Reviewer 2

We would like to thank the reviewer for their valuable comments

The paper describes measurements of single particle composition from a wildfire plume in Canada. The authors perform cluster analysis to demonstrate that there were 5 different types of particles in the biomass plume, indicating that the emissions are not internally mixed. They demonstrate that BrC appears to be associated with lower/non volatility organics.

Aerosol optical properties and aerosol mixing state are critical issues to resolve regarding the effects of biomass burning on climate. This paper provides new insight into these attributes of wildfire emissions that are consistent with recent laboratory studies and field work. This is an interesting and well written paper. I recommend that it be published after the authors address the following comments.

Specific

Are there issues with sensitivity / uncertainty of single particle analysis? I am not that familiar with the capabilities of the SP-AMS in this regard. The paper mentions issues with the ATOFMS (e.g. high sensitivity to K) but did not really discuss this with the new results. I don't see this changing the conclusions that there are multiple particle classes in the emissions, but it may alter the relative importance of the different classes. More discussion of the uncertainty of the LS-SP-AMS are needed.

Response: In addition to the optical detection limit of light scattering signal (< 0.2 V), multiple scattering signals observed in a trigger event and particles generating weak total ion signals (< 10 ions) were excluded in cluster analysis. The size distribution of total ion signals of the single particle measurement is shown in Figure S3a and the orange dashed line represents the threshold values (10 ions) for real particles.

Similar to the response to Reviewer 1's comments, 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), making the direct comparison of particle number difficult. However, the comparison of particle number fraction of K-rich particles measured by the two instruments suggests that the LS-SP-AMS may underestimate the K-rich particle number. This uncertainty has been added to 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, 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, 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 works 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.

A shortcoming of the experiment design is the very short residence time (1.9 s) in the thermodenuder. The aerosol will certainly not reach equilibrium in this system. Therefore classifying the residual material as low- or non-volatile may be misleading. It may simply be semivolatile material that has not had sufficient time to evaporate. A simple time scale analysis can be done to estimate whether the system has reached equilibrium (e.g. May et al. JGR 2013 doi:10.1002/jgrd.50828). If it has not this should be noted and the caveat added about the residual mass may not actually be low volatility.

Response: We agree that aerosol particles may not reach thermal equilibrium in our system although the thermodenuder was operated at high temperature (250^oC), and thus our measurement only represents the upper limit of low-volatility BBOA materials. This information has been added to Section 3.5 of the revised manuscript.

"However, the short residence time (1.9 s) of ambient aerosol particles in the thermodenuder may result in non-equilibrium measurements and thus overestimate low-volatility aerosol mass (An et al., 2007; May et al., 2012)."

References:
An, W. J., Pathak, R. K., Lee, B. and Pandis, S. N.: Aerosol volatility measurement using an improved thermodenuder: Application to secondary organic aerosol, J. Aerosol Sci., 38, 305-314, 2007.

May, A. A., Levin, E. J. T., Hennigan, C. J., Riipinen, I., Lee, T., Collett, J. L.,Jr., Jimenez, J. L., Kreidenweis, S. M. and Robinson, A. L.: Gas-particle partitioning of primary organic aerosol emissions: 3. Biomass burning, J. Geophys. Res.-Atmos., 118, 11327-11338, 2013.

Figure 4 – Not sure how much this figure adds. Four of the diagrams are pretty similar (Org dominated) with one showing contribution of K. The contribution of K in one particle type is illustrated in Figure 3. The limited contribution of rBC was made in text.

Response: A ternary diagram is a common approach to present the mixing state of particles measured by ATOFMS in order to visualize the relative contributions of organic, rBC and K in the BBOA-K particles. For that reason we have decided to keep a ternary diagram of BBOA-K and move it to Figure 3. Due to the limited contributions from the other ternary diagrams, they have been moved to the supplementary information.

Figure 6 – The figure shows regression lines and states r2 values. I was interested in the value of the slopes and their physical interpretation – these slopes should mean something. Basically this way of presenting the data did not really make sense to me. A bit more text describing how to interpret would be helpful. Also, the caption says estimated mass rBC and non- and low-volatility mass – wasn't this measured downstream of the thermodenuder?

Response: The slopes of the linear regression in Figure 5a (blue dashed line) is 1.38 g/cm^3, which can be interpreted as the average density of thermo-processed particles assuming all particles are spherical and internally mixed, and is similar to the effective particle densities of biomass burning smoke observed in recent laboratory chamber experiments (1.18-1.45 g/cm^3) (Li et al., 2015). In addition, the slope of the linear regression in Figure 5b (blue dashed line) is 2.02 m^2/g, which can be interpreted as the average mass absorption efficiency (MAE) of thermo-processed particles. The above information has been added to Section 3.5 and Figure 5 of the revised manuscript. Note that the MAE of low-volatility BBOA materials can be determined based on the theoretical closure calculation (please see the last response in this document).

The mass of thermo-denuded particles was estimated by the calculation presented in Section 3.5 of the revised manuscript and Section S6 of the Supplementary Information.

Reference:
Li, C., Ma, Z., Chen, J., Wang, X., Ye, X., Wang, L., Yang, X., Kan, H., Donaldson, D. J. and Mellouki, A.: Evolution of biomass burning smoke particles in the dark, Atmos. Environ., 120, 244-252, 2015.

"It is clear that rBC mass alone cannot explain the observed aerosol volatility (R2 = 0.31, black solid circles in Fig. 6a)." This sentence does not make sense. Are you trying to say that rBC mass by itself cannot explain the mass downstream of thermodenuder? Which then implies that there is other low volatility material beyond rBC? What about non-spherical particle issues and SMPS measurements?

Response: Thank you for pointing this out. Yes, that is what we are trying to say. Considering the uncertainties of SMPS measurement due to the non-spherical and fractal structure of rBC particles, the sentence has been revised to highlight the possibility that rBC mass alone may explain the observed aerosol volume of thermo-processed particles during the BB period only if their effective density is very small (less than 0.3 g/cm^3).

"In contrast, significant enhancement of rBC was not observed during the BB period and rBC only has a weak correlation with the aerosol volume of thermo-processed particles for the entire sampling period (R^2 = 0.31, slope = 0.43 g/cm^3, black solid circles and dashed line in Figure 5a). Note that particle mobility diameter measured by SMPS is a function of particle shape and morphology. The non-spherical and fractal structure of rBC can lead to an underestimation of removal efficiency of aerosol mass in the thermodeunder. Although it seems unlikely, rBC mass alone may explain the observed aerosol volume of thermo-processed particles during the BB

period only if their effective density is less than 0.3 g/cm^3.”

“the strong absorption characteristics observed during the BB period cannot be explained by the presence of rBC alone, because the rBC loading was roughly constant throughout the sampling period (R2 = 0.33, black solid circles in Fig. 6b).” This is based just on r2. Or is it based on optical closure using the measured rBC mass and mass absorption cross section? Need to clarify.

Response: The original argument is based on a high value of the correlation coefficient between absorption and mass of thermo-processed particles. In the revised version, a theoretical closure calculation is performed to estimate the mass absorption efficiency of low-volatility BBOA materials. Assuming the MAE of rBC (MAE$_{rBC}$) from biomass burning ranged from 5.3 to 6.4 m^2/g (Lack et al., 2012), the average MAE of low-volatility of BBOA (MAE$_{BBOA}$) observed during the BBOA period is approximately equal to 0.8-1.1(±0.4) m^2/g based on a theoretical closure calculation (i.e., absorption at 405 nm measured by PASS-3 = m$_{rBC}$ (MAE$_{rBC}$) + m$_{BBOA}$ (MAE$_{BBOA}$), where m$_i$ = mass concentration of species i), which is comparable to MAE of primary organic aerosol emitted from biomass burning (e.g., Lack et al., 2012, 2013). The above estimation indicates that the low-volatility BBOA contributes approximately 33-44% of total light absorption at 405 nm of the thermo-processed particles during the BB period. Furthermore, Healy et al. (2015) showed that absorption of ambient and thermally denuded particles at 405 nm are comparable during the BB period, indicating that almost all of the BBOA absorption was associated with low-volatility materials. This information has been added to Section 3.5 of the revised version. The significance of this finding has been highlighted in the Abstract and Conclusion.

References:

Healy, R. M., Wang, J. M., Jeong, C. -., Lee, A. K. Y., Willis, M. D., Jaroudi, E., Zimmerman, N., Hilker, N., Murphy, M., Eckhardt, S., Stohl, A., Abbatt, J. P. D., Wenger, J. C. and Evans, G. J.: Light-absorbing properties of ambient black carbon and brown carbon from fossil fuel and biomass burning sources, J. Geophys. Res.-Atmos., 120, 6619-6633, 2015.

Lack, D. A., Bahreni, R., Langridge, J. M., Gilman, J. B. and Middlebrook, A. M.: Brown carbon absorption linked to organic mass tracers in biomass burning particles, Atmos. Chem. Phys., 13, 2415-2422, 2013.

Lack, D. A., Langridge, J. M., Bahreini, R., Cappa, C. D., Middlebrook, A. M. and Schwarz, J. P.: Brown carbon and internal mixing in biomass burning particles, Proc. Natl. Acad. Sci. U. S. A., 109, 14802-14807, 2012.