Anonymous Referee #3
Received and published: 6 November 2015
This manuscript reports the real-time characterization of non-refractory submicron aerosol in an urban and rural site in SE USA using the ACSM. Source apportionments of the organic aerosol were made at each site during different seasons. The results presented in this manuscript fall within the scope of this journal, but major revisions need to be made before this manuscript can be accepted.

General comments:

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

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

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

Specific comments:

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

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

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

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

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

	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	22/19/2012 – 20/12/2012	22/09/2013 – 20/12/2013

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

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

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

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

Pg 22387 line 16: Do you mean Eq. (1) in Budisulistiorini et al. (2015)?

Yes, it is Eq. 1 in Budisulistiorini et al. (2015). We revised the text accordingly.

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

We added the information as suggested.

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

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

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

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

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

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

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

Pg 22390 line 21: r2 = 0.2-0.5 is a low correlation, not moderate. Also, the authors need to specify in the manuscript what they mean by moderate and high correlation.

We have addressed similar question from Referee #2.

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

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

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

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

We moved this sentence before discussion of PMF factors.

Pg 22397 line 22: I do not agree with the authors' suggestion that m/z 75 can be used as a marker ion for IEPOX-OA. This mass peak does not appear to be significant in the IEPOX-OA mass spectra shown by the authors (in Fig. 2) and Budisulistiorini et al. (2013).

The ion fragment at m/z 75 along with *m/z* 53, 82, and 100 were recommended by Lin et al. (2012) to aid in identification of IEPOX SOA of PMF analysis. Here, we examined contribution of those ions to IEPOX-OA factor over different seasons and sites. The *m/z* 75 might not be prominent ion in the mass spectra; however, its time trend is well correlated with *m/z* 82. Therefore, m/z 75 and 82 could be used to identify of IEPOX-OA factor, which is consistent to the Lin et al. (2012) recommendation.

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

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

"The moderate correlations with isoprene ozonolysis and photooxidation tracers suggest that 91Fac could be related to isoprene chemistry but not specifically related to the IEPOX pathway. However, the fair correlations of 91Fac with monoterpene SOA tracers suggest multiple sources could contribute to its formation. Laboratory studies found that combined isoprene-, α-pinene-, and β-caryophyllene-derived SOA mass (Chen et al., 2015) as well as β-pinene+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."

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

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

References

Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I., and Ng, N. L.: Secondary organic aerosol formation from the β-pinene+NO3 system: effect of humidity and peroxy radical fate, Atmos. Chem. Phys., 15, 7497–7522, 2015

Budisulistiorini, S. H., Canagaratna, M. R., Croteau, P. L., Marth, W. J., Baumann, K., Edgerton, E. S., Shaw, S. L., Knipping, E. M., Worsnop, D. R., Jayne, J. T., Gold, A., and Surratt, J. D.: Real-time continuous characterization of secondary organic aerosol derived from isoprene epoxydiols in downtown

Atlanta, Georgia, using the Aerodyne aerosol chemical speciation monitor, Environ. Sci. Technol., 47, 5686- 5694, 2013
Budisulistiorini, S. H., Li, X., Bairai, S. T., Renfro, J., Liu, Y., Liu, Y. J., McKinney, K. A., Martin, S. T., McNeill, V. F., Pye, H. O. T., Nenes, A., Neff, M. E., Stone, E. A., Mueller, S., Knote, C., Shaw, S. L., Zhang, Z., Gold, A., and Surratt, J. D.: Examining the effects of anthropogenic emissions on isoprene-derived secondary organic aerosol formation during the 5 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee, ground site, Atmos. Chem. Phys. 15, 8871-8888, 2015
Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite Jr., J. R., Carlton, A. G., Lee, S.-H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211–5228, 2015
Henry, K. M. and Donahue, N. M.: Photochemical Aging of α-Pinene Secondary Organic Aerosol: Effects of OH Radical Sources and Photolysis, J. Phys. Chem. A, 116, 5932–5940, 2012
Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical Composition of Secondary Organic Aerosol Formed from the Photooxidation of Isoprene, J. Phys. Chem. A, 110, 9665–9690, 2006
Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S.-H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, Proc. Natl. Acad. Sci., 112, 37–42, 2015