

Response to Review 2

We sincerely thank the reviewer for the valuable comments and suggestions. Below we list our point-by-point replies to the comments and the descriptions of the changes we made in the revised manuscript.

Zhai and coauthors describe a series of experiments used to investigate the chemical, physical and optical properties of particles generated through the combustion of rice straw, chosen to represent local crop residues in Southern China. The motivation is to provide data that will help modelers to better assess regional and global radiative climate impacts of particles from this source. A combination of instrumentation is applied to calculate effective densities in two ways, employing a scanning mobility particle sizer, single particle mass spectrometer and an aerosol particle mass analyzer. Extinction, scattering and calculated absorption coefficients are also derived from a cavity attenuated phase shift spectrometer. These properties are assessed for untreated and thermally denuded rice straw combustion particles. While the experiments are worthwhile, there are some issues regarding the approaches taken, and the results need to be framed in the context of existing work in a more rigorous way. Suggested revisions are below:

Major comments:

- 1) Why is the rice straw dried at 100 °C prior to use? Presumably local farmers do not do this and simply burn the residue with its natural water content. Wouldn't this change the burn conditions, smouldering etc? Would it be more representative to burn untreated fuel?

Response: Water content in crop residues varies in a wide range and has a great impact on the burning efficiency and emissions (Hayashi et al., 2014; Oanh et al., 2011). Crop residue moisture has been shown to be positively correlated with particle emissions in the range of 5~35 wt. %. However, empirical emission inventory calculation has to simplify the variation from the water content in biofuels. Pretreatment of biomass fuel in burning simulation is a practical and necessary procedure to ensure the result can be comparable with other studies under the defined conditions (e.g. dehydration at 100 °C for 24 h to ensure water content of the residue within 2 wt. %), which has been applied in many previous studies (Hayashi et al., 2014; Li et al., 2015; Oanh et al., 2011; Zhang et al., 2011).

In this work, water content in the rice straw we collected from the field was less than 5 wt. %. The dehydration to reach a water content within 2 wt. % had not much influence on the burning emissions.

- 2) Why is a relatively low laser desorption ionization energy (0.6 mJ per pulse) selected here? Routinely single particle mass spectrometers of this design employ energies on the order of 1 mJ per pulse. How were the ART-2a cluster parameters chosen- are they simply selected from previous work? If so cite the source and reason for selection.

Response: In this work, laser energy for the desorption/ionization could be varied between 0.5 and 1 mJ with a spot size of ~ 0.3 mm. Higher laser power could yield more elemental compositions and fragments of organics. Lower laser fluencies could yield a greater amount of molecular information. 0.6 mJ/pulse is a proper laser

desorption/ionization energy for SPAMS. The laser power density of SPAMS (0.6 mJ with a spot size of 0.3 mm) is comparable to that of ATOFMS (~1.0 mJ with a spot size of ~1.0 mm).

When using ART-2a method, the learning rate could affect the rate of convergence which will result in different amount of clusters. Generally, with the same vigilance, a higher learning rate could result in a greater amount of clusters. The vigilance could also influence the amount of clusters. At low vigilance, the result of ART-2a is not accurate with rough resolution. At high vigilance, too many clusters could be generated with vague features of mass pattern. The ART-2a parameters used in this paper were based on previous work and the experience in our group (Song et al., 1999; Huang et al., 2013; Spencer et al., 2007).

We have added the references in Line 165 as “*Base on previous work (Huang et al., 2013; Spencer et al., 2007), parameters for ART-2a used in this work such as vigilance factor, learning rate, and iterations were 0.85, 0.05, and 20, respectively*”.

- 3) Is a flow rate of 0.6 L min⁻¹ within the manufacturer’s operating range for the thermal denuder?

Response: Yes. According to the manufacturer’s specification, the flow range of thermodenuder (Model 3065, TSI Inc.) is 0.2 to 2 L/min with optimal flow at 0.5 to 1 L/min (<http://www.tsi.com/Low-Flow-Thermodenuder-3065>).

- 4) The transmission efficiency of the thermal denuder was tested using NaCl particles. Why not simply examine the transmission efficiency of size selected biomass combustion particles at room temperature to validate agreement with the NaCl transmission efficiencies at room temperature.

Response: In general, particle loss in any TD is caused by diffusional and thermophoretic processes, which are both size- and temperature-dependent (Wehner, et al., 2002). Thus, the loss measurements for a series of particle diameter and heater temperatures are essential.

Since sodium chloride (NaCl) is easy to generate and evaporates only at 600 °C, it was used to detect the transmission efficiency and particle loss of thermodenuder in our work and many previous work. Similar tests have been done to detect transmission efficiency in previous work (Huffman et al., 2008; Cheung et al., 2016).

Also, for the absorption enhancement calculation, the transmission efficiency needs to be taken into account. The formula on line 553 simply relates b_{abs} before and after the denuder. Any losses of BC through diffusion and impaction in the denuder will be incorrectly assigned as absorption reduction through a removal of coating materials (absorption enhancement effect).

Furthermore, why is the “shrink factor” used to account for volatilized coating materials? Firstly, the shrink factors shown in Fig S7 demonstrate a wide range of values, with multiple modes, and using a single value does not seem appropriate. In any case accounting for shrinking should not be necessary. Shrinking of the coatings is desirable for this test. The idea is that the bulk BC mass should be conserved through the denuder

(applying the correct transmission efficiency factor should result in BC mass entering the denuder being roughly equivalent to “transmission corrected” BC mass exiting the denuder), but that the coating materials should evaporate. Any reduction in absorption can thus be assigned to either reduced optical “lensing” due to the reduction of coating sizes or evaporation of any non-BC absorbing material. Applying the transmission efficiency correction and removing the shrink factor should be tested.

Response: In our work, we have taken the transport efficiency of TD into account for all the thermo-denuded related measurements including the absorption enhancement calculation. As written in Line 282, *“the measured η were used to correct the particle number concentration in the calculation of all the measurements related to thermal-denuded process”*.

As for shrink factor, particles might shrink to smaller sizes after thermal treatment. In this experiment, we heated the particles before the DMA size selection. Thus, the mono-dispersed particles at the fixed size obtained after heating actually were not from the particles with the same original dried-particle diameter. For measurement like absorption enhancement, the particle optical data before and after thermal-denuded process are compared directly. Thus, it is essential to take the particle shrink factor into consideration.

Here, we accepted the comment of Reviewer 3 and we added a new part (2.6) named as shrink factor (Line 285) to give a detailed description on the shrinking effect.

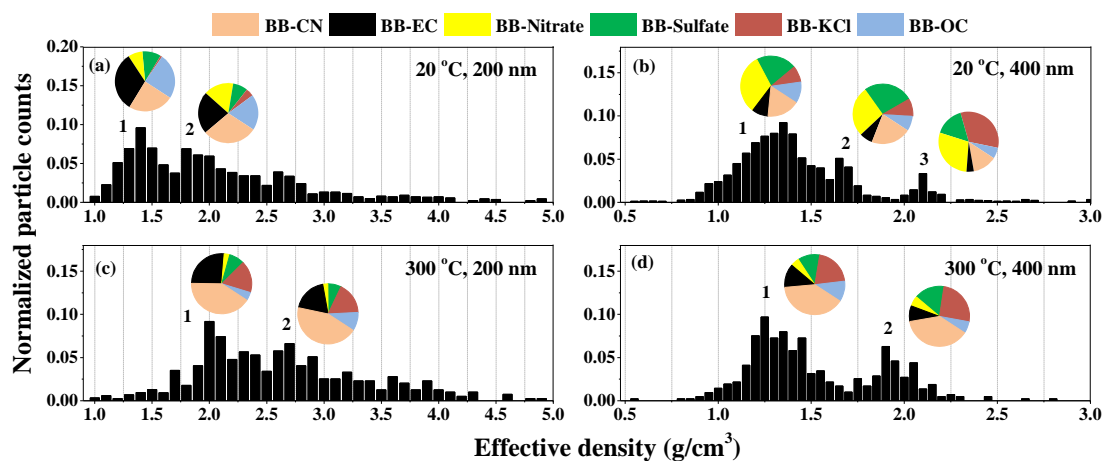
“The thermal-denuded method to separate the coating of particles for absorption enhancement calculation as well as other experiments related to particle volatility has been used in previous work (Nakayama et al., 2014; Chan et al., 2011; Lack et al., 2012). However, the particles might shrink to smaller sizes after thermal treatment. The particle shrinkage should be taken into consideration for size-selected volatility experiments which could be neglected in previous work. One main reason should be due to the extremely low concentration for size-selected particles after thermal-denuded process up to 300 °C. The concentration of the size-selected particles might be too low to be detected in the following instruments.

Therefore, we developed an approximation of the particle shrinkage calculation. A tandem DMAs (TDMA) was utilized to detect the size change of particles. Here, we used the ratio of the particle diameter after heating (d_{m2}) to the diameter before heating (d_{m1}) as the shrink factor (d_{m2}/d_{m1}) of particles (shown in Figure S3). An approximation of the peak value for the dominant shrink factor mode was used for each diameter. The selection of particle diameter after thermal-denuded process was based on the original dried-particle diameter multiplied the shrink factor of each diameter (discussed in supplementary). ”

- 5) The x-axis of Figure 3 should show include effective density also. It would also be very useful to show an effective density distribution plot for each of the different particle classes. This will allow the authors to provide better evidence to support their postulations regarding potential composition-density relationships throughout.

Response: We accepted this suggestion and the suggestion in minor comment 1. We

changed our figure as following and combined the original Fig. 3 and S3 into one figure.



- 6) Overall, there needs to be much better discussion of the findings here in the context of similar work previously performed by other groups. In terms of single particle mass spectrometry analyses of biomass burning particles (and relating biomass particle composition to optical and physical properties) there is a host of relevant studies that should be discussed. See (Silva et al., 1999; Zauscher et al., 2013; Bi et al., 2011; Guazzotti et al., 2003; Schwarz et al., 2008; Moffet and Prather, 2009; Moffet et al., 2008; Pagels et al., 2013). In terms of efforts examining relationships between biomass burning chemical composition measured through mass spectrometry and optical absorption enhancements see (McMeeking et al., 2014; Healy et al., 2015) and other ambient combustion particle absorption enhancements (Cappa et al., 2012; Liu et al., 2015) among others. One point which is posed as a new conclusion (evidence for external mixing of K and organic aerosol in biomass burning particles using single particle mass spectrometry) has been recently reported by others (Lee et al., 2016).

Response: We accepted the reviewer's advice and added discussion of the findings of similar work previously as the reviewer suggested.

Line 337: *Evidence of external mixing sodium and potassium salts in ambient environment was also observed by single particle mass spectrometry in previous work (Zauscher et al., 2013; Bi et al., 2011).*

Line 339: *A recent work performed by Lee et al. (2016) reported that K^+ was not uniformly mixed in biomass burning particles with less than 20% particles containing high K^+ content.*

Line 344: *The similar results of the externally mixed aerosol population have been found by Moffet et al. (2008) with an observation of a wide range of densities ($1.1\text{-}3.4 \text{ g/cm}^3$).*

Line 443: *The mass spectra of individual biomass burning particles have been studied in previous work (Silva et al., 1999; Zauscher et al., 2013).*

Line 572: *McMeeking et al. (2014) found that the strongly light-absorbing biomass burning particles tended to have a weak wavelength dependent absorption while the weakly light-absorbing particles tended have a strong wavelength dependent absorption, which is consistent with our results. In this work, the high values of AAE (~ 6.23) and SSA*

(~0.89, at 530 nm) suggested the light absorbing of rice straw burning particles were relatively weak compared to the particles emitted from other types of biofuels.

Line 585: Previous studies have reported the absorption enhancement values in a range of 1.2-1.6 for biomass burning particles (Moffet and Prather, 2009; McMeeking et al., 2014). However, some other studies suggested that BC absorption enhancement due to lensing is minimal and climate models might overestimate the warming effect by BC (Healy et al., 2015; Cappa et al., 2012).

Line 605: Other than coating thickness, absorption enhancement of particles could be related with the mixing state and morphology (Liu et al., 2015).

Minor comments:

- 1) Some SI figures should be in the main manuscript (S3 and S6)

Response: We have accepted the reviewer's advice and combined Fig. 3 and S3 into one figure.

However, the mass pattern of each cluster from biomass burning particles has been reported in previous work (Huo et al., 2016; Zauscher et al., 2013). The single particle mass pattern of biomass burning particles is not the major finding in this work. Thus, we would rather put Fig. S6 in the supplementary.

- 2) Figure S4: the legend does not specify the method used for effective density calculation

Response: The description of different methods for effective density calculation was given in the figure caption of Fig. S4.

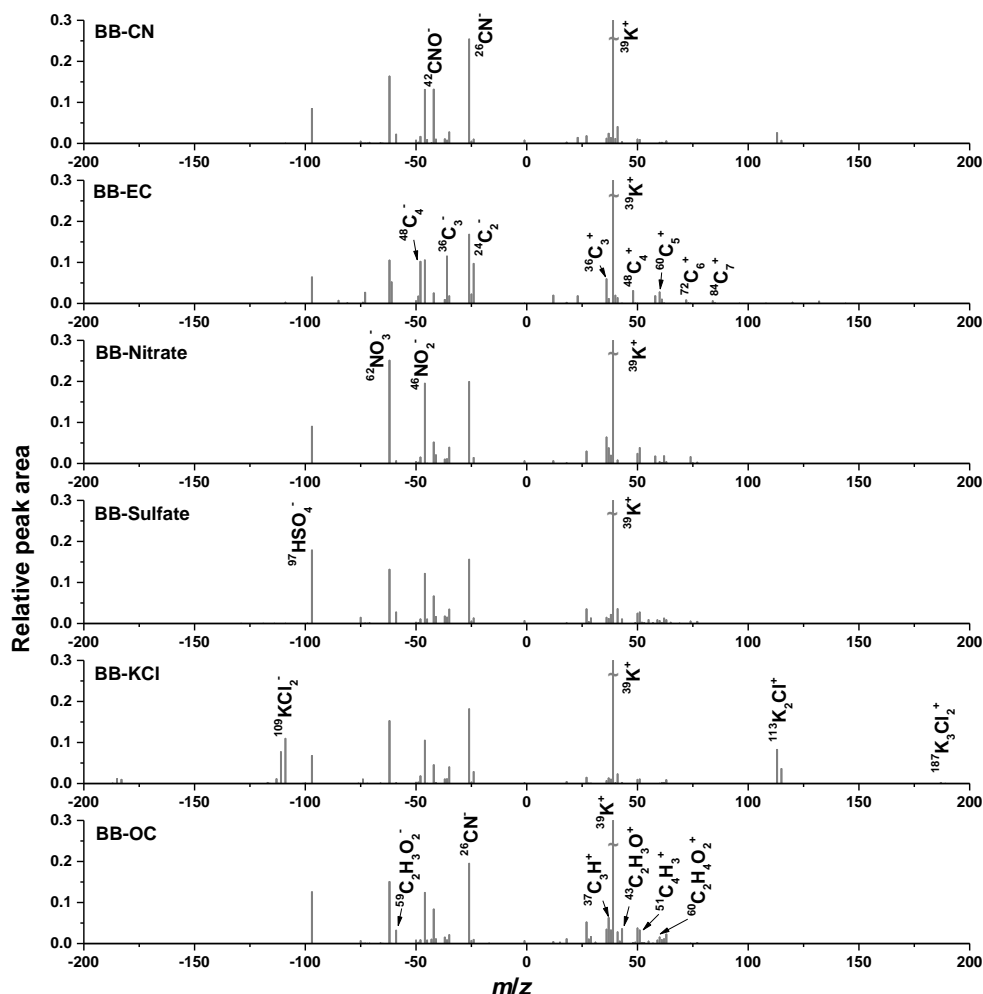
“Size-resolved effective density of biomass burning particles determined by two methods. ρ_{eff}^I is the effective density obtained from mobility and mass measurements (based on the DMA-APM-CPC system) while ρ_{eff}^{II} is obtained from mobility and aerodynamic measurements (DMA-SPAMS system). The effective density of each size is the average peak value of the dominant mode from different scans. Error bars represent the standard deviations of the five replicate test results.”

Section 3.2: Do all of the particle types need the prefix BB? All particles discussed are from biomass.

Response: We used prefix BB for particle types to distinguish the subgroups of biomass burning particles from the other particle types in the ambient environment which were named as OC, EC, etc. for short in many previous works (Bi et al., 2011; Huang et al., 2013).

Also, the order of the particle types does not match Fig S6

Response: We changed the order of particle types in Fig. S6.



- 3) Line 392: Test for statistically significant differences

Response: Overall, these two methods had consistent results. The differences between the average values from the two methods were less than 8% for all particle sizes. We noticed that ρ_{eff}^{II} were generally smaller than ρ_{eff}^I , which could be due to the systematic error from different measurements.

We added the above discussion in our manuscript.

- 4) Line 386: Simply remove the intermediate size from the plot if it is not represented in the other plot

Response: The optimum sampling size range of SPAMS is 0.2-2.0 μm . To make the comparison of two methods in Fig. S4 meaningful, we would like to keep the data of 300 and 350 nm particles.

- 5) Line 453: Is there a way to demonstrate this? See suggestion of effective density plots for each particle class earlier

Response: We accepted the reviewer's advice and changed Fig.3.

- 6) Line 487: This is not an offset, simply a bulk measurement.

Response: We rewrote the sentence as "It's worth noting that the optical measurement

was based on bulk measurement by CAPSs, which is not sensitive to the diversity of particle mixing state.”

References:

- Cheung, H. H. Y., Tan, H., Xu, H., Li, F., Wu, C., Yu, J. Z., and Chan, C. K.: Measurements of non-volatile aerosols with a VTDMA and their correlations with carbonaceous aerosols in Guangzhou, China, *Atmospheric Chemistry and Physics*, 16, 8431-8446, 10.5194/acp-16-8431-2016, 2016.
- Hayashi, K., Ono, K., Kajiuira, M., Sudo, S., Yonemura, S., Fushimi, A., Saitoh, K., Fujitani, Y., and Tanabe, K.: Trace gas and particle emissions from open burning of three cereal crop residues: Increase in residue moistness enhances emissions of carbon monoxide, methane, and particulate organic carbon, *Atmos. Environ.*, 95, 36-44, 10.1016/j.atmosenv.2014.06.023, 2014.
- Huang, Y., Li, L., Li, J., Wang, X., Chen, H., Chen, J., Yang, X., Gross, D., Wang, H., and Qiao, L.: A case study of the highly time-resolved evolution of aerosol chemical and optical properties in urban Shanghai, China, *Atmos. Chem. Phys.*, 13, 3931-3944, 2013.
- Huffman, J. A., Ziemann, P. J., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Development and Characterization of a Fast-Stepping/Scanning Thermodenuder for Chemically-Resolved Aerosol Volatility Measurements, *Aerosol Sci. Technol.*, 42, 395-407, 10.1080/02786820802104981, 2008.
- Huo, J., Lu, X., Wang, X., Chen, H., Ye, X., Gao, S., Gross, D. S., Chen, J., and Yang, X.: Online single particle analysis of chemical composition and mixing state of crop straw burning particles: from laboratory study to field measurement, *Frontiers of Environmental Science & Engineering*, 10, 244-252, 10.1007/s11783-015-0768-z, 2016.
- 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, 10.1016/j.atmosenv.2015.09.003, 2015.
- Oanh, N. T., Bich, T. L., Tipayarom, D., Manadhar, B. R., Prapat, P., Simpson, C. D., and Liu, L. J.: Characterization of Particulate Matter Emission from Open Burning of Rice Straw, *Atmos. Environ.*, 45, 493-502, 10.1016/j.atmosenv.2010.09.023, 2011.
- Song, X. H., Hopke, P. K., Fergenson, D. P., and Prather, K. A.: Classification of single particles analyzed by ATOFMS using an artificial neural network, ART-2A, *Anal. Chem.*, 71, 860-865, 10.1021/ac9809682, 1999.
- Spencer, M. T., Shields, L. G., and Prather, K. A.: Simultaneous measurement of the effective density and chemical composition of ambient aerosol particles, *Environ. Sci. Technol.*, 41, 1303-1309, doi: 10.1021/es061425+, 2007.
- Wehner, B., Philippin, S., and Wiedensohler, A.: Design and calibration of a thermodenuder with an improved heating unit to measure the size-dependent volatile fraction of aerosol particles, *Journal of Aerosol Science*, 33, 1087-1093, 10.1016/s0021-8502(02)00056-3, 2002.
- Zauscher, M. D., Wang, Y., Moore, M. J. K., Gaston, C. J., and Prather, K. A.: Air Quality Impact and Physicochemical Aging of Biomass Burning Aerosols during the 2007 San Diego Wildfires, *Environmental Science & Technology*, 47, 7633-7643, 10.1021/es4004137, 2013.

Zhang, H., Hu, D., Chen, J., Ye, X., Wang, S. X., Hao, J. M., Wang, L., Zhang, R., and An, Z.: Particle size distribution and polycyclic aromatic hydrocarbons emissions from agricultural crop residue burning, *Environ. Sci. Technol.*, 45, 5477-5482, 10.1021/es1037904, 2011.