Reviewer 1

We would like to thank for the reviewer for their valuable comments.

General: This article covers measurements of a biomass burning plume sampled in Toronto using a state-of-the-art LS-SP-AMS, ATOFMS and a variety of other instrumentation. There are a few things that can use highlighting, discussion and clarification and I outline those items below. The experimental section is well-written and referenced. References to an unpublished paper (Willis et al 2015) covering details of an AMS factor analysis make it difficult for me to interpret the factor analysis results presented here. I therefore suggest that the authors present an overview of the PMF results in the supplementary section. The authors can do a better job of stating a clear hypothesis – it is stated that the primary goal of this paper is to examine the mixing state of K, rBC, and BBOA – but why exactly? Also, the quantitative capabilities of the AMS measurement can use some more discussion. With a stated mass resolution of 2000 is it really possible to reliably quantify K mixing state? I know that O:C ratios are potentially quantified with AMS, is that possible here? The strengths of this paper include tying the properties of the different particle types to optical properties and volatility. Overall the paper is interesting and is worthy of publication in ACP and I commend the authors for a solid piece of work.

Response: Please see our response to these scientific comments below.

Specific:

Abstract: it would be nice to have more background about the potential sources of the BBOA given that these appear to be field measurements. There is no mention of the geographic region in the abstract. What sort of biomass burning plume is this? Is it representative of biomass burning plumes worldwide?

Response: The abstract has been modified accordingly as shown below:

"Biomass burning organic aerosol (BBOA) can be emitted from natural forest fires and human activities such as agricultural burning and domestic energy generation …… In this work, single particle measurements from a soot-particle aerosol mass spectrometer coupled with a light scattering module (LS-SP-AMS) were performed to examine the mixing state of BBOA, refractory black carbon (rBC) and potassium (K$^+$, a tracer for biomass burning aerosol) in an air mass influenced by wildfire emissions transported from Northern Quebec to Toronto, representing aged biomass burning plumes…"

P. 32160, around line 10: There should be a better stated hypothesis here. Why is it so important to determine the mixing state of K and BBOA? What does it mean to optical and hygroscopic properties if they are internally or externally mixed?

Response: A few sentences have been added to the Introduction of the revised manuscript as shown below:

"…Potassium (K) is abundant in biomass burning plumes and can be used as a tracer of biomass burning aerosol particles. Potassium salts such as KCl, KNO_3 and K_2SO_4 are hygroscopic in nature, and hence the mixing states of potassium salts, BC and BBOA may affect the cloud formation ability and light scattering of individual biomass burning particles. Furthermore, the mixing state of biomass burning aerosol particles can be potentially used as a tracer of different types of burning. Internal mixtures of organic, BC and potassium salts have been observed in biomass burning aerosol to different extents using electron microscopy techniques (Li et al. 2003)…."

P. 32160, lines 14-16: Awkward sentence

Response: This sentence has been revised as shown below.

"The primary objective of this study is to investigate the mixing state of potassium, rBC and organic aerosol in aged biomass burning particles, which in this case originated from wildfire emissions transported from Northern Quebec to Toronto, Ontario."

P. 32160, lines 16-19: Awkward sentence

Response: This sentence has been revised as shown below.

"We use single particle measurements to provide chemical insight into the volatility and optical properties of biomass burning particles observed in this study."

P. 32163, line 16-21: It is stated that the PMF results will not be discussed here because they are discussed in Willis et al 2015. However, Willis et al 2015 is in review. This leaves me to conclude that the relevance of these results are dependent on how another paper is peer reviewed. I suggest that the authors work with Willis et al to provide a summary of the PMF analysis in the supplementary section of this paper. I have questions about other factors obtained via PMF (see below) and the reference of Willis et al is useless to me at this point.

Response: In addition to the reference to our previous work, some detail of PMF analysis has been added to Section 2.2 of the revised version (see below). Furthermore, time series and mass spectra of four factor solutions are presented in Figures S1 and S2. Note that Willis et al. (2015) has been accepted for publication in Atmospheric Chemistry and Physics, and that the final version will be published in the near future.

"In brief, the bilinear model was solved using the PMF2 algorithm in robust mode (Paatero and Tapper, 1994) and a final solution was selected using the PMF Evaluation Tool (PET) version 2.06 according to the method described by Ulbrich et al. (2009) and Zhang et al. (2011). A four-factor solution was selected by examining the solutions for up to eight PMF factors. Two factors allowed the separation of local/fresh traffic emissions from more aged/transported aerosol. Three

factors allowed the separation of BBOA from a background oxygenated organic aerosol (OOA). Increasing the number of factors from three to four allowed for the separation of local/fresh traffic emissions into HOA-rich and rBC-rich factors. Moving beyond four factors, splitting and/or mixing of BBOA and background OOA factors became evident, so solutions with more than four factors were not considered. Time series and mass spectra of the four-factor solution are presented in Figures S1 and S2."

P. 32165, line 16: Were the K+ and Org_rBC distributions obtained using the same instrument?

Response: Both K^+ and Org_{rBC} size distributions were measured by LS-SP-AMS. The manuscript has been revised to avoid potential confusion.

P. 32166, lines 1-4: Was this calculated only for rBC containing particles? This is confusing - I suggest the authors give more detail on this calculation and its interpretation in the supplementary section. It is confusing because the authors are invoking spherical morphology while using effective densities for fractal soot.

Response: The calculation is only for rBC-containing particles. The calculation is only for rBC-containing particles. Our instrument detected rBC-containing particles exclusively because the tungsten vaporizer was removed. Even though spherical particle morphology is assumed in the calculation, different effective densities of rBC are used to simulate the effect of the fractal structure of ambient rBC on the coating thickness (i.e. rBC core with different porosity). The above information has been added or clarified in the revised version of manuscript as shown below. In addition, Figure S4 (Figure S1 in the original version) has been updated to show the calculation results by assuming rBC effective densities of 0.3, 0.8 and 1.4 g/cm^3. The coating thickness is relatively insensitive to variations in the effective density of rBC core.

"Since a resistively heated tungsten vaporizer was removed from our LS-SP-AMS, only rBC and its coating materials were detected in this study. Assuming a core-shell structure, a spherical rBC core, a uniform thickness of coating, and a BBOA density of 1.3 g/cm^3, the single particle measurements can be used to calculate the coating thickness of the rBC core. To simulate the effect of the fractal structure of ambient rBC, the effective density of rBC was varied between 0.3 and 1.4 g/cm^3 (i.e., rBC core with different porosity). Figure S4 presents the two-dimensional histograms (mf_{rBC} vs. particle aerodynamic diameter, d_{va}) of BBOA particles identified by cluster analysis, with calculated coating thickness curves overlaid for comparison. For example, a 320 nm BBOA particle (i.e., d_{va} ~ 400 nm, assuming the effective densities of a porous rBC core and BBOA materials are 0.8 and 1.3 g/cm^3, respectively) that consists of 5% of rBC by mass would have a BC core of radius ~68 nm covered by ~92 nm of BBOA material. The coating thickness is relatively insensitive to variations in the effective density of rBC core (Figure S4)."

P. 32166, line 9-14: One should not need to solely rely on cluster analysis to tease out trends of HOA type aerosol. For example, the time series for hydrocarbon like OC marker peaks can be plotted. Does such a time series give the typical HOA temporal signature? Also, only the BBOA

factor from the PMF analysis is shown. Was the PMF analysis able to extract an HOA factor? This would be a salient point of discussion.

Response: The PMF results have been added (Section 2.2 and Figures S1 and S2) to illustrate the presence of HOA in this study. It can be found that the PMF analysis for the wider sampling period (i.e., May 31-June 17, 2015) gives two factors (HOA-rich and rBC-rich factors) that are related to local/fresh traffic emissions. Furthermore, cluster analysis that covered a wider range of the sampling period (i.e., May 31-June 17, 2015) in the same field study could identify a HOA-rich particle class as reported in our previous work (Willis et al., 2015). However, most HOA-rich and rBC-rich particles were not detected in the single particle mode possibly due to their small particle size (i.e., smaller than the cut off size of light scattering detection). The above information has been added to Section 3.2 of the revised manuscript.

"A particle class associated with a high mass fraction of hydrocarbon-like organic aerosol materials (HOA-rich particle class reported in Lee et al. (2015)) was not identified. Given that HOA-rich particles were clearly observed during the BB period based on the PMF results (Section 2.2 and Figures S1 and S2), it is possible that the single particle measurement of LS-SP-AMS actually detected a small number of HOA-rich particles during the BB period but cluster analysis could not separate them from the more dominant BBOA particle classes due to similar mass spectral characteristics. It is also important to note that cluster analysis over a wider range of the sampling period (i.e., May 31-June 17, 2015) in the same field study could identify HOA-rich particle class as reported in our previous work (Willis et al., 2015)."

P. 32166, Line 15: what do the percentages correspond to? Number % or mass % of particle type? Mass % of sulfate?

Response: The percentages correspond to Number %. This information has been added to the text and Table 1.

P. 32166, line 27: How was the potassium deconvoluted from the organics here? Was there enough resolution to distinguish between K and organic fragments? I think that some detail on this would be important for the interpretation of K in some of the other BBOA clusters where K may not be as abundant (but still present). If the authors could provide an example of a deconvolution of K peaks from organic peaks this would provide strong evidence of the quantitative capabilities for the technique.

Response: Cluster analysis was performed using unit mass resolution (UMR) mass spectra, and thus the relative contributions of K^+ and organic fragments to m/z 39 cannot be distinguished. Nevertheless, organic fragment (i.e. $C_3H_3^+$) at m/z 39 only gives a small contribution to the mass spectra of PMF-BBOA factor determined by the high resolution ensemble measurements, suggesting that most ion signal of m/z 39 observed in the BBOA-K particle type is due to the presence of K^+. In addition, if m/z 39 is used as a proxy for K^+, the results represent the upper limit of K^+ in each particle class. All the above information has been added to Section 3.3 of the revised manuscript.

"Cluster analysis was performed using UMR mass spectra, and thus the relative contributions of K^+ and organic fragments to m/z 39 cannot be distinguished. Nevertheless, the organic fragment (i.e., $C_3H_3^+$) at m/z 39 only gives a small contribution to the mass spectra of PMF-BBOA factor determined by the high resolution ensemble measurements, suggesting that most of the ion signal at m/z 39 observed in the BBOA-K particle type is due to the presence of K^+."

"Assuming that the relative ionization efficiency of K^+ (RIE_K) is equal to 2.9 (Drewnick et al., 2006) and using m/z 39 as a proxy for K^+, the upper limits of average mass fractions of K^+ for BBOA-K and the other BBOA-related particle types are approximately 20% and < 1%, respectively."

P. 32167, Line 6: Is it possible that the particles having low K are from sources having low K. Another possibility is that the BBOA having low K is SOA. Please discuss.

Response: We agree that, in addition to primary emissions, large quantities of gas-phase organics co-emitted from biomass burning may lead to significant secondary organic aerosol (SOA) production, contributing to the observed BBOA-related particle types with low K^+ content. This information has been added to Section 3.3 of the revised manuscript.

P. 32167, Lines 16-18: One way to compare the two techniques is to compare the NUMBERS of biomass particles classified by ATOFMS and LS-SP-AMS. Was this attempted? If not, I suggest the authors look into this. Inevitably, the ATOFMS is much more sensitive to K and it is not clear how well K can be deconvoluted from organics for the AMS technique and thus the potassium signal may be below the AMS detection limit. Have any studies looked into the quantitative capabilities of the AMS for potassium for biomass burning aerosols? Discuss.

Response: The ATOFMS and the LS-SP-AMS deployed in this study have very different counting efficiencies in terms of particle number (more than 200,000 vs. 7000 particles, respectively), making the direct comparison of particle number difficult. However, the comparison of the particle number fraction of K-rich particles measured by the two instruments suggests that the LS-SP-AMS may underestimate K-rich particle number. This uncertainty has been added to the revised manuscript.

Similar to the above response, cluster analysis was performed using UMR mass spectra, and thus the relative contributions of K^+ and organic fragments to m/z 39 cannot be distinguished. Nevertheless, we believe that most ion signal of m/z 39 observed in BBOA-K particle type is due to the presence of K^+ based on the mass spectra of PMF-BBOA factor determined by the high resolution ensemble measurements. If m/z 39 is used as a proxy for K^+, the results represent the upper limit of K^+ in each particle class. Furthermore, we agree that the potassium ion signal observed in other BBOA-related particle classes (i.e. BBOA-1 to 4) may be below the AMS detection limit. Figure S3b shows that only 27% of the total particle number used in the clustering gave ion signals above the detection limit of m/z 39 (~2 ions). Lastly, although previous work attempted to quantify potassium mass in aerosol particles using AMS (e.g.,

Drewnick et al., 2006), relative ionization efficiency of potassium (RIE_K) is still uncertain for AMS measurements in general. All of the above information has been discussed in Section 3.3 of the revised manuscript.

Reference:
Drewnick, F., Hings, S. S., Curtius, J., Eerdekens, G. and Williams, J.: Measurement of fine particulate and gas-phase species during the New Year's fireworks 2005 in Mainz, Germany, Atmos. Environ., 40, 4316-4327, 2006.

P. 32167, Line 25: is it possible to quantify O:C?

Response: Based on the empirical parameterization of the improved-ambient method reported by Canagaratna et al. (2015) and measured f_{44} values, the oxygen-to-carbon (O:C) ratio (i.e. O:C = 0.079 + 4.31 x f_{44}) of BBOA-4 is estimated to be 0.43, which is higher than O:C ratios of other BBOA-related particle types (0.14-0.34). In addition to organics, CO^+ and CO_2^+ signals can be generated by rBC (Corbin et al., 2014) and thus our estimates likely represent the upper limit of O:C ratios. This information has been added to Section 3.4 of the revised manuscript.

Reference:
Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253-272, 2015.

Corbin, J. C., Sierau, B., Gysel, M., Laborde, M., Keller, A., Kim, J., Petzold, A., Onasch, T. B., Lohmann, U., and Mensah, A. A.: Mass spectrometry of refractory black carbon particles from six sources: carbon-cluster and oxygenated ions, Atmos. Chem. Phys., 14, 2591-2603, 2014.

P. 32169, Lines 13-17: Is there any difference in volatility for the BBOA-K and the rest? Is it possible that the mixing state of the particles can affect the volatility of the particles?

Response: We did not conduct direct single particle measurements of thermally denuded particles so that we cannot directly comment on the volatility of BBOA-K and other particle types. However, BBOA-K and BBOA-1 are mainly composed of low molecular weight organics, suggesting that the two particle classes may be more volatile compared to BBOA-2, BBOA-3 and BBOA-4 as we highlighted in the last paragraph of Section 3.5. The mixing state may affect the measured volatility if aerosol particles composed of less volatile, highly viscous organics but our measurement cannot directly provide information on this topic.

P. 32170, Line 27: It is stated that the properties of the BBOA particles depends on burning conditions, but would also guess that this is also a strong function of source or fuel type as well. I suggest the authors consider that possibility.

Response: We agree that fuel types can also play a role in affecting chemical properties of BBOA. This information has been added to the revised manuscript.