation of PMF factors resolved from OA ~~measurements~~measured at ~~the~~ JST ~~site during~~in 2012.


Winter
Spring
Summer (SOAS)
Fall
BBOA
91Fac
IEPOX-OA
LV-OOA
60
40
20
0
6
4
2
0
12
8
4
0
8
6
4
2
0
Mass Conc. (µg m^{-3})
1/3/2013
1/5/2013
1/7/2013
1/9/2013
1/11/2013
Date and Time (Local)

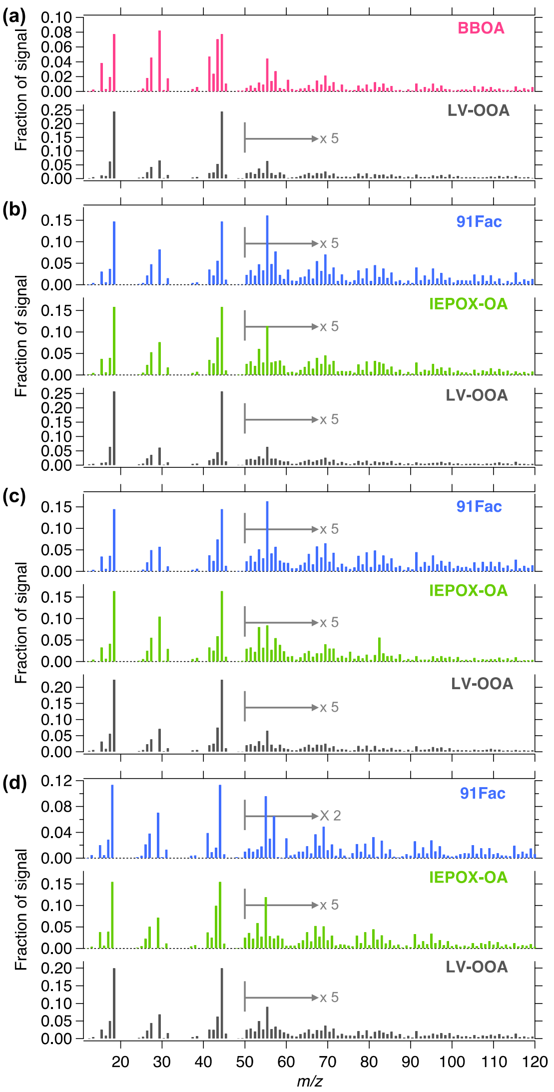


Figure 6. Mass spectra of PMF factors resolved from (a) winter, (b) spring, (c) summer, and (d) fall OA measured at LRK in 2013.

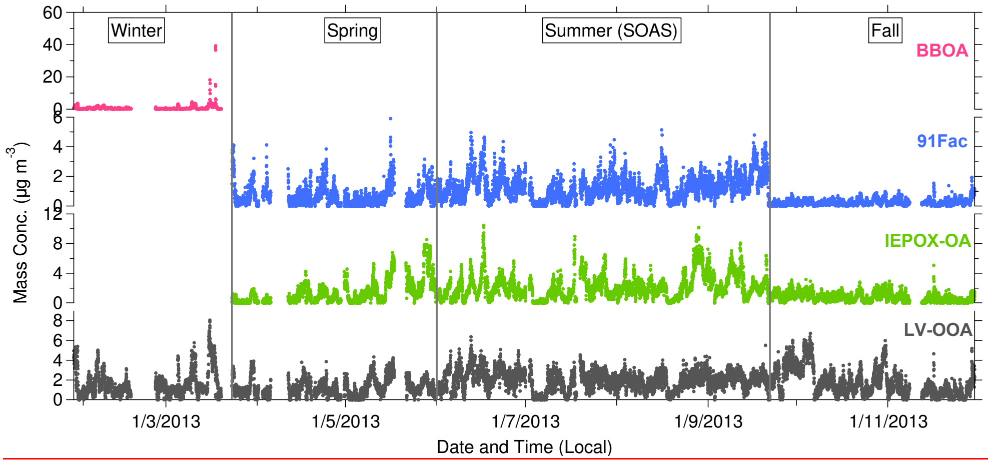


Figure 6. Annual temporal variation of PMF factors resolved from OA measured at LRK in 2013. OA measurements ~~at the LRK site during 2013. Measurements~~ in the summer ~~coincided with~~included results from Southern Oxidant Aerosol Study (SOAS) campaign that ~~results~~ have been published in Budisulistiorini et al. (2015).

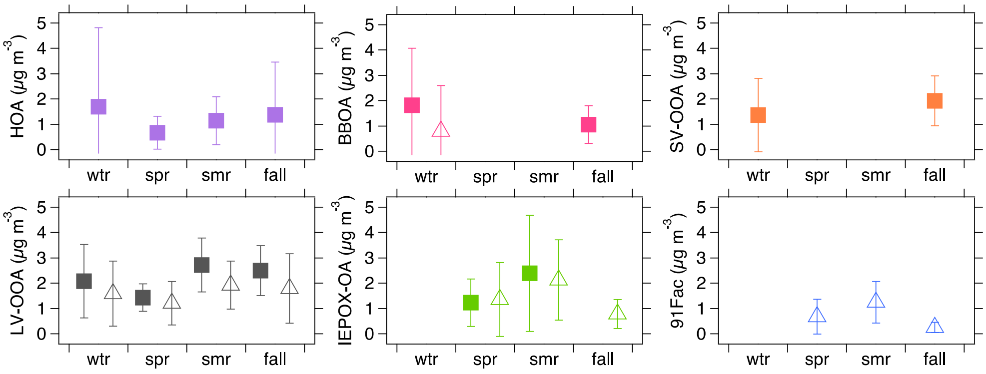
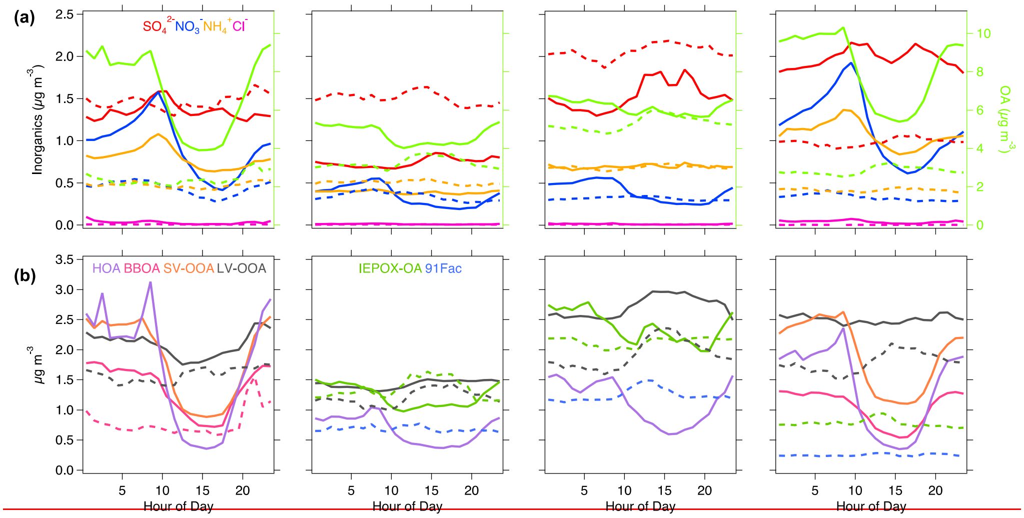


Figure ~~7~~8. Seasonal average mass ~~concentration~~concentrations of PMF factors resolved from JST (solid squares) and LRK (open triangles). Error bars are shown as ± 1-standard deviation.



~~**Figure 8.**~~

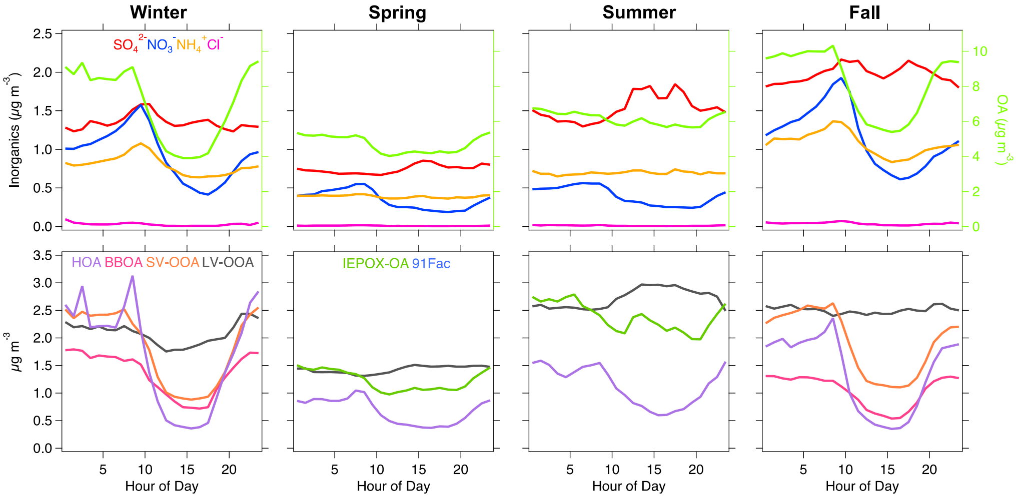


Figure 9. Diurnal variations of ~~(a)~~ OA and inorganic species measured by ACSM (upper panel) and ~~(b)~~ OA factors resolved by PMF analysis (lower panel) from winter, spring, summer, and fall measurements at ~~the~~ JST ~~site (solid lines)~~in 2012.

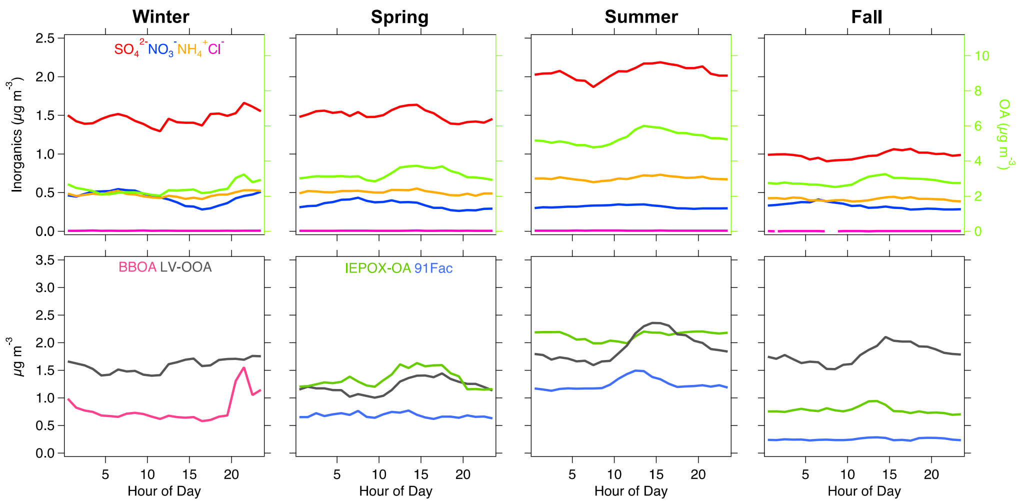
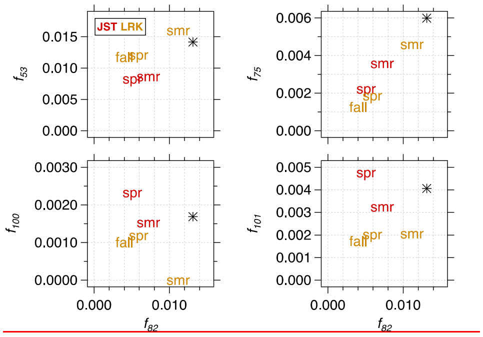


Figure 10. Diurnal variations of OA and inorganic species measured by ACSM (upper panel) and OA factors resolved by PMF analysis (lower panel) from winter, spring, summer, and fall measurements at LRK ~~site (dash lines).~~ in 2013.


JST LRK
smr
fall
spr
spr
smr
0.015
0.010
0.005
0.000
f_{53}
0.006
0.004
0.002
0.000
f_{75}
0.0030
0.0020
0.0010
0.0000
f_{100}
0.005
0.004
0.003
0.002
0.001
0.000
f_{101}
0.000
0.010
f_{82}
0.000
0.010
f_{82}

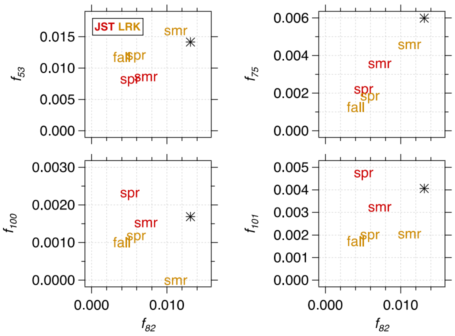


Figure 11.~~**Figure 9.**~~ Scatterplots of the *m/z* 53 (possibly $C_4H_5^+$), *m/z* 75 (possibly $C_3H_7O_2^+$), m/z 100 (possibly $C_5H_8O_2^+$) and *m/z* 101 (possibly $C_5H_9O_2^+$) normalized fragment ions from the IEPOX-OA mass spectra versus the *m/z* 82 normalized fragment ion from the same 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).