

Response to Review 3

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.

This manuscript reports the size-resolved chemical composition, effective density and optical properties of rice straw burning particles using different online instruments including DMA-APM-CPC, single particle aerosol mass spectrometer, and cavity attenuated phase shift (CAPS) spectroscopy.

First of all, the focus of this study is unclear and hence the significance and atmospheric implication should be explicitly highlighted in the abstract, introduction and conclusion.

Response: In this work, we focus on the size dependent mixing states of biomass burning particles and their correlations with the optical properties. To make this main point clear, we rewrote the abstract, revised some parts of the introduction and result discussions. Below is the new abstract:

“Biomass burning aerosol has important impact on the global radiative budget. A better understanding of the correlations between the mixing states of biomass burning particles and their optical properties is the goal of a number of current studies. In this work, effective density, chemical composition, and optical properties of rice straw burning particles in the size range of 50-400 nm were measured using a suite of online methods. We found that the major components of rice straw burning particles included black carbon (BC), organic carbon (OC) and potassium salts, but the mixing states of particles were strongly size-dependent. Particles of 50 nm had the smallest effective density (1.16 g/cm^3), due to a relatively large proportion of aggregate BC. The average effective densities of 100-400 nm particles ranged from $1.35\text{-}1.51 \text{ g/cm}^3$ with OC and inorganic salts as dominant components. Both density distribution and single-particle mass spectrometry showed more complex mixing states in larger particles. Upon heating, the separation of the effective density distribution modes testified the external mixing state of less volatile BC or soot and potassium salts. Size-resolved optical properties of biomass burning particles were investigated at two wavelengths ($\lambda=450$ & 530 nm). The single scattering albedo (SSA) showed the lowest value for 50 nm particles (0.741 ± 0.007 & 0.889 ± 0.006) because of the larger proportion of BC content. Brown carbon played an important role for the SSA of 100-400 nm particles. The Ångström absorption exponent (AAE) values for all particles were above 1.6, indicating the significant presence of brown carbon in all sizes. Though freshly emitted, the light absorption enhancement (E_{abs}) was observed for particles larger than 200 nm because of the non-BC material coating. Concurrent measurements in our work provide a basis for discussing the physicochemical properties of biomass burning aerosol and its effects on global climate and atmospheric environment.”

Secondly, the results should be discussed in more detail. In particular, the observations regarding particle effective densities and single particle compositions should be better integrated in this manuscript in order to provide a more complete picture on the relationship of particle mixing state, morphology and effective density.

Response: We accepted most of the reviewer's suggestions. Please see the detailed responses to specific comment 3-5.

Lastly, there is an issue about the data quality in Section 3.3.3 (See specific comments) that should be addressed by the authors.

Response: We accepted most of the reviewer's suggestions. Please see the detailed responses to specific comment 1 and 6.

The manuscript should be proofread carefully before submission. Overall, I don't recommend this manuscript to be published in Atmospheric Chemistry and Physics in the current format. Below is the specific comments.

Specific comments:

1. Absorption enhancement results (Section 3.3.3 and Figure 5): Figure 1 demonstrated that aerosol particles were pre-treated by a thermodenuder before generating monodisperse particles using a DMA. The size-selected particles were then characterized by a few real-time instruments. Using such experimental setup, the size-resolved absorption enhancement factors reported in Figure 5 are actually not meaningful. The primary reason is that those enhancement factors were not determined by comparing particles with the same original dried-particle diameter. The whole particle size distribution should shift towards the lower particle size after thermal treatment (i.e. removal of coating materials). The original size of heated particles should be greater than that of particles without heating as shown in Figure S7. It is unclear how the shrink factor and transmission efficiency of particles presented in Section 3.3.3 can resolve this fundamental problem. Detail clarification is required to keep the related discussion in the manuscript.

Response: In this work, we have taken the transmission 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. Thus, the mono-dispersed particles at the fixed size obtained after heating actually are 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 reviewer's advice 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). ”

Furthermore, this manuscript emphasizes a few times that aerosol coating can act as a lens to enhance light absorption of aerosol particles in general. Nevertheless, the major conclusion of this work regarding light absorption enhancement (relative to pure BC) is due to the presence of atmospheric brown carbon from biomass burning emissions and without much discussion on the lensing effect. It is recommended to change the tone/wording in the text to avoid any potential confusion to the readers, especially for those are not familiar with this research topic.

Response: For absorption enhancement, the major point in this work is that absorption enhancement has been observed in freshly emitted biomass burning particles, compared to the numerous works on aged ambient aerosol. We believe that the absorption enhancement in this experiment was caused by the particle coating rather than the presence of brown carbon. In the manuscript, we claimed the contribution of the thick coating to the absorption enhancement for particles larger than 200 nm. We only attributed the stronger absorption enhancement at the wavelength of 450 nm to the presence of brown carbon when compared with the 530 nm data.

2. Figure 2 and Section 3.1.3: Similar to the comment #1, it is essential to highlight in the manuscript that the individual column in Figure 2 is not presenting results obtained from particles with the same original dried-particle diameter. The current writing is somewhat misleading. However, the findings observed from this figure is still useful even though direct comparison of plots displayed in the same column is inappropriate.

Response: We accepted the reviewer’s advice and added the description in Line 385 as following:

“It is worth noting that the thermal-denuded particle density distribution here was not from the particles with the same original dried-particle diameter. However, our observations are still meaningful since the evolution trends of density distribution after heating were similar despite of the particle size. ”

3. To better organize the discussion of particle effective density, it is recommended to combine Section 3.1.2 and 3.1.4 in the manuscript.

Response: We accepted this suggestion and combined Section 3.1.2 and 3.1.4 together.

4. Effective density and chemical composition (Section 3.1.3):

1) Lines 358-360: Without quantitative chemical characterization in a single particle basis, it is hard to prove if some BC was externally mixed with other components based on the effective density measurement alone. BC particles with highly fractal structure and thin organic coating can lead to the similar observations, depending on the uncertainty of effective density measurement.

Response: We agree with the reviewer's point of "BC particles with highly fractal structure and thin organic coating could also lead to the low density mode in effective density distribution". In the revised manuscript, we softened our statement as:

"The separation of the peaks after heating suggested that the some less volatile BC or soot with effective density of $\sim 1.0 \text{ g/cm}^3$ was possibly externally mixed with other compositions."

2) Lines 365-378: According to Figure 2, peaks are always observed at around 1.7-1.8 g/cm³ for the heated particles with diameter less than 400 nm. Please comment whether this observation is due to the presence of extremely low volatility organic aerosol materials generated. Furthermore, what are the vaporization temperature of KCl and other potassium salts.

Response: We accepted the reviewer's suggestion and added the important role the extremely low volatility organic compounds might play in the dominant effective density mode at 300 °C in the revision.

The vaporization temperatures of KCl and other potassium salts are above 700 °C (Knudsen et al., 2004), which we have added in our manuscript.

The revision in part 3.1.3 is as following (Line 407):

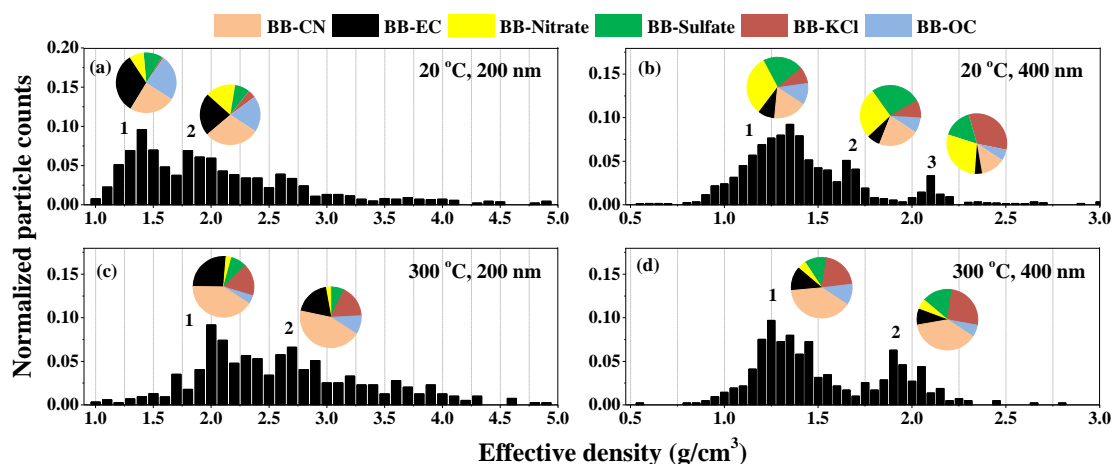
"Besides, Bond et al. (2006) reported that the density of light-absorbing carbon should be 1.7-2.1 g/cm³ which is quite high compared with the density of the volatile organics (0.61-0.90 g/cm³). Saleh et al. (2014) had shown that the light-absorbing organics in biomass burning particles were extremely low volatility organic compounds. Thus, we assume these extremely low volatility organics should play an important role in the dominant effective density mode at 300°C."

Upon heating, the density mode of KCl and partly K₂SO₄ at $\sim 2.0 \text{ g/cm}^3$ was ambiguous as the dominant mode shifted right and overlapped with the KCl mode (dash lines shown in Figure 2). However, at 300 °C, the dominant mode of 400 nm particles was at 2.05 g/cm³ which fitted the density of potassium salts, indicating the main material of 400 nm heated ($\sim 800 \text{ nm}$ unheated, detected by a tandem DMAs) biomass burning particles should be potassium salts with vaporization temperatures above 700°C (Knudsen et al., 2004)."

5. Section 3.2 and Figure 3: The authors may over-interpret their observations. The average chemical compositions are not sufficient enough (i.e. they are too similar) to explain the effective densities of the two particle modes presented in Figure 3a (200 nm). Similarly,

the first two particle modes in Figure 3b (400 nm) have the very similar average chemical compositions.

Response: In the revised manuscript, we changed Fig. 3 as below:



Different chemical composition proportions could be one of the reasons of different effective density of each mode. Other reasons could be due to the difference of particle morphology such as sphericity and shape factor. Here, we focused the aspect of chemical composition since this part (Section 3.2) was mainly based on the SPAMS cluster analysis.

In the pie charts of 200 nm particles at room temperature, the second mode with larger effective density could be due to less BB-EC and more BB-KCl and BB-CN. Thus, the effective density of the second mode is higher than the first one.

However, the chemical compositions were similar in the first and second modes of 400 nm particles at 20 °C. We assume these two modes were derived from one mode. We revised the related discussion in Line 488.

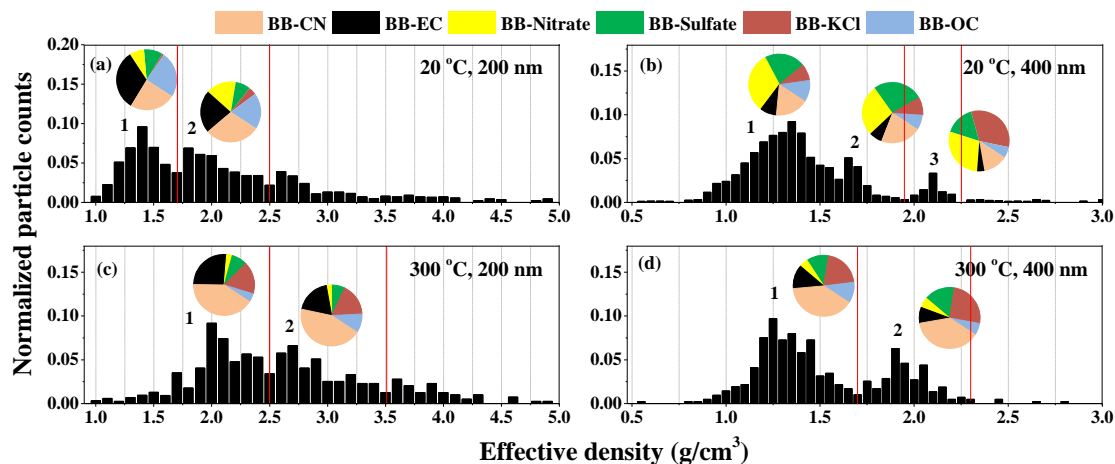
“For 400 nm mobility selected particles, the pie charts of particle type were almost identical for the first and second modes (as shown in Fig. 3b, 20 °C). Thus, we assume these two modes were derived from one effective density mode.”

What are the particle number distributions of each cluster (lines 430-432)? Their particle number distributions should be able to extract from the results of cluster analysis. Estimation of effective densities of some clusters is possible with such additional information.

Response: Indeed, the number distributions of each particle cluster could be extracted from cluster analysis. However, the cluster analysis by SPAMS in terms of chemical compositions is a qualitative one. We cannot estimate the effective densities via absolute number distribution of each cluster. Besides, the morphology of particles in each cluster varied from one another which is difficult to give a quantitative estimation.

Furthermore, it is unclear how to separate the particle modes in Figure 3 for constructing the pie chart. Please provide sufficient detail.

Response: We used the smallest value between two modes as the separation point (as the red lines shown in the figure below).



6. Section 3.3.2, Lines 533-541: What is the particle size for data reported in Table S2?

Response: The data reported in Table S2 was the particles that freshly emitted from combustion of biomass. The size distribution was shown in Fig. S1 (~20-660 nm).

Significant drop of AAE for the thermodenuded particles are observed. Please comment on the significance and relative contributions of extremely low volatility brown carbon to the total light absorption properties of biomass burning aerosol observed in this study and compare their results with existing literature.

Response: The significant drop of AAE should be attributed to the large proportion of organics evaporated at 150-300 °C. However, at 300 °C, the AAE was still above 1.6, indicating the presence of the extremely low volatility brown carbon in biomass burning particles. We have revised the AAE part in our manuscript as following (Line 564):

“The SSA and AAE values of total biomass burning particles are shown in Table S2. The decrease of SSA values upon heating was due to the vaporization of secondary inorganic species like NH_4NO_3 and less absorbing organics. The AAE values for all particles at 150 °C and 300 °C were ~19% and ~64%, lower than those at room temperature (20 °C). The significant decrease of AAE at 300 °C could be due to the vaporization of light-absorbing organics in the temperature range of 150-300 °C. However, the AAE value at 300 °C was still above 1.6, indicating the presence of extremely low volatility light-absorbing organics in biomass burning particles. 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 to 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.”

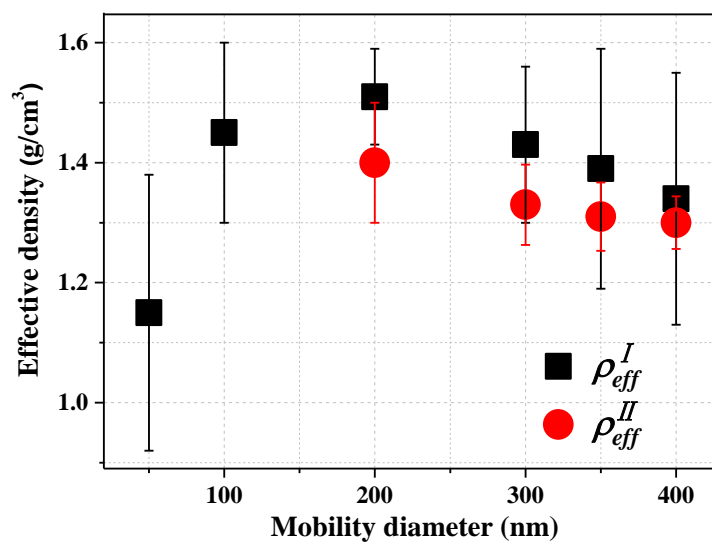
Minor and technical comments:

1. Please replace “bi-model” by “bi-modal” throughout the entire manuscript.

Response: Changed.

2. Figure S4: The legend displays the same for both types of effective density. Please correct.

Response: We redrew the Figure S4 as below:



3. Please use “low” and “high” to describe density.

Response: Changed.

4. Line 198: Should it be “...increased as the size increased...”?

Response: We revised the sentence as “the SSA ($\lambda=450$ nm) of 100-400 nm particles increased as the size increased” (Line 529).