Reply to the comments of anonymous reviewer #1 on manuscript entitled " Emission characteristic of refractory black carbon aerosols in the fresh Asian biomass burning: a perspective from laboratory experiment "

We appreciate very much the insight comments and recommendations of the reviewer in improving this paper and our future research. Here, we will response to all the comments one by one as follows:

General comments:

The present manuscript describes a series of laboratory experiments on wheat straw and rape or rapeseed plants to quantify emission ratios and mixing state of refractory black carbon (rBC) using the Single Particle Soot Photometer (SP2). The ultimate objective of this study is to provide data that can augment field measurements of biomass burning (BB) events as well as providing important BB inventory used by models. The primarily findings of value to the community include the quantification of the delta-rBC/delta-CO ratio as a function of MCE (modified combustion efficiency); dependence of rBC mass mode diameter on MCE; and dependence of rBC mixing state on MCE for the two fuel sources studied. The biggest disappoint of this study is the lack of measurements of the rBC optical properties as a function of MCE. From a climate forcing point-of-view, quantification of BB optical properties is central to bounding the contribution of these events to aerosol radiative forcing. Consequently, this study is very myopic - only two fuels are examined and the experiments carried out are rBC- centric. This being said, the data is expected to find value in emission inventories and thus should be considered for publication after comments, listed below, are addressed.

Reply: We fully agree with the reviewer's suggestions, that measurement of optical properties of rBC as a function of MCE will benefit the better understanding aerosol radiative forcing effect of biomass burning, because rBC particles that produced at different combustion phase of biomass mass have distinct light-absorbing capacity due to coating of non-refractory matters. At present the observational studies for the absorption enhancement effect of rBC-containing particles are still scant and conflicting. To clarify its radiative effect, more observational and experimental results are needed. Open biomass burning (OBB) is one of great important sources of rBC. In particular in East China, substantial amount of crop residue were unorganizedly burned in the field, which lead to degradation of air quality and serious health problems. Better constraining the emission factor of rBC of OBB plays a key role in reducing the uncertainty of emission inventory and improving simulations of Chemical Transport Model (CTM).

The initial idea of this study is to investigate the emission ratio of rBC (ΔrBC/ΔCO) from open burning of residues of two major economic crops (wheat and rape plant) in East China (including Jiangsu, Anhui and Shandong province), because intensive burning of these crop residues in the field often resulted in Air Quality Index > 500 (hazardous level) during harvest season, which imposed great detrimental effect on human and environment. Long-range transport of Asian biomass burning was also frequently reported in Japan. For this reason, a Japan-China joint field campaign was performed at agriculture area in the East of China, we collected samples of crop residues and performed burning experiments in the laboratory. Taking advantage of SP2, the incandescent delaytime and coating thickness were also investigated to understand the physical characteristics of freshly emitted rBC particles. As reviewer pointed out, simultaneous measurements of optical properties and mixing state of rBC particles as a function of MCE was critically important to evaluate its climate effect. Liu et al., (2014) reported aerosol single

scattering albedo (ω) dependence on biomass combustion efficiency in laboratory and field study. The author reported that MCE could explains 60% of the variability in ω, while the 40% unexplained variability could be accounted for by other parameters such as fuel type. Besides, for open burning of agriculture residues in the field, the plumes were quickly mixed and diluted after being emitted in the ambient condition. rBC particles tend to be coated with more non-refectory matter (semi-volatile organics, inorganics etc.) with photochemical aging. Consequently, chemical and optical properties of rBC particles from burning may change during transport, whereas ΔrBC/ΔCO ratio could preserve for long. As far as I know, a photo-acoustic soot spectrometer (such as PASS-3, DMT) could measure scattering/absorption coefficient at three wavelengths, and it was normally used to investigate the light absorption enhancement by mixed condition black carbon particles (Liu et al., 2014, Liu et al., 2017). Unfortunately, we did not have it during experiment. For all these reason, concurrent measurement of optical properties of rBC-containing particles in this study was not conducted in this study. In our next research, we would like to follow reviewer's suggestions to perform comprehensive measurements on the dependence of both mixing state and optical properties of rBC particles on the combustion state of biomass burning.

Liu, S., et al. (2014), Aerosol single scattering albedo dependence on biomass com- bustion efficiency: Laboratory and field studies, Geophys. Res. Lett., 41, 742–748, doi:10.1002/2013GL058392.

Liu, D., et al. (2017) Black-carbon absorption enhancement in the atmosphere determined by particle mixing state, Nature Geosci, advance online publication, 10.1038/ngeo2901.

Specific comments:

The authors correctly indicate that the combustion process is the driving force that dictates variations in emission characteristics. It is clear that the authors characterized stages of the burn as either flaming or smoldering, yet offer no boundary conditions as to when a burn was flaming vs smoldering. If MCE was used, what value determined if the data points were from an active flaming condition or smoldering condition? And, if as the authors point out, both stages could occur at the same time. On page 9, line 13, the authors state that "when the combustion shifted from the flaming dominant to the smoldering-dominant state. . ." what is the criteria used to characterize one stage over the other?

Reply: We will clarify this point in the revised manuscript. In this study, the MCE value = 0. 95 was deemed as a criteria to distinguish flaming- dominant and smoldering-dominant combustion basically. Nevertheless, a conservative criteria (MCE < 0.90) was used to indicate smoldering-dominant combustion, in accordance with our previous study (Kondo et al., 2011). During the experiments, we found a prominent phenomenon that occurrence of peak of number concentration of non-rBC particles was obviously later than that of rBC particles (as shown in Figure 1), and the MCE value of ~0.95 normally fall in the middle of these two peak. It can be an indicator that the dominant combustion phase shifted from the flaming to smoldering. As mentioned, the mass of each sample was ~20 g, the combustion period was normally short that both flaming and smoldering stages sometimes could occur at the same time at the different part of biomass. To reduce such uncertainty, we used a fire-integrated increment of mixing ratios of CO and CO2 and an averaged MCE of each combustion cases to represent the dominant combustion phase in the following discussion. We will clearly state the MCE criteria in the revised manuscript.

Kondo, Y., et al. (2011), Emissions of black carbon, organic, and inorganic aerosols from biomass burning in North America and Asia in 2008, J. Geophys. Res., 116, D08204, doi:10.1029/2010JD015152.

This reviewer is rather surprised that the authors fit the rBC size/mass distribution data to a Gaussian (page 1, line 19; page 9, line 27) as opposed to a lognormal. It is well-known that most aerosol distributions are skewed (e.g., exhibit a long tail at larger sizes) and thus are better described with a lognormal function (Hinds 1999). On page 9, line 28, the authors make reference to figure 2a that presumably shows an example dM/dlogDp plot. Such a plot does not exist. The authors are strongly encouraged to add this figure along with a lognormal fit.

Reply: We consented to the reviewer's comments, and checked both Lognormal fit and Gaussian fit of mass size distribution of rBC particles (Normalized dM/dlogDp v.s. Mass Equivalent Diameter of rBC) for all the combustion cases. As suggested, the aerosol distributions are normally skewed. Indeed, lognormal function fitting is slightly better than that of Gaussian function in most instances. This phenomena is more prominent in smoldering-dominant case that that in flaming-dominant cases (as shown in Figure 1). We will correct the expressions in the revised manuscript, and add dM/dlogDp plot in the Figure 2a.

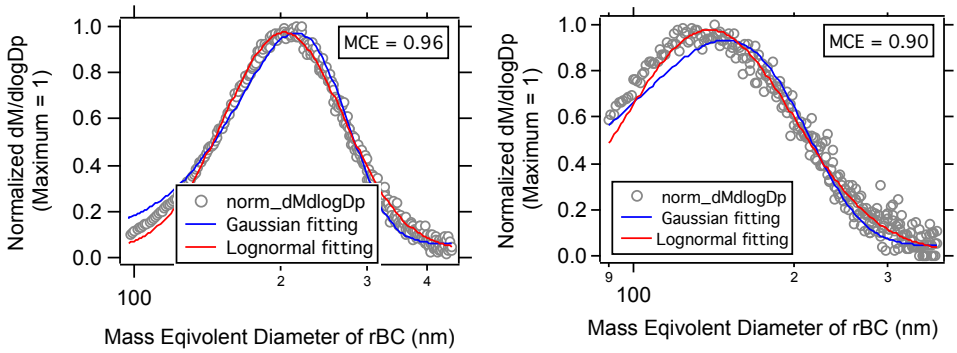

Figure 1 Gaussian and lognormal fitting for normalized mass size distribution of rBC for flaming- (left) and smoldering- dominant case (right).

Central in their study is the use of MCE. The authors are encouraged to read the 2016 publication by Collier et al., (Regional Influence of Aerosol Emissions from Wildfires Driven by Combustion Efficiency: Insights from the BBOP Campaign; (2016) Environ. Sci. Technol.50, 8613−8622) with specific attention to Figure 4). While the Collier paper focuses on wildfires, the dependence of aerosol emissions on MCE the authors might this study relevant to theirs.

Reply: As mentioned by the reviewer, our main conclusion is consistent with Dr. Collier's results that characteristics of biomass burning aerosols are strongly dependent on the MCE. As a matter of fact, in this study we found that the ratio of number concentration of non-rBC (w/o incandescent signal, such as semi-volatile organic matter) to that of rBC particles also showed an obviously increasing tendency with decrease of MCE, implying of high emissions potential of OA in smoldering combustion. It was also consistent with Dr. Collier's study. We would like to cite Dr. Collier's research to support our conclusion in the revised manuscript.

Page 1, Line 15: The authors cite in their abstract that "A single particle soot photometer (SP2) was adopted to measure rBC-containing particles at high temporal resolution and with high

accuracy," yet do not explicitly discuss what was "adopted" to realize the high temporal resolution and high accuracy. If the authors altered some hardware/software aspect of the SP2 that improved upon its "out-of-the-box" capabilities, then they should explicitly discuss those changes. If nothing was not done, than eliminate this statement as it is misleading.

Reply: Since we did not alter hardware/software aspect of SP2, we would like follow the reviewer's advise and remove the statement "at high temporal resolution and with high accuracy ".

Page 4, line 19: The authors write " All of the biomass was stored in sealed plastic bags to preserve its original state." Sealing a sample will not prevent loss of semivolatile materials. Have the authors accounted for this or attempted to quantify this?

Reply: We agree with the reviewer's comments that the semi-volatile matters in the fresh biomass will loss even they were sealed in hermetic bag. In this study, the agriculture residues that were collected in the field were almost dry (Figure 2). In northern and eastern China peasant usually dry their crop residues first and burn them intensively. For the dried biomass, the loss of semi-volatile matter should be negligible, compared with vigorous combustion processes. In this study, we did not measure the water content and carbon content. However, we would like to follow reviewer's suggestion to consider the influences of physical properties of biomass on the emission characteristics of rBC in our next study.

Figure 2 Photo of dry rapeseed plants that were collected in the field.

Page 4, line 22: "flexible rubber hose". This reviewer assumes that the authors mean "conductive" tubing. If so, please state that.

Reply: In this study, we use conductive silicon tube for sampling flow and measurement. To avoid overloading of aerosol particles in the heat-resistant combustion box (~144 L), the smoke was ventilate from top of the combustion box to outside of laboratory through a flexible rubber tube (OD: ~ 15cm) at a high flow rate (120 m3/h). Figure 3 is the diagram of the biomass burning experiment, described in previous literature: Inomata, S., Tanimoto, H., Pan, X., Taketani, F., Komazaki, Y., Miyakawa, T., Kanaya, Y., and Wang, Z.: Laboratory measurements of emission factors of nonmethane volatile organic compounds from burning of Chinese crop residues, Journal of Geophysical Research: Atmospheres, 120, 5237-5252, 2015.

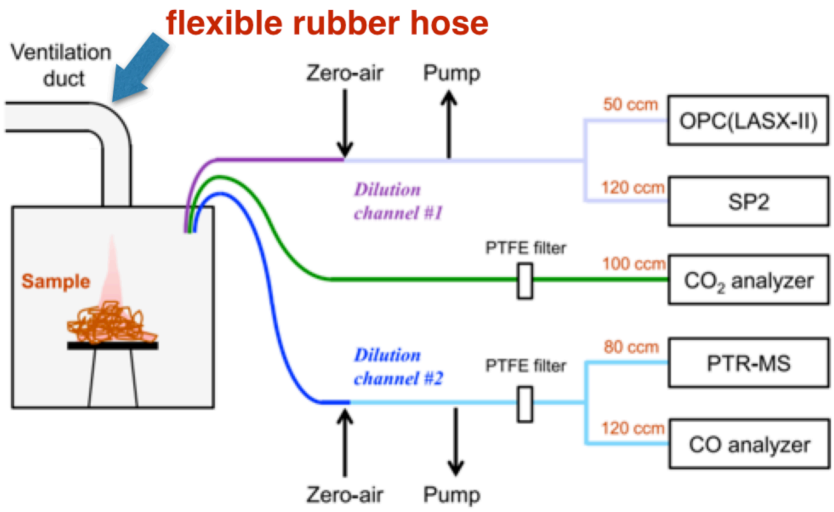

Figure 3. A schematic diagram of the laboratory biomass burning experiment

Page 4, line 24/25: The authors indicate that four samples were placed in humid conditions for 30-minutes to absorb moisture. How was the moisture content quantified? Why only 30-minutes? What was the goal? To 'coat' the fuel with some moisture or increase the moisture content of the fuel? The moisture content would be expected to potentially impact the MCE and, in turn, the rBC/CO ratio and thus better quantification would be warranted.

Reply: In this study, we prepared only four wet samples for investigating the impact of physical condition (dry or humid) of biomass on the emission characteristics of rBC particles. Because all the biomass samples were dry, we did artificial treatment on the samples by exposing them in humid condition. The biomass moisture reached about 96% as determined from one measured sample (Inomata et al., 2015). During the burning experiments, relatively more smoldering condition were achieved for the wetted samples with averaged MCE values of 0.88, 0.90, 0.91 and 0.96. We found that emission of both rBC and NMVOCs were suppressed. In our next study, we would like to measure the moisture content of biomass to quantitatively investigate the effects.

Page 7, line 14/15: The authors assume that the non-refractory coating possesses a refractive index of 1.5 - 0i. While likely valid, the authors are encouraged to acknowledge that while BB events are a major source of brown carbon (BrC), it is highly unlikely that shortwave light absorbing OA will absorb at 1064 nm - the laser wavelength utilized by the SP2.

Reply: Great thanks for the reviewer's reminds and suggestions; we will keep it in mind.

Page 9, line 28/29: As stated above, Figure 2a does not exist.

Reply: We will add the figures in the revised manuscript.

Page 10, line 25 - 28. While some trends appear to be present, the lack of water content quantification limits how much can be concluded with respect to comparing dry and wet wheat straw. The authors are encouraged to address this either by estimating the change in water

content that a 30-minute exposure of a 99% RH environment could create or acknowledge that the lack of water content quantification limits the quantitative comparison of dry and wet wheat straw emission ratios.

Reply: We would like to follow the reviewer's advise to make it clear in the manuscript that the burning experiment on wet biomass only provide quantitative results because of lack of water content quantification of biomass, although ΔrBC/ΔCO ratio for burning of wet biomass was observed to be lower than that of dry biomass. Previous study (Chen, L. W., et al., Moisture effects on carbon and nitrogen emission from burning of wildland biomass, Atmospheric Chemistry and Physics, 10, 6617-6625, 2010.) using off-line filter-based analysis (IMPROVE_A protocol) indicated that emission factor (g/KgC) of EC did not change or even decrease as increase in moisture level of biomass. Their result was consistent with ours. We would like to quantify the relationship between water content and emission characteristics of rBC in our next research.

Page 11/12 and Figure 4. The linearity between the incandescence delay time and shell/core ratio is somewhat surprising. In the application and comparison of the two methods of analyzing the rBC mixing state - incandescence delay and coating thickness was the LEO method applied to the incandescence delay time analysis? Not only will the LEO method impact the scattering signal amplitude, it could impact the scattering peak location relative to the rBC incandescence peak. Therefore, as the shell/core ratio increases evaporative losses might be expected to exert a greater impact the location of the uncorrected and LEO corrected delay times.

Reply: Yes, as pointed out by the reviewer, the S/C ratio in Figure 4 was calculated on the basis of LEO method only for the rBC-containing particle with delay time (Δt) > 0.8 μs, and the rBC particles with negative delaytime was excluded in LEO fitting analysis because in such cases rBC particles may locate at off-center positions or attach to the surfaces of non-rBC matters. To be clear that, LEO fitting method was adopted to estimate the original scattering signal amplitude of rBC-containing particle before the evaporative loss started. Whereas, Δt is observed difference in scattering peak location and incandescence peak location. They are independent parameters. To derived the rBC-containing particles' original scattering signal amplitude, LEO fitting method just needs two basic information (1) the position of center of the laser beam in the observed scattering signal profile, and we determined this position on the basis of SP2's Position Sensitive detector (PSD, Gao et al., 2007) and standard procedures (Laborde et al., 2012); Briefly, it was calculated using equation: $t_{split} + \Delta t_{split\text{-}center}$. Here, t_{split} is the observed position that PSD scattering signal (Channel 3) was inverted, and $\Delta t_{split\text{-}center}$ is a predetermined parameter describing time difference between center of laser beam (t_{center}) and t_{split} that was obtained on the basis of PSL experiment. (2) "leading edge" data that were used for Gaussian fitting. In this study, the leading edge data are selected according to the criterion of $t < -2.5\sigma$. Here, σ denotes the standard deviation of the Gaussian function of the laser intensity profile, as described in literature (Moteki et al., 2014). Therefore, the LEO method has nothing to do with scattering peak location relative to the rBC incandescence peak.

Regarding the linearity between S/C ratio and Δt, we are sorry for the misleading of the statement in the manuscript. Figure 4 mainly describes the relationship between S/C ratio and Δt for rBC-containing particles with rBC cores (MED = 200 ± 10 nm). As shown, the histograms of both the S/C ratio and Δt showed a predominant peak with a relatively long tail. A multiple-peak Gaussian fitting analysis showed that there were two modes with S/C ratio = 1.18 and S/C ratio = 1.34, corresponding to Δt = 1.74 μs and Δt = 3.18 μs. It reflected that the rBC particles had different levels of coatings in different combustion state. Meanwhile, Δt value for biomass burning aerosol was larger than that of ambient EC in the suburbs of Tokyo (Moteki et al., 2007)

at the same S/C ratio. This phenomenon was possibly related to both chemo-physical properties of coating matters and irregularity of rBC particles. Further experiments are need.

Page 13, line 19/20: The authors state that "The coating thickness of freshly emitted rBC particles from OBB was relatively small (20 nm), and this thickness was reported to increase to 65 ± 12 nm (Schwarz et al, 2008) and up to 100 nm (Taylor et al., 2014) when they experienced transport over hours or days." The authors are cautioned here. As Schwarz et al. state: "Although the sources of these emissions are unknown, their location and season of occurrence suggest that neither BB plume is from agricultural sources, but from brush fires." Similarly, Taylor et al., interrogated a boreal forest fires. The source fuel examined by the authors is agricultural in origin, not wilfires. Therefore caution must be exercised when extrapolating to expected aging behavior using two very different source fuels. As a matter of fact, this Reviewer is not convinced of the statement "We found that the aging of particles was more important than their sources in determining the coating thickness of rBC particles." More discussion is needed to buttress this statement.

Reply: We consent to the reviewer's comment that it was hardly to attribute the difference in coating thickness of rBC particle among studies only to atmospheric aging because fuel types, combustion condition were different. We will add type of biomass in the Table 3 and revise the interpretation in the revise manuscript. Besides, we noticed that, for the rBC particles outflowed from urban area, the number fraction of thickly-coated rBC particles (S/C ratio > 2 @ rBC_{MED} = 180 nm) could increased from 30% to 60% of total rBC particles as their photochemical age increased from 2h to 14 h (Moteki et al., 2007). It reflected that the photochemical process was of great importance in variation of the mixing state of rBC particles. At present, more field/airborne observational evidences of biomass burning aerosols were needed to explain the variability in coating thickness of rBC particles.

Please insert error bars on Figure 6 if possible

Reply: We will add error bar in the Figure 6.

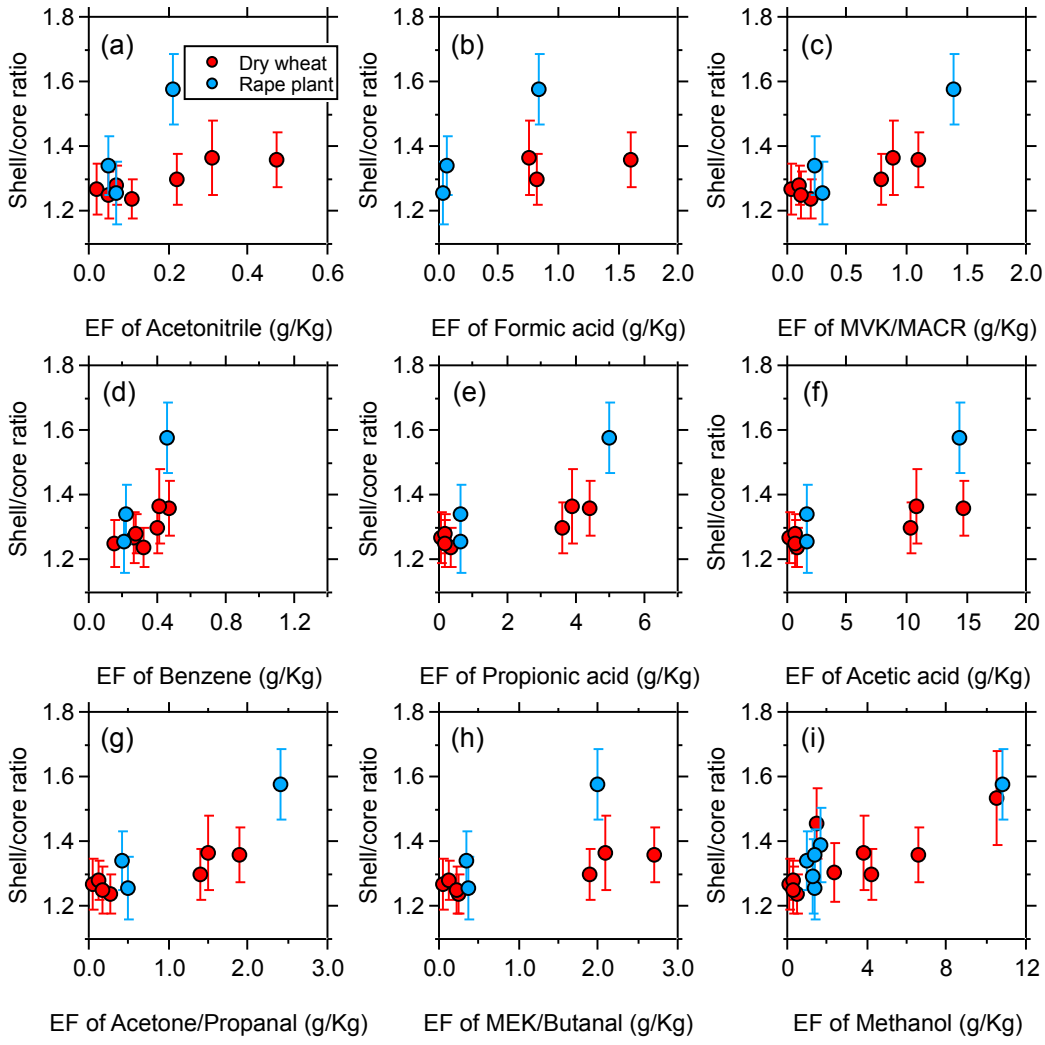

Figure 6. Variations in the shell/core ratios of rBC particles with MED = 200 ±10 nm as a function of the emission factor of each experiment. Here, EF is defined as the amount of each compound released per unit amount of dry fuel consumed. The red, green and blue colors indicate the dry wheat straw, wet wheat straw and rapeseed plant samples, respectively.

Reply to the comments of anonymous reviewer #2 on manuscript entitled " Emission characteristic of refractory black carbon aerosols in the fresh Asian biomass burning: a perspective from laboratory experiment "

We appreciate very much the insight comments and recommendations of the reviewer in improving this paper and our future research. Here, we will response to all the comments one by one as follows:

This manuscript reports results of rBC emissions and emission ratios from two different agricultural fuel types, which can be emitted during open agricultural burning and are relevant to both China and other regions where wheat and rapeseed are grown worldwide. The authors do a good job of citing previous work on ambient rBC emissions and the large uncertainties and variation in the data from different locations and sources. Unfortunately this work only focuses on rBC and does not measure non-rBC mass or aerosol optical properties. A large source of uncertainty in the aerosol optical properties from OBB is due to the presence of BrC as well as rBC, which the authors acknowledge in the introduction, but do not attempt to measure or quantify. For example, even with the assumption that the non-rBC aerosol is dominated by organics (and not direct measurement), this work could predict total aerosol optical properties and BrC absorption using the Saleh et al. 2015 (already cited) and Pokhrel et al. 2017 correlations of mass ratios with measured aerosol optical properties from different fuel types during a similar laboratory study on different biomass burning fuel emissions. A measurement of the total aerosol, Organic Aerosol and/or non-refractory aerosol mass to report rBC/OA or rBC/Total aerosol mass is used to bound BrC as referenced above as well as the total aerosol optical properties (single scatter albedo, SSA) that has been found to also be independent of fuel type and as a function of MCE. SSA is relevant to the total aerosol radiative impacts of OBB as reported Liu et al., 2014. For all of these reasons, the addition of non-rBC measurements if available for this data set would greatly enhance the impact of this work on the total aerosol optical and physical properties from near-field source emissions of two major crops from China, wheat and rapeseed, and any attempt to add this kind of total aerosol information if possible would be greatly supported.

Reply: We consented to the reviewer's comments that open biomass burning (OBB) emits not only refractory BC (rBC) particles but also substantial mounts of organic aerosols (OA), the latter of which mostly consists of light-absorbing carbon (BrC). The chemical/physical and mixing state of BrC with rBC were not well understood, which resulted in great uncertainty in evaluating the climate effect of biomass burning aerosol. Recent studies (Saleh et al., 2014, Pokhrel et al., 2017) make advances in better quantify the absorptivity and direct radiative effect of BrC mass by introducing an applicable parameter (BC-to-OA ratio)(Saleh et al., 2015). They also revealed that absorptivity of BrC depend largely on its combustion condition at the source (Saleh et al., 2014, Collier et al., 2016), reflecting of the importance to investigate the optical properties of fresh biomass burning aerosols. In the present study, initial idea is to investigate the emission characteristics of rBC from open burning of agriculture residues in East China to better constrain uncertain of rBC emission inventory and to improve the performance of regional chemistry model, because intensive crop residues burning in the field often resulted in local Air Quality Index > 500 (hazardous level) in harvest season in East China. Because of the limit in instruments, the optical property of OBB aerosol was not simultaneously measured during experiments. Nevertheless, we would like to follow the reviewer's advice to incorporate optical measurements of OBB-related aerosols in our further research.

Regarding reviewer's suggestion to predict BrC absorption on the basis of assumption that the non-rBC aerosol is dominated by organics and BC-to-OA ratio. Note that, SP2 only counts the number concentration of light scattering particle or non-rBC particles with diameter larger than 166 nm due to limitation of avalanche photodiode detector, and the size of non-rBC particles are derived on the basis of predetermined calibration curve using polystyrene sphere latex particles (PSL, Size Standard Particles, JSR Corporation, Japan). Therefore, precise estimation on optical properties of organics aerosols was difficulty due to lacking the size-resolved density, morphology information. In particular, the information about existing state of non-rBC mass (internally mixed or external mixed with rBC) for the particle with a diameter less than 166 nm was also unknown. As a whole, it is better to predict the optical property of OBB aerosol on the basis of direct measurement. Now we are purchasing a centrifugal particle mass analyzer (CPMA), we will use a DMA-CPMA-SP2 tandem system to quantify the mass concentration of rBC and non-rBC, as well as the optical properties of rBC-containing particles. By selecting a specific particle size range (for example, 200 ~ 300 nm), the mixing state and absorptivity of BrC will be quantified properly.

General comments:

The rBC sample was diluted by a factor of 46 while the gas-phase measurements were diluted by a factor of 22. There a concern that such a large dilution of the rBC would make quantification of the total rBC mass from the fire emissions have very large uncertainties in the measurements. A study of the uncertainties induced by the dilution system was studied for the aerosol sampling, but was not quantified for the gas-phase measurements. Are the authors not concerned that the different dilution ratios for the aerosol measurements and the gas-phase measurements might not introduce uncertainties in the measurements as the emissions ratios are the main deliverable of this manuscript?

Reply: We agree with reviewer that different dilution factor could result in different uncertainties in both aerosol-phase and gas-phase measurement, and finally influences the emission ratio of rBC. During biomass burning experiment, we used a high dilution factor (~46) for aerosol channel to satisfy the maximum detection limits of SP2. As a matter of fact, the same dilution factor (46) was also examined for gas-phase measurement. We found that uncertainty (2%) of carbon monoxide measurement was negligible. Because an ultrafast CO analyzer (model AL5002, Aero- 30 Laser GmbH) has relatively high detection limit (detection range 0–100 ppmv, detection limit 1.5 ppbv, integration time 1 s), we selected a low dilution factor (22). Besides, the inlet of gas-phase and aerosol-phase sampling tube was ~40 cm beside the flame of biomass, therefore except for 46 times excess dilution, biomass smoke has already underwent great dilution at the sampling location due to mixing with excess fresh air. In this study, we considered that the emission ratio of rBC (ΔrBC/ΔCO) preserved because they were emitted in seconds and they did not experience in-cloud and below-cloud scavenging processes. In future work, we will follow reviewer's suggestion to use the same dilution ratio when both rBC and CO concentrations were measured.

It is also unclear as to why the authors did not conduct dilution studies to see if the rBC coating was changing by introducing a 1/46 dilution ratio. Sampling a range of initial fuel sample emissions including smaller burn sizes (< 20 g) from the same fuel types would have greatly enhanced this study.

Reply: We agree to the reviewer's suggestions. As implied, different dilution condition will impact the gas-aerosol equilibrium of semi-volatile organic matter, the latter of which tend to influence the mixing state of rBC particles due to continuous condensation/evporation

processes. In this study, we did not quantify the effect of dilution on the coating thickness of rBC particles because the total dilution factor can not be exactly determined since the sampling inlet was besides the combustion flame, and biomass smoke has already diluted due to mixing with fresh air in the combustion chamber. Besides, to avoid saturation of SP2 measurement, the burning biomass was only ~20 gram, and the rapid evolution of the combustion process also resulted in difficulty in discriminating the dilution effect. Therefore, large-scale burning experiment (like FLAME experiments) is much applicable for investigating dilution effects, and parallel measurements using two SP2 with different dilution factors is another option. In our future research, we would like to follow the reviewer's advice to investigate the dilution effect.

What is the width of the rBC size distributions from each experiment? While MMD of rBC MED is reported for each experiment, for example, what is the sigma or range in rBC size distributions? Is the rBC a tight size distribution/at what diameter does the rBC drop off for both the high and low ends? A table with this information and/or a graph of the rBC size distribution averages or examples would make a good addition to this manuscript in understanding the size range of rBC emissions.

Reply: Great thanks for the reviewer's suggestions. We will add the information in the table 2. Besides, We make a correction in the curve fitting of mass size distribution of rBC particles according to the comments of the reviewer #1. As a matter of fact, Lognormal function fitting is better than that of Gaussian function in most instances. This phenomena is more prominent in smoldering-dominant case that that in flaming-dominant cases (as shown in Figure 1). We will correct the expressions in the revised manuscript, and add dM/dlogDp plot in the Figure 2a.

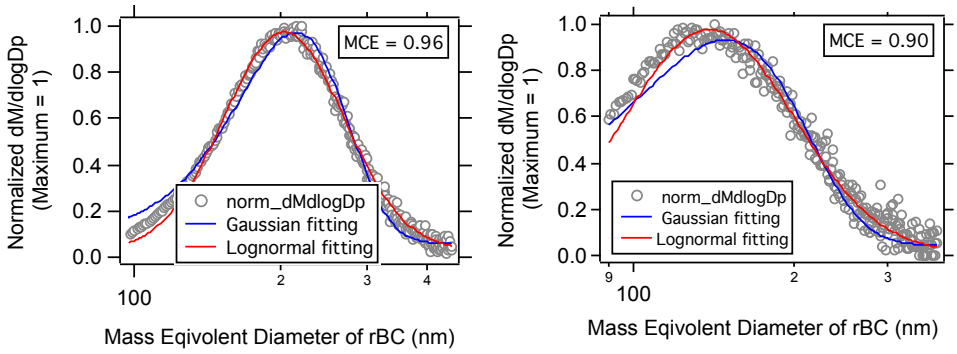

Figure 1 Gaussian and lognormal fitting for normalized mass size distribution of rBC for flaming- (left) and smoldering- dominant case (right).

Could the data from each burn be separated into smoldering and flaming analysis? What was the reason for using a fire-integrated MCE analysis when the first Figure separates the different phases? How was the separation of combustion conditions done for that figure? Was it using 0.9 as referenced in the introduction (Page 3 Line 10-11) or 0.95 in the results section (Page 11 Line 2) to separate the phases (or some- thing else)? This information is referenced in different ways in the results section, but should be clearly defined in the experimental section and remain constant throughout the results section (which it may be but it's not clear to the reader how this was done).

Reply: As mentioned in the manuscript, the combustion processes evolved rapidly. Flaming and smoldering combustion sometimes occurred at the same time at different part of biomass, and clear discrimination between flaming phase and smoldering phase was difficult. Therefore, we used a fire-integrated MCE to represent the general burning condition of biomass. Regarding the criterion, a value of MCE > 0.95 and a value of MCE < 0.9 was used in literatures as criterion to separate flaming and smoldering phase, respectively. We followed the same criterion in the manuscript. Figure 1 shows two examples reflecting the temporal variations of number concentrations of rBC and non-rBC particles. We found a prominent phenomenon that occurrence of peak of number concentration of non-rBC particles was obviously later than that of rBC particles, and the MCE value = 0.95 always fall in the middle of these two peak. It can be an indicator that the combustion shifted from the flaming-dominant to smoldering-dominant state. We will clearly state the MCE criteria in the revised manuscript.

In the absence of other size distribution or measurements of the non-refractory or scattering aerosol, if this SP2 is able to measure scattering particles up to 1 micron in diameter, could the scattering data be presented in addition to the rBC data to give a more representative picture of the total aerosol emissions and optical properties?

Reply: As suggested by the reviewer, we would like to add size-distribution information about both the rBC and non-rBC particles during the burning experiment, as shown Figure 2 below. SP2 only detects light-scattering or non-rBC particles with diameter larger than ~ 166 nm. Presuming that non-rBC particles were in spherical configuration, the volume size distribution could be also determined. In the present study, non-rBC particles less than 166 nm in size (the lower detection limit of the SP2) accounted for limited fraction (4%) of the total aerosol volume. The maximum size of non-rBC particle was estimated to be ~ 750 nm. It is worth noting that we found that there were two modes for the volume size distribution of non-rBC particles with a peak at 307 nm and another peak at 606 nm. The second minor peak was related to an extreme smoldering case (discussed in paper, Inomata et al., 2015, JGR), since the number concentration was very low.

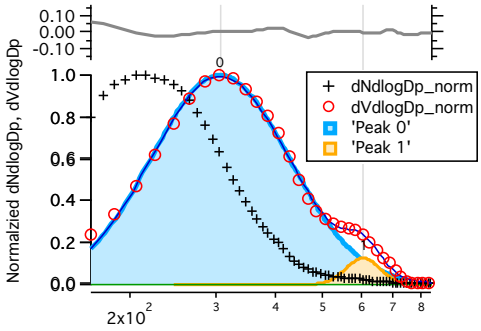

Figure 2 Normalized number size distribution (dN/dlogDp) and normalized volume size distribution (dV/dlogDp) for non-rBC particle during experiment.

Similar to the response of the first reviewer, the authors focus on the combustion state influencing the rBC emissions. What about the effect or concern for differences due to different fuel types, e.g. agricultural fuels versus wildfire fuels? Fuel types vary largely for OBB, and this should not be neglected. The authors are advised to modify the interpretation of the results

and text at times to accommodate this as another reason for the large variability in reported rBC emissions from both laboratory and ambient measurements.

Reply: We consented to the reviewer's insight comments. To avoid misleading, we will specify the type of biomass in the table 3 and correct our statements in the revised manuscript. As the reviewer implied, there are large differences in carbon/water contents and physical structure for different biomasses, which may result in their different inflammability, as well as mixing state of rBC particles, though some studies (e.g. Collier et al., EST, 2016) pointed out that general characteristics of biomass burning aerosols depended strongly on the combustion processes of a fire, and Saleh et al., (2014, NG) reported that aerosol absorptivity depends largely on burning condition, not fuel type.

The addition of the wet data needs further substantiation in the methods, focus in the text, and data interpretation. Without this it should be removed from the text (or alternatively moved to SI).

Reply: As suggested, we will move this part to supporting information.

Specific Comments:

Page 1, Line 14: Are "rape plants" the same as rapeseed? If so, suggest adding"also known as rapeseed" to the text.

Reply: We will use rapeseed plants in the context for consistency.

Page 1, Line 15: Do the authors mean "used" when they say "adopted"? Adopted implies a change was made to the standard SP2 rBC sampling regime. If this was done, please state and explain, and if it was not, please change the text to "used" or similar wording as the SP2 is a standard instrument for measuring rBC.

Reply: In the revised manuscript, we will replace "adopted" by "used".

Page 1, Line 1 – Page 2, Line 1: "This study highlights that open biomass burning produces the majority of coated rBC particles, which have considerable ability to affect cloud processes and influence regional climate." This significance statement in the abstract overstates the results reported in this paper. It is unclear how the authors can state that biomass burning produces the majority of rBC coated particles in the atmosphere from a laboratory study of two different agricultural fuel types. A similar statement could be made along the lines of agricultural fuel types produce coated rBC particles, . . . ", which would not over interpret the reported results.

Reply: As suggested, we will revise the overstatement in manuscript, as follows: " This experimental study found that mixing state of rBC particles from biomass burning strongly depend on the its combustion processes, and overall MCE should be took carefully into consideration while the climate effect of rBC particles from open biomass burning was simulated."

Page 2, Line 3-4: What about cloud albedo?

Reply: We will add "cloud albedo" in the sentence.

Page 2, Line 7: It would be helpful to define OBB since this is not common terminology for a general audience. The reviewer suggests defining OBB to include agricultural and wildfire emissions, but mainly suggests adding a sentence to define OBB clearly to the reader.

Reply: we will add a terminology in the manuscript.

Page 2, Line 9: Do the authors mean VOCs or SVOC's? Both are common terms and are not used interchangeably.

Reply: Thanks for pointing out the typo, and I will delete the "VOCs" since it is not used in the context.

Page 2, Line 10: Suggest removing "in smoke"

Reply: "in smoke" is removed in the revised manuscript.

Page 2, Line 19 – 20: "Hygroscopic growth of rBC-containing particles also results in much more compact rBC cores." Is there a reference to support this statement? Suggest moving the Fan 2016 reference to a modelling study in the following sentence here and at the beginning of the sentence adding "Modelling studies indicate that the . . . " unless a measurements reference can also be added to support this statement.

Reply: We revised the sentence as suggested, as follows: " Modeling study indicated that hygroscopic growth of rBC-containing particles also results in more compact rBC cores (Fan et al., 2016). "

Page 2, Line 21-22: "Second, the rBC particles are often located at off-center positions or may possibly be attached to the surfaces of non-rBC particles." Are there any references that can substantiate this sentence? If none can be found, please remove this sentence or change it to a statement implying these morphologies are possible but not implying the significance of off-center rBC particles in ambient aerosols.

Reply: The sentence will be changed to "Second, the rBC particles sometimes were also reported to be attached on the surface of non-rBC matters (Moteki et al., 2014)."

Page 2, Line 28: add Liu 2015b to the list of citations for BrC influencing overall rBC absorption enhancements.

Reply: I will cite Liu et al., 2015b in the manuscript.

Page 3, Line 4-5: Suggest relating tar balls to secondary organic aerosol SOA from BB sources to link the two terminologies. Are tar balls one type of SOA defined as being low volatility and from BB sources? Are there any known optical properties that can be ascribed to this particle type, e.g. likely to contain BrC? A brief summary/explanation of the definition of what a tar ball is in terms of its formation, sources, physical and optical properties would benefit a larger audience.

Reply: In the revised manuscript, we will state that " It was reported that "tar-ball" that mostly consisted of BrC and secondary organic aerosols with low volatility were also emitted during smoldering combustion (Pósfai et al., 2004)."

Page 3, Line 12: When defining the rBC emission ratio, rBC is rBC mass concentration, correct? Likewise CO is a mixing ratio? Suggest adding this information to the initial definition here.

Reply: Initial definition will be added in the revised manuscript, as folows: "The rBC emission ratio (ΔrBC/ΔCO), which is defined as the enhancement of mass concentration rBC (in unit of ng/m3) with respect to its background versus that of CO (in unit of ppbv, parts per billion volume), ... "

Page 3, Line 27: "The variability in ΔrBC/ΔCO among observational studies also result from differences in sampling locations and conditions." After this section would be a good time to introduce the topic of variability due to fuel type as suggested in the general comments.

Reply：I will follow the reviewer's suggestion to revise the content of second paragraph in page3, as follows: "The rBC emission ratio (ΔrBC/ΔCO), which is defined as the enhancement of mass concentration rBC (in unit of ng/m^3) with respect to its background versus that of CO (in unit of ppbv, parts per billion volume), is an applicable indicator for constraining the rBC emission inventory for models (Pan et al., 2011). The variability in ΔrBC/ΔCO among observational studies mostly results from differences in measurement techniques, fuel type, and burning conditions. For example, observations made onboard the NOAA WP-3D aircraft yielded ΔrBC/ΔCO values of 9 ± 2 ng/m^3/ppbv (Spackman et al., 2008) and 17.4 ng/m^3/ppbv (Schwarz et al., 2008) for brush fire plumes during the TexAQS field campaign. Airborne observations on the NASA DC-8 aircraft indicated that the ΔrBC/ΔCO values were 8.5 ± 5.4 ng/m^3/ppbv for plume of boreal forest and agriculture fires in Asia, and 2.3 ± 2.2 ng/m^3/ppbv for wildfire plume in North America (Kondo et al., 2011). Observations using a multi-angle absorption photometer (MAAP, which employs the filter-based light absorption technique; here we consider BC instead of rBC) at mountain sites (30.16°N, 118.26°E, 1840 m a.s.l.) in South China yielded high ΔBC/ΔCO values (10 - 14 ng/m^3/ppbv) when the site was subjected to burning of crop residues (Pan et al., 2011)."

Page 4, Line 19 – 20: Suggest removing "to preserve its original state" since while this storage would limit deposition onto the samples it would not preclude semivolatile evaporation and/or water loss etc.

Reply：As suggested, the statement "to preserve its original state" will be deleted. As a matter of fact, the farmer normally dries agriculture residues in the sun for days before the biomasses are burned. The samples that we collected in the field were dehydrated so that evaporation of semi-volatile and water vapor should be negligible.

Figure 3 Photo of dry rapeseed plants that were collected in the field.

Page 4, Line 26: "To monitor the evolution of the combustion process of biomass, the mixing ratios of CO2 and CO in the OBB smoke were measured simultaneously." The gas phase mixing ratios were measured "to monitor the combustion conditions" of the rBC, correct? The statement here seems to imply aging, which these experiments are more representative of near-field emissions and do not probe aerosol aging in the plume as might be interpreted with the current sentence. The reviewer also cautions the authors to imply that all fires proceed from flaming to smoldering combustion conditions both here and other locations in the text since OBB can vary over time and does not always proceed as straightforward as a laboratory study.

Reply: We agreed to the reviewer's comments. Here, mixing ratios of CO and CO2 were measured to calculate Modified Combustion Efficiency (MCE), the latter of which is a applicable metric to estimate the combustion phase of biomass. To avoid misleading, we will revise the statement in the revised manuscript, as follows: "As mentioned, MCE is a useful metric for describing the combustion phase of biomass burning, and the calculation of MCE requires simultaneous measurements of CO and CO2 concentration. Here, mixing ratio of CO2 was measured using a Li-7000 CO2 analyzer..."

Page 5, Line 31-33: Suggest showing at least an example of the rBC size distribution from one or an average from several burns ideally as a figure in the main text, and alternatively in the SI. Is a Gaussian fit best or does lognormal fit the rBC mass equivalent diameter data better?

Reply: We will add the mass size distribution of rBC particle in the manuscript. We found that lognormal curve fitting is slightly better than that of Gaussian function for rBC particles in most burning instances, in particular for smoldering-dominant case, as shown in Figure 4. We will correct the statements.

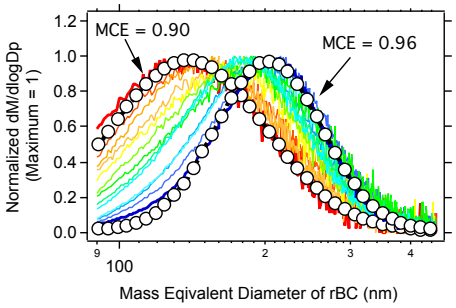

Figure 4 Normalized mass size distribution of rBC particles for all the burning cases.

Page 6, Line 3-4: The SP2 scattering channel was not saturated for the 500 nm and 1000 nm PSL's? The lower limit of the scattering detection is listed as 166 nm. What is the upper limit for this instrument? If this SP2 can detect scattering particles up to 1 micron in diameter, it would advantageous to report this data in addition to the rBC measurements.

Reply: Great thanks for the reviewer's suggestion. Regarding calibration, scattering signal for PSL particle at both Dp = 500 nm and Dp = 1000 nm were saturated for APD of SP2. Nevertheless, peak height of scattering signal for PSL particle at Dp = 500 nm could be estimated properly according Gaussian fitting by SP2. Unfortunately, it was not available for

PSL particle at Dp = 1000 nm due to strict data screening. Maximum size of non-rBC particle was estimated to be ~ 750 nm, and the We will report the information in the revised manuscript.

Page 8, Line 10: Fire-integrated MCE's are reported and listed in Table 2. What is the variability over the course of each burn? Could the range of MCE's from each experiment also be included in this table?

Reply: We will include 10th, and 90th percentile values for each experiment.

Page 9, Line 8-10: Could this be related to how the burns were started? Information on the fires were started/lit should be added to the information in the experimental section as well as being considered as an potential explanation for this initial rBC peak in number at the start of sampling.

Reply: We will add information about the ignition of biomass in the experimental section, as suggested.

Page 9, Line 22: ". . . because the combustion process differed significantly." Does this imply that the experiments do not generally proceed from flaming to smoldering as well as the examples in Figure 1? Please explain what this sentence means as it was not clear to the reviewer.

Reply: We will revise the expression to avoid misleading. In general, the combustion proceed from flaming to smoldering for most case, however the time duration of in flaming or smoldering were different. We will also add the total duration of combustion processes in the Table. Of course, we cannot avoid the situations that both flaming and smoldering combustion occurred at different position of fuel at the same time. Therefore, we considered using a fire-integrated MCE to present the overall combustion condition.

Page 9, Line 24: "45 times dilution". Earlier this was stated as 46 – please explain the reason for the difference.

Reply: We will correct the mistake.

Page 9, Line 27-29: Reference is made to the rBC displaying "a perfect Gaussian distribution for all burning cases." Reference is also made to a Figure 2a, which appears to not exist in this version of the text. This size distribution information should be added to the Figure. Is the rBC distribution averaged over the course of the whole experiment? rBC distributions are not often perfect Gaussians, therefore, the addition of this information to the Figure should be included.

Reply: As suggested, we will include the mass size distribution of rBC particles as shown previously.

Page 9, Line 31: Change " tends to produce larger particles" to "tends to produce larger rBC particles".

Reply: We will change to "tend to produce larger rBC particles"

Page 10, Line 2: "small" seems to contract the data in Figure 2 and previous sentence since the rBC MMD increases for flaming combustion.

Reply: Sorry for misleading, I will revise this statement as follows: " This result indicates that flaming combustion tends to produce larger rBC particles than smoldering combustion. It is consistent with previous studies, which reported that rBC particles formed considerably in intense flaming combustion due to less efficient transport of oxygen into the interior flame zone. As a result, growth in the size of rBC particles was rapid because the coagulation rate of particles is roughly proportional to the square of their number concentration (Lee and Chen, 1984)."

Page 11, Line 1 – 4: But are these reported differences in delta rBC/delta CO statistically significant? Based on the uncertainties, there does not look to be enough difference within the uncertainties of the measurements to warrant significant difference and subsequent interpretation.

Reply: We will add more information and revise the manuscript as follows: "the average ΔrBC/ΔCO ratio was 13.9 ± 10.1 ng/m^3/ppbv for the burning cases with a fire-integrated MCE > 0.95. This value was probably a low estimation since both flaming and smoldering combustions were included in the calculation. However, by selecting the cases with both the 10th and 90th percentiles MCE value > 0.90, we found that the average ΔrBC/ΔCO ratio was 23.1 ± 11.4 ng/m^3/ppbv ...".

Page 11, Line 29-30: What is the reason for focusing on the time delay analysis data when the LEO-fitting coating thickness analysis that yields more information with fewer uncertainties was also extensively done? Was the LEO-fitting analysis only done on the MED = 200 rBC core-containing particles? 200 nm MED is relatively large for most rBC studies, and even for some of the data presented here where MMD's are reported down to 144 nm MED rBC for some of the experiments. How much do the results change if 150, 180 or 220 MED cores were used for the LEO analysis?

Reply: As pointed out by the reviewer, LEO-fitting analysis could provide direct information about the coating thickness of rBC particle. Nevertheless, the delaytime of occurrence of incandescent peak *after* scattering peak also was informative for the reader to understand the real situation when the particle was passing through the laser. For instance, number of previous studies (Sedlacek et al., 2012, GRL; Moteki et al., 2007, GRL; Taketani et al., 2014, JGR, Miyakawa et al., 2015, AE, etc.) directly used the delaytime to indicate the degree of aging/coating of rBC-containing particles. rBC-containing particle in non-shell-core structure could also be determined if the delaytime value was a negative value (Sedlacek et al., 2012).

Regarding the LEO-fitting analysis, we agree with the reviewer's concerns that most of rBC particles had small size (less than 200 nm), and coating thickness could be calculated on the basis of LEO-fitting method. It was worthy noting that low detection limit of scattering particles was ~ 166 nm, implied that information about the rBC-containing particles with a diameter less than 166 nm was missing, and it will be problematic statistically to identify the relationship between coating thickness and MCE. Although we did analysis for all the data, we just reported the rBC particles with larger MED in the manuscript.

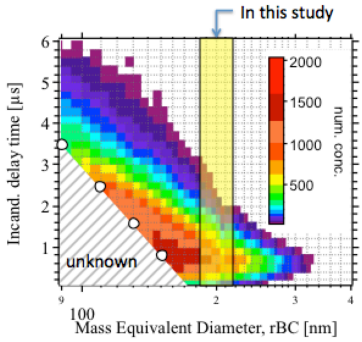

Figure 5 An example of variation of delaytime as a function of MED of rBC. Line-shaded area indicates that the information is missing. The yellow-color shaded area indicate the data that was analyzed in the manuscript.

Page 12 and Figure 4: Can you separate the data into flaming and smoldering to substantiate the claim that the two modes present in all the data are due to the different combustion phases?

Reply: In this study, we found that S/C ratio for rBC particles with MED = 200 nm increase as MCE decrease in most of burning case (Figure 6 shows two examples). As demonstrated, S/C ratio was ~ 1.2 when MCE > 0.95 (flaming-dominant phase) and ~ 1.4 when MCE < 0.90 (smoldering-dominant phase), in accordance with the estimated results from multi-Gaussian curve fitting. Because the data in flaming and smoldering phase overlapped significantly (as Figure 4 shown in the manuscript), it is better to demonstrate the differences using multi-Gaussian curve fitting method. We will add more information in the Figure 4 in the manuscript for better understanding of readers.

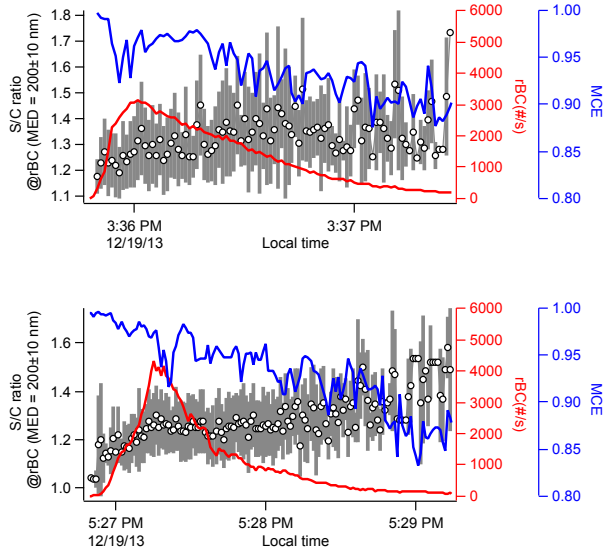

Figure 6 Two examples demonstrating that S/C ratio increase as MCE decrease for rBC particles with MED = 200 nm during combustion process.

Page 13, Line 6-13: Add the range of S/C reported for the ARCTAS data to the text. How much weight can be placed on a S/C change of 1.2 to 1.4? Could some of the other studies help to substantiate why this is a significant difference? More explanation and reference to other datasets here in the text would be advised since the data in Figure 5 appears to have a lot of scatter in the data and poor r2 fit values.

Reply: We will report the range of S/C ratio from ARCTAS data, and revise the statement as follows " Airborne measurements during the ARCTAS campaign (Kondo et al., 2011) showed an increasing tendency for the values of the S/C ratio (1.3 ~ 1.66) with increase of MCE, and the authors explained that this phenomena was because flaming phase plumes were more aged than the smoldering plumes, a 205 ± 40% increase of the volume of the coating materials resulted in a larger S/C ratio than that of rBC particles in smoldering plume."

We consented to the reviewer's comments that a S/C ratio increasing from 1.2 to 1.4 was not significant. As a matter of fact, the volume of non-rBC coatings could increase by 140% when S/C ratio increases by 20%, which will possibly lead to mass ratio of rBC to non-rBC (M_R = $m_{non\text{-}BC}$ /m_{rBC}) around 2.7. Recent study (Liu et al., NG, 2017) reported that the absorption enhancement due to optical lensing effect was significantly important at M_R = 3 for biomass burning aerosols. Liu et al., (2014, GRL) also reported that MCE could explain 60% of variability in single scattering albedo of biomass burning aerosols. It implies that the moderate variation in mixing state of biomass burning aerosol may have significant effect on its optical properties. As suggested by the reviewer, we will perform the optical measurement of rBC particle from biomass burning in our next research.

Liu, D., et al., (2017), Black-carbon absorption enhancement in the atmosphere determined by particle mixing state, Nature Geosci, advance online publication, 10.1038/ngeo2901

Liu, S., et al. (2014), Aerosol single scattering albedo dependence on biomass combustion efficiency: Laboratory and field studies, Geophys. Res. Lett., 41, 742–748, doi:10.1002/2013GL058392.

Page 13, Line 14 – 15: Is this for all the data? Is there a difference in the different fuel types or MCE flaming versus smoldering conditions if the data were to be averaged from all experiments and separated into different categories? Adding the range of thicknesses sampled should also be added to the text here as the coating thicknesses look to cover the full ranges reported by the aircraft data referenced in the text.

Reply: Yes, histogram analysis of coating thickness was performed for all the data. We found that it shows a lognormal distribution with a mode value of 20 nm and the standard deviation of 0.54. Coating thickness was mainly ranging from ~ 11 nm to 54 nm. The same analysis was also done for rBC particles with MED = 250 nm, what the difference was that histogram showed a Gaussian distribution with a mode value of ~17 nm. We will add the information in the revised manuscript.

Page 13, Line 19 – 29: Since Figure S4 indicated coating thicknesses of 0 – at least 60 nm sampled from this data, is it possible to state that atmospheric aging results in increased rBC coatings? The data presented here and in Table 3 is from a large variety of fuel types, combustion conditions, and atmospheric aging timescales that this level of interpretation requires more investigation isolating different fuel types and atmospheric aging timescales.

Reply: We consent to the reviewer's comment that it was hardly to attribute the difference in coating thickness of rBC particle among studies only to atmospheric aging because fuel types, combustion condition were different. We will add type of biomass in the Table 3 and revise the interpretation in the revise manuscript. Besides, we noticed that, for the rBC particles outflowed from urban area, the number fraction of thickly-coated rBC particles (S/C ratio > 2 @ rBC_{MED} = 180 nm) could increased from 30% to 60% of total rBC particles as their photochemical age increased from 2h to 14 h (Moteki et al., 2007). It reflected that the photochemical process was of great importance in variation of the mixing state of rBC particles. At present, more field/airborne observational evidences of biomass burning aerosols were needed to explicit the variability in literature.

Page 14, Line 4-5: The S/C ratio appears to increase with the EF of the NMVOC's for dry data while the wet wheat S/C does not look to depend on EF of NMVOC's. It also looks as if the S/C for the wet data is at the maximum for the dry data. More discussion of these differences should be included in the text if this is found to be significant. If not, then the wet data should be removed from the manuscript as it does not have much interpretation of the data collected here anywhere else in the manuscript.

Reply: We will delete the data from burning of wet wheat, as suggested by the reviewer.

Page 14, Line 9-10: Without a reference for this hypothesis or substantiation from the data presented here, this should be removed as it is too speculative.

Reply: We will remove the sentence from the manuscript.

Technical Corrections:

Page 2, Line 3: remove "the" from ". . . play a vital role in the climate change. . ."

Reply: "the" is removed in the sentence.

Page 2, Line 5: remove "their" from "its their"

Reply: "their" is removed in the sentence.

Page 2, Line 11: remove ", evidently"

Reply: "evidently" is removed in the sentence.

Page 2, Line 19: remove "much"

Reply: "much" is removed in the sentence.

Page 3, Line 27: "The variability in ΔrBC/ΔCO among observational studies also result from differences in sampling locations and conditions." – change "result" to "results"

Reply: "result" is replaced by "results".

Page 4, Line 10: Change ". . . we conducted open burning experiments. . . " to ". . . we conducted laboratory burning experiments. . . ".

Reply: To avoid misleading, we replaced "open" by "laboratory" here and all other parts in the manuscript.

Page 4, Line 20: Remove "generally"

Reply: "generally" is removed in the sentence

Page 5, Line 32: change "fitted" to "fit"

Reply: "fitted" is replaced by "fit".

Page 13,Line 9: Remove "As a matter of fact"

Reply: "As a matter of fact" is removed in the sentence.

Page 14, Line 5: Change "open" to "laboratory"

Reply: "open" is changed to "laboratory" in the manuscript.

Page 14, Line 13: Remove "urgently"

Reply: "urgently" is removed in the sentence.

Page 14, Line 26: Remove "obviously"

Reply: "obviously" is removed in the sentence.

Page 14, Line 27: Add "rBC" to say "result indicated that the rBC coagulation/growth. . ."

Reply: "rBC" is added here.

Table 1: Change "C/S ratio" to "S/C ratio"

Reply: "C/S ratio" is corrected to "S/C ratio"

Table 2: Should the last column say "MED of rBC MMD"?

Reply: MED is abbreviation of Mass Equivalent Diameter, and MMD is Mass Mode Diameter, we will add annotation in the Table 2.

Figure 1: Needs the information added to the figure or figure text on the different color blocks of data shown in yellow, red and blue.

Reply: The information about the color blocks in yellow, red and blue is add in caption of Figure 1.

Figure 2: Needs an explanation of the lines presented in the figure and the circle around one set of data. Also the text refers to 2a and 2b within the Figure which are not present.

Reply: We will add the explanation of the lines and circle in the figure. The missing figures 2a and 2b will be added in the manuscript.

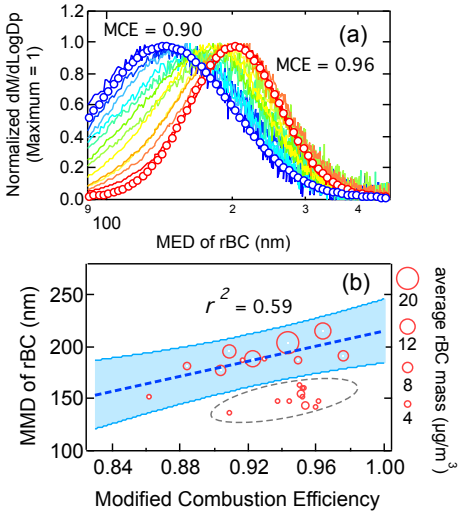

Figure 4: Would changing the color scale on the number of rBC in the Figure enhance the ability for the reader to discern the two modes that can be separated with the histograms? Label the modes flaming and smoldering on the figure would also make the main points of the Figure more clear to the reader.

Reply: We will polish the Figure 4 as suggested by the reviewers.

Emission characteristics of refractory black carbon aerosols from fresh biomass burning: a perspective from laboratory experiments

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Abstract. The emission characteristics of refractory black carbon (rBC) from biomass burning are essential information for numerical simulations of regional pollution and climate effects. We conducted combustion experiments in the laboratory to investigate the emission ratio and mixing state of rBC from the burning of wheat straw and rapeseed plants, which are the main crops cultivated in the Yangtze River Delta region of China. A single particle soot photometer (SP2) was used to measure rBC-containing particles at high temporal resolution and with high accuracy. The combustion state of each burning case was indicated by the modified combustion efficiency (MCE), which is calculated using the integrated enhancement of carbon dioxide and carbon monoxide concentrations relative to their background values. The mass size distribution of the rBC particles showed a lognormal shape with an mode mass equivalent diameter (MED) of 189 nm (ranging from 152 nm to 215 nm), assuming an rBC density of 1.8 g/cm^3. rBC particles less than 80 nm in size (the lower detection limit of the SP2) accounted for ~5% of the total rBC mass, on average. The emission ratios, which are expressed as ΔrBC/ΔCO (Δ indicates the difference between the observed and background values), displayed a significant positive correlation with the MCE values and varied between 1.8 – 34 ng/m^3/ppbv. Multi-peak fitting analysis of the delay time (Δt, or the time of occurrence of the scattering peak minus that of the incandescence peak) distribution showed that rBC-containing particles with rBC MED = 200 ± 10 nm displayed two peaks at Δt = 1.7 μs and Δt = 3.2 μs, which could be attributed to the contributions from both flaming and smoldering combustion in each burning case. Both the Δt values and the shell/core ratios of the rBC-containing particles clearly increased as the MCE decreased from 0.98 (smoldering-dominant combustion) to 0.86 (flaming-dominant combustion), implying the great importance of the rapid condensation of semi-volatile organics. This laboratory study found that mixing state of rBC particles from biomass burning strongly depend on the its combustion processes, and

overall MCE should be took carefully into consideration while the climate effect of rBC particles from open biomass burning was simulated.

1 Introduction

Black carbon aerosols in the atmosphere play a vital role in climate change by absorbing solar radiation and altering the formation, lifespan and albedo of clouds (Novakov et al., 2005;Ramanathan and Carmichael, 2008;Bond et al., 2013). It was operationally defined according to its light absorption capacity, chemical reactivity and/or thermal stability (Lack et al., 2014). One definition is refractory black carbon (rBC), which corresponds to the carbon mass derived from laser-induced incandescence (LII) emission at a boiling point at 4000 K. Open biomass burning (normally refers as the burning of living or dead vegetation such as agriculture residue, grass, forest, leaves, shrub etc. due to anthropogenic activities and natural causes, abbreviated as OBB) is one of the important sources of rBC, and it contributes ~42% of atmospheric loadings in the global emissions budget (Bond et al., 2004). In addition to rBC, OBB also simultaneously emits substantial amounts of semi-volatile organics that undergo extremely complicated mixing processes with rBC during transport. Jacobson (2001) pointed out that the light absorption by internally coated rBC by inorganic/organic matter could increase, due to the "lensing effect," in which a non-absorbing coating directs more light to the cores of rBC particles. However, the debate on the absorption enhancement capacity of rBC-containing particles is still ongoing, because discrepancies exist between observations and theoretical predictions based on Mie scattering models (Shiraiwa et al., 2010;Cappa et al., 2012) and among observation results from different locations and using different sources (Healy et al., 2015;Liu et al., 2015b;Massoli et al., 2015;Ueda et al., 2016). The widely accepted explanations are as follows. First, the morphologies of rBC particles differ among different sources, and the process of particle aging in the atmosphere changes the physical structure of the particles. For instance, several studies have found that rBC particles with a fractal structure tend to collapse to a more closely packed shape when they are thickly coated (Adachi et al., 2010;Chen et al., 2010;He et al., 2015). Modeling study indicated that hygroscopic growth of rBC-containing particles also results in more compact rBC cores (Fan et al., 2016). Second, the rBC particles sometimes were also reported to be attached on the surface of non-rBC matters (Moteki et al., 2014). Either of these circumstances renders the core-shell model invalid or introduces biases into the results. Sedlacek et al., (2012) reported that a large fraction (60%) of rBC-containing particles with non-core-shell structures exist in biomass burning plumes. Methodologies have also been developed to distinguish particles with attached rBC (bare rBC on the surfaces of non-rBC particles) from rBC-containing particles with the core-shell structure (Moteki et al., 2014). In addition, OBB is an important source of brown carbon (BrC), which has distinct light absorbing features with different wavelength dependence, and their coexistence of rBC and BrC also influences the overall absorption enhancement of rBC-containing particles (Lack et al., 2012;Liu et al., 2015a;Liu et al., 2015b;Saleh et al., 2015).

Biomass normally consists of celluloses/hemicellulose, organics and water. The emissions of rBC from OBB is determined

by the composition (carbon content) of the biofuel and the evolution of combustion (Yokelson et al., 1997;Andreae and Merlet, 2001). Briefly, the combustion process of biomass begins with the pyrolysis of biofuel molecules and the evaporation of flammable mixtures (i.e., volatile compounds) and water, which is followed by flaming combustion that converts most carbon substances to carbon dioxide (CO_2). rBC particles are also produced in large quantities at this stage due to the oxygen-limited conditions and high temperatures. The last stage is smoldering combustion, which predominantly emits carbon monoxide (CO) and organics (Andreae and Merlet, 2001). It was reported that "tar-ball" that mostly consisted of BrC and secondary organic aerosols with low volatility were also emitted during smoldering combustion (Pósfai et al., 2004). Detailed descriptions of the physical properties of biomass burning particles have been provided in the literature (Reid et al., 2005;Akagi et al., 2011). The modified combustion efficiency (MCE), which is defined as $\Delta CO_2/(\Delta CO_2+\Delta CO)$ (Δ is the difference in measured concentrations between the OBB plume and the corresponding background value), has been used to indicate the relative amounts of flaming and smoldering combustion during a fire for characterizing the emission of rBC and organic matter. An MCE value > 0.95 is normally regarded as flaming-dominant combustion, whereas MCE < 0.9 represents smoldering-dominant combustion (Kondo et al., 2011;Pan et al., 2012;Pan et al., 2013;May et al., 2014).

The rBC emission ratio (ΔrBC/ΔCO), which is defined as the enhancement of mass concentration rBC (in unit of ng/m^3) with respect to its background versus that of CO (in unit of ppbv, parts per billion volume), is an applicable indicator for constraining the rBC emission inventory for models (Pan et al., 2011). The variability in ΔrBC/ΔCO among observational studies mostly results from differences in measurement techniques, fuel type, and burning conditions. For example, observations made onboard the NOAA WP-3D aircraft yielded ΔrBC/ΔCO values of 9 ± 2 ng/m^3/ppbv (Spackman et al., 2008) and 17.4 ng/m^3/ppbv (Schwarz et al., 2008) for brush fire plumes during the TexAQS field campaign. Airborne observations on the NASA DC-8 aircraft indicated that the ΔrBC/ΔCO values were 8.5 ± 5.4 ng/m^3/ppbv for plume of boreal forest and agriculture fires in Asia, and 2.3 ± 2.2 ng/m^3/ppbv for wildfire plume in North America (Kondo et al., 2011). Observations using a multi-angle absorption photometer (MAAP, which employs the filter-based light absorption technique; here we consider BC instead of rBC) at mountain sites (30.16°N, 118.26°E, 1840 m a.s.l.) in South China yielded high ΔBC/ΔCO values (10 - 14 ng/m^3/ppbv) when the site was subjected to burning of crop residues (Pan et al., 2011). The large variability also resulted from difference in sampling altitude. For instance, airborne-based measurements tend to capture flaming-dominant plumes because they are more easily injected to high altitudes than smoldering-dominant plumes (Kondo et al., 2011). In fact, rBC emissions are heavily dependent on the combustion state of biomass. Field measurements using a semi-continuous ECOC analyzer (Thermo-Optical-Transmittance technique, IMPROVE protocol) during OBB episodes in East China yielded ΔEC/ΔCO values of 17.4 ± 5.2 ng/m^3/ppbv for flaming-dominant cases and 11.8 ± 2.3 ng/m^3/ppbv for smoldering-dominant cases (Pan et al., 2012). Biomass burning experiments in the laboratory on 15 individual plant species sampled in the United States indicated that ΔrBC/ΔCO increased by up to 40 ng/m^3/ppbv as MCE increased to 0.95, and this result was largely insensitive to the biomass type used (May et al., 2014). Note that, ΔrBC/ΔCO values decreased significantly with aging of OBB plumes, owing mostly to the below-cloud and in-cloud scavenging processes as a result of

large fractions of water-soluble organic species (Mazzoleni et al., 2007;Gilardoni et al., 2016). Observations made in both East Asia and North America indicate a strong dependence of ΔrBC/ΔCO on accumulated precipitation along backward trajectories (Kondo et al., 2011), implying that the rBC-containing particles became hydrophilic and were removed by wet deposition during transport. This result is consistent with observations of OBB plumes at the top of Mt. Tai (36.26°N, 117.11°E, 1534 m a.s.l.) in North China, which indicated that ΔBC/ΔCO values for OBB plumes decreased substantially due to cloud scavenging processes (Pan et al., 2013).

The Yangtze River Delta Region (YRDR) is one of the most important agricultural regions in China, and it accounts for 29% of total grain production. Wheat and rapeseed plants are two major crops. After harvest, some of the crop straws are burned in the open air at fields, resulting in severe air pollution over the regional scale. Although field measurements on variations in the concentrations of rBC and CO and their ratios in OBB plumes have been reported, their physical characteristics may change significantly due to the rapid aging/mixing processes of semi-volatile organic vapors. Therefore, laboratory studies are very important to obtain insight into the initial emission features of rBC particles in China. In the present study, we conducted laboratory burning experiments using two crop residues (wheat straws and rapeseed plants) obtained from the YRDR. The mass concentration and size distribution of rBC particles in the OBB plume were measured using a single particle soot photometer (SP2). The physical properties of nascent rBC-containing particles, the evolution of the size distribution, the mixing state of the rBC particles, and their dependence on the combustion state was investigated. The information presented in this paper is helpful for constraining/reducing uncertainties in OBB emission inventories and the estimates of their climatic effects by models.

2 Experiments

2.1 Description of the burning experiments

We conducted burning experiments in the laboratory using samples of wheat straw and rapeseed plants that were collected in an agricultural area of East China during a field campaign in 2010 (Pan et al., 2012). All of the biomass was stored in sealed plastic bags to preserve its original state. During experiments, the biomass sample was placed on an aluminum foil net rack in a heat-resistant combustion box with an approximate volume of 144 L, and it was ignited by a butane-fuel lighter from the bottom. Afterwards, the biomass burned until it went out completely. In general, a total of twenty-four samples (the mass of each sample was ~20 g) were tested. The OBB smoke was removed from the room by a venting fan through a flexible rubber hose at a flow rate of 120 m^3/h. The wheat straw samples were classified into two groups. Twenty samples were burned in the chamber without artificial treatments, and four of the samples were placed in humid conditions (RH>99%) for 30 minutes to absorb moisture for comparison. Detailed information on the setup of the OBB experiments is provided in the literature (Inomata et al., 2015). As mentioned, MCE is a useful metric for describing the combustion phase of biomass burning, and the calculation of MCE requires simultaneous measurements of CO and CO_2 concentration. Here, mixing ratio of CO_2 was measured using a Li-7000 CO_2 analyzer (Li-COR Inc.; detection range 0–3000 ppmv, RMS noise

35 ppbv, integration time 0.5 s) through a separate 1/8 inch, ~1.5-m-long Teflon tube. The mixing ratio of CO was concurrently measured with an ultrafast CO analyzer (model AL5002, Aero-Laser GmbH; detection range 0–100 ppmv, detection limit 1.5 ppbv, integration time 1 s). Comparison with a non-dispersive infrared CO gas analyzer (Thermo 48C; precision 10.0 ppbv, RMS noise 5.0 ppbv, average time 1 min) indicated that the measurement uncertainty was within 5%.

To avoid instrument overloading due to the extremely high concentrations of particles and trace gases, the inlets of the sampling lines were situated ~40 cm away from the combustion smoke. The sampling flows were subsequently diluted in a dilution system by mixing dry zero air produced by a zero gas generator (Thermo Inc., model 111). The flow rate of injected zero air was precisely controlled with a mass flow controller (Kofloc Inc., model 3660; accuracy ± 1.0% at 25°C). The uncertainty of the dilution system was evaluated using known-size dry polystyrene sphere latex particles (PSL, Size Standard Particles, JSR Corporation, Japan). The PSL aerosols were produced by a nebulizer at a flow rate of 3.5 L/min and passed through a diffusion dryer (model 3062, TSI Inc., USA) and then size-selected using a differential mobility analyzer (DMA, model 3081, TSI Inc., USA). The number concentration of PSL particles was measured using a laser aerosol spectrometer (LAS-X II, PMS(GB) Ltd., UK; uncertainty 5%, flow rate 50 ccm) with and without dilution. The errors of the dilution system were found to be 6%, 2%, 2%, 4%, and 5% for particles with mobility diameters of 120 nm, 200 nm, 300 nm, 500 nm, and 1000 nm, respectively, at a dilution ratio of ~50. During the burning experiment, a 50-cm-long, 1/4-inch flexible conductive silicone tube (TSI Inc., USA) and stainless steel Swagelok fittings were used for the aerosol tubing (dilution factor: 46), and polytetrafluoroethylene (PTFE) tube and fittings were used for the measurement of gases (dilution factor: 22). Abbreviations and symbols used in this paper is shown in Table 1.

2.2 Instruments

2.2.1 Single particle soot photometer

A single-particle soot photometer (SP2, Droplet Measurement Technologies Inc.) was used to examine the evolution of the number concentration and mixing state of the OBB particles. The SP2 employs a continuous intra-cavity Nd:YAG laser beam (1064 nm, TEM00 mode, Gaussian) to produce a strong laser power field and detects the laser-induced incandescence signal emitted from individual rBC particles when they are heated to their boiling point (~4300 K) (Gao et al., 2007). The peak value of the incandescent signal was converted to the rBC mass based on a calibration curve determined using fullerene soot (FS) particles (stock 40971, lot: L20W054, Alfa Aesar, USA). The calibration procedure used in quantifying rBC masses was the same as that used in previous studies (Moteki and Kondo, 2010;Miyakawa et al., 2016). The effective density function of FS was determined on the basis of a DMA–aerosol particle mass (DMA-APM) system in Yutaka Kondo's laboratory at the University of Tokyo and was consistent with previous results (Moteki and Kondo, 2007;Gysel et al., 2011) (Fig. S1). In our study, the mass of the individual FS particles ranged from 0.35 to 89.5 fg, which corresponds to 80–700 nm in mass equivalent diameter (MED), assuming an rBC density of 1.8 g/cm^3 and ideally spherical particles. Due to variations in morphology and composition under ambient conditions, the incandescent signal may not always be linearly

proportional to the mass of rBC particles. The uncertainty of the derived rBC mass on the basis of the incandescent signal was estimated to be ~ 30%, and the uncertainty of the derived MED values was estimated to be ~ 10%. The mass size distribution of the rBC in the OBB plume typically peaked at 180 ~ 200 nm (<10 fg). Extrapolation using a lognormal function fit to the observed size distribution suggested that the missing rBC particles with MED < 80 nm and MED > 500 nm only cause minor mass underestimation (~5%). The size-dependent detection efficiency of SP2 for FS particles was also evaluated on the basis of a DMA-SP2-CPC (model 3010, TSI Inc., USA) system, and we found that the SP2 detection efficiency was in the range of 0.94 ~ 0.98 for particles with MED values larger than 80 nm (shown in Fig. S2).

The scattering signal of the SP2 was calibrated using PSL particles with known sizes (170 nm, 200 nm, 254 nm, 300 nm, 500 nm and 1000 nm). It is worth noting that only PSL particles with sizes larger than 166 nm can be detected adequately, implying that the ambient measurement of the SP2 will underestimate the total number concentration of light-scattering particles because the particles that are smaller than this size threshold are not counted. A two-elemental avalanche photodetector was employed in the SP2 to determine the actual position of the particle in the laser beam, which allows for delay time and coating thickness analysis of rBC particles with core-shell structure (Gao et al., 2007). Detailed information on the SP2 is provided in the literature (Schwarz et al., 2008;Schwarz et al., 2010;Moteki et al., 2014).

2.2.2 Determination of the coating thicknesses of rBC-containing particles

As mentioned above, when the rBC-containing particles pass through the laser beam, the rBC component needs a short period of time to absorb energy to gradually evaporate the coating materials. This means that the time when the rBC reached its boiling point was later than the time of occurrence of the peak of scattering. For the rBC-containing particles with core-shell structure, the coating thickness can be semi-qualitatively represented by the delay time of the LII peak (Δt), which is defined as the elapsed time between the occurrence of the peak of the scattering signal and the peak of the incandescence signal; a positive value of this quantity indicates that the peak of the incandescence signal occurs after the peak of the scattering signal. In principle, the larger the Δt value is, the more likely the rBC core is to be thickly coated. Such phenomena have been frequently reported in a number of studies (Moteki et al., 2007;Subramanian et al., 2010). In our experiment, a histogram analysis of the Δt value demonstrated that there was a small Δt^* peak at 0.8 ± 0.5 (2σ) μs for the uncoated FS particle with MED < 400 nm. Apparently, this Δt^* peak did not result from the coating effect, but the intrinsic error of the photodetector of the SP2. We regarded the particles with Δt values larger than 1.3 (mean + 2σ) μs as being coated. A detailed classification of thinly coated and thickly coated particles is discussed in section 3.4. In practice, estimation of the coating thickness of rBC cores in terms of Δt values is sometimes problematic because, first, the Δt values showed a discontinuous increase with an increase in coating thickness, depending on both the rBC core and the coating material. A laboratory study of graphite particles coated with organic liquids indicated that the Δt value jumped from less than 1 μs to 3 μs after the coating thickness of particles exceeded a threshold value (Moteki and Kondo, 2007). Such variations provide only a measure of the minimum detectable coating thickness, and they do not permit precise estimation.

Second, the Δt value can be negative in cases where the peak of the incandescence signal occurs *before* the peak of the scattering signal (Sedlacek et al., 2012). Negative Δt values have been reported not only in biomass burning plumes (Sedlacek et al., 2015) but also in laboratory experiments (Moteki and Kondo, 2007). An accepted explanation is that the rBC component is located at or near the surface of non-refractory matter (such particles are said to belong to the non-core-shell type or the attached type). When such particles passed through the laser beam, the rBC did not absorb a sufficient amount of energy to evaporate the non-rBC substances, and the occurrence of fragmentation allowed some of the remaining non-rBC substances to pass though the laser, producing a scattering signal after the incandescence signal was induced. Moteki et al., (2014) suggested the use of the time-dependent variation of the scattering cross section (C_s) to discriminate the coated rBC particles from the attached type and proposed a measurable parameter, a logarithm of the ratio of C_s before evaporation ($C_{s\text{-}be}$) to C_s at the onset of incandescence ($C_{s\text{-}oi}$), $\log(C_{s\text{-}be}/C_{s\text{-}oi})$, to quantify the contributions from the different types.

Following the same principle, we calculated the coating thickness of rBC-containing particles with the core-shell structure on the basis of the leading-edge-only (LEO) fitting method (Gao et al., 2007). The physical interpretation of this method has been described in the literature (Gao et al., 2007;Laborde et al., 2012). In the LEO fitting approach, the laser intensity profile of the SP2 was predetermined from an analysis of the PSL particles, and the "leading edge" data are selected according to the criterion of $t < -2.5\sigma$. Here, σ denotes the standard deviation of the Gaussian function of the laser intensity profile. Using a strict threshold (e.g., $t < -3\sigma$) can reduce the risk of the onset of evaporation of the coating; however, it significantly increases the possibility of incorrect Gaussian fitting. The optical diameter of the undisturbed rBC-containing particles was estimated using Mie scattering theory and the LEO-fitted scattering peak height, presuming a refractive index of $m = 1.5 - 0i$ for the coating materials. To test the validity of the LEO fitting method, laboratory experiments were performed using FS particles (Alfa Aesar 40971, lot: L20W054) coated with oleic acid (molecular weight 282.46, boiling point 360°C). The instruments used in this procedure are the same as those described in the literature (Moteki and Kondo, 2007). FS particles with mobility diameters of 100 nm, 150 nm, and 200 nm were selected using the DMA and then coated with oleic acid using a heated oleic oil bath. The coated particles with shell mobility diameters of 180 nm, 200 nm, 250 nm, 300 nm, and 350 nm were selected by a second DMA and then measured using the SP2. We excluded the doubly-charged particles from the data analysis because both the core and shell sizes of these particles were apparently larger than those of the singly charged ones. The shell diameters of the coated particles were well determined using the LEO fitting method. Linear regression analysis of the calculated and the measured shell diameters demonstrated a good positive correlation with a high correlation coefficient ($r^2 = 0.9$), as shown in Fig. S3. The coating thickness of rBC was calculated using $(\boldsymbol{D_p - D_c})/\mathbf{2}$, where $\mathbf{D_p}$ and $\mathbf{D_c}$ are the shell and core diameters, respectively, of the rBC-containing particles. The shell/core (S/C) ratios were calculated using $\mathbf{D_p/D_c}$. The total uncertainty of the S/C ratio values was calculated to be 14%.

2.2.3 Non-methane volatile organic compounds (NMVOCs)

In the present study, the mixing ratios of the NMVOCs in the gas phase in the OBB smoke were measured simultaneously using a high-sensitivity proton-transfer-reaction mass spectrometer (PTR-QMS 500, IONICON Analytik GmbH) with a time resolution of 1.9 s. Four primary ions ($H_3{}^{18}O^+$, NO^+, $O_2{}^+$ and $H^+\bullet(H_2O)_2$) were used, and more than 20 product ions ($NMVOC\bullet H^+$) were selectively monitored, according to predetermined multiple ion detection (MID) settings. The detection limit and dwell time of PTR-QMS for NMVOCs were generally less than 0.3 ppbv and 0.1 s, which are fully satisfactory for the measurement of OBB smoke. Detailed information on the configuration of the instrument is provided in the literature (Inomata et al., 2015).

2.3 Determination of combustion states and the rBC emission ratios

As mentioned, the excess mixing ratios of CO (ΔCO) and CO_2 (ΔCO_2) are normally used to estimate the modified combustion efficiency (MCE) of biomass, which was defined as $\Delta CO_2/(\Delta CO_2 + \Delta CO)$). In the present study, the mixing ratios of CO and CO_2 were measured at a time resolution of 1 s. Although the real-time variation in MCE was obtained, comparisons were difficult because the combustion states and durations varied significantly among the different cases. Here, a fire-integrated modified combustion efficiency was calculated on the basis of equation (1).

$$\mathrm{MCE} = \frac{\sum \Delta CO_2}{\sum \Delta CO + \sum \Delta CO_2} = \frac{\sum([CO_2]_{plume} - [CO_2]_{baseline})}{\sum[CO]_{plume} - [CO]_{baseline}) + \sum([CO_2]_{plume} - [CO_2]_{baseline})} \quad (1)$$

where $\sum$ represents the time-integrated total mixing ratios of ΔCO and ΔCO_2, and [X] is the mixing ratio of species X, expressed as ppmv. Correspondingly, the emission characteristics of rBC were indicated by the rBC emission factor $\Delta rBC/\Delta CO$, which was calculated on the basis of equation (2).

$$\Delta rBC/\Delta CO = \frac{\sum([rBC]_{plume} - [rBC]_{baseline})}{\sum([CO]_{plume} - [CO]_{baseline})} \quad (2)$$

where [rBC] is the mass concentration of rBC in unit of ng/m^3. The baseline of the mass concentration of rBC and the mixing ratios of CO and CO_2 were determined from the linear interpolation of the data before and after each combustion experiment.

3 Results and discussion

3.1 Evolution of the combustion process

Fig. 1 shows two sample time series of the number concentrations of rBC and non-rBC particles and the mixing ratios of CO and CO_2 in the smoke for a wheat straw combustion case (Fig. 1a) and a rapeseed plant combustion case (Fig. 1b). The evolution of the concentrations of particles and gases were similar, although the carbon content and combustion duration differed between the two biomass types. This result indicates that the combustion process was overwhelmingly important in

determining the variations in emission characteristics. As described in the literature (Andreae and Merlet, 2001;Reid et al., 2005), smoldering combustion normally occurs after flaming-dominant combustion ceases, resulting in two isolated peaks for the mixing ratios of CO and CO_2. However, we did not observe such a clear boundary between these two stages in our burning experiments. This result occurred primarily because the combustion durations were short (less than 200 s), and both flaming and smoldering combustion might occur simultaneously in different parts of the biomass. The mixing ratios of CO displayed a broader tail than those of CO_2, implying that the relative importance of smoldering combustion increased at the end; this effect is particularly clear in Fig. 1b.

The temporal variations in the number concentration of rBC were highly correlated with those of CO_2. This phenomenon is in accordance with previous conclusions that the production of rBC particles is mostly related to flaming-dominant combustion processes (Pan et al., 2012). In the high-temperature and low-oxygen environment present in the inner part of flames, the evaporated unsaturated alkanes tend to pyrolyze to soot precursor particles (i.e., PAHs), which is followed by the aggregation and considerable growth of the rBC particles. The non-rBC particles appear to be mostly emitted under low-temperature burning conditions (Reid et al., 2005). Directly after the biomass was ignited, a small peak (yellow shading in Fig. 1) in the number concentration was sometimes observed, which could be related to the emissions from combustion of butane fuel of lighter. As flaming temperature increased up to 800K, rBC particles were produced in significant quantities, and these particles provided substantial numbers of condensation nuclei for semi-volatile compounds. As a result, the number concentration of non-rBC particles decreased to almost zero (red shading in Fig. 1). When combustion shifted from the flaming-dominant to the smoldering-dominant stage during the second half of the burning period (blue shading in Fig. 1), the number concentration of non-rBC particles increased again. This observation can be explained by the secondary condensation growth of pyrolyzed compounds that occurred because the temperature was not high enough to cause their complete oxidation. The number size distribution and volume size distribution of non-rBC particles during burning experiments are shown in Fig. S4. Overall, these observations confirmed the results of previous studies that indicate that particle formation in OBB is essentially a nuclei-limited condensation process, and rBC and CO_2 were mostly produced by flaming combustion, whereas organic matter and CO were emitted from the smoldering combustion (Reid et al., 2005).

Table 2 summarizes the information on the sample types, the mixing ratios of CO and CO_2, the mass concentration of rBC particles and MCE for all burning experiments. Although the combustion proceeded generally from flaming to smoldering phase, both flaming and smoldering combustion sometimes occurred at the same time at different position of fuel. Besides, the time duration of in flaming or smoldering were different case by case. Here, the fire-integrated MCE value was used to represent the overall combustion condition for each combustion case. As shown, the averaged MCEs have no significant differences for the combustion of dry wheat straw (0.86 ~ 0.98), wet wheat straw (0.88 ~ 0.96), and dry rapeseed plants (0.91 ~ 0.96). The average mass concentration of rBC after 46 times dilution ranged from 0.25 to 19.8 $\mu g/m^3$, and the average mixing ratio of CO after 22 times dilution ranged from 95 to 5003 ppbv.

3.2 Variations in rBC size as a function of MCE

The masses of rBC particles as a function of mass equivalent diameter (MED) displayed a lognormal distribution for all burning cases. For better expression, each dM/dlogDp distribution was normalized so that its maximum value = 1 (Fig. 2a). We found that the mass mode diameter (MMD) for each combustion case clearly increased from 152 nm to 215 nm as the overall MCE value increased from 0.862 to 0.964. The correlation (r^2 = 0.59) was significant at the 95% confidence interval (Fig. 2b). This result indicates that flaming combustion tends to produce larger rBC particles than smoldering combustion. It is consistent with previous studies, which reported that rBC particles formed considerably in intense flaming combustion due to less efficient transport of oxygen into the interior flame zone. As a result, growth in the size of rBC particles was rapid because the coagulation rate of particles is roughly proportional to the square of their number concentration (Lee and Chen, 1984). In this study, these consecutive processes were interrelated and could not be decoupled in the analysis. Nevertheless, this mechanism explained the outliers (contained within the dashed ellipse shown in Fig. 2b), in that the number concentration of rBC particles was not sufficient to support substantial growth. For smoldering combustion, the production of rBC precursors (i.e., PAHs) was less effective because of the low temperature.

As mentioned, the MMD of rBC particles in OBB plumes was determined by the combustion condition; however, its variations during the evolution of the OBB combustion process has not been fully investigated, because the separation of the combustion stage for *in situ* measurement was difficult. A recent study (Taylor et al., 2014) reported that the MMD of rBC particles was 152 nm. This value is apparently smaller than the frequently presented values (180 ~ 200 nm), and the authors attributed the differences to nucleation scavenging processes during transport. Published studies on OBB plumes are mostly based on airborne SP2 measurements. Andreae and Merlet (2001) noted that airborne measurements tend to be biased toward flaming combustion because the plumes formed during the flaming stage was more likely to be injected to higher altitudes than those formed during the smoldering stage (Kondo et al., 2011). Another explanation involved rapid coagulation processes, in which small rBC monomers might easily form agglomerates or clusters driven by organic coatings when the temperature of the plume decreased. This process likely occurs so quickly (on the time scale of seconds) that ambient measurements (OBB plume age > 1 hour) cannot detect this process.

3.3 Emission ratio of rBC particles

Fig. 3 shows the dependence of the ΔrBC/ΔCO ratio on the MCE for all combustion cases. For comparison, the results from previous OBB experiments in the laboratory, as well as from field measurements and emission inventories are also plotted on the same figure. As shown, the ΔrBC/ΔCO ratio increased from 1.5 ng/m^3/ppbv to 34 ng/m^3/ppb as the MCE increased from 0.91 to 0.98. The results of fitting a power function were similar with those from previous studies (McMeeking et al., 2009;May et al., 2014), even though different types of biomass were combusted. This result indicates that the MCE value is a key parameter for determining the rBC emission intensity from OBB, irrespective of the difference in the types of biomass used. In the present study, we tested two biomass conditions (dry and wet) for wheat straw. For combustion cases involving

wet wheat straw, we found that the values of the ΔrBC/ΔCO ratio were always less than 7.1 ng/m^3/ppbv as the MCE value increased up to 0.96, and these values are much smaller than that (25.3 ng/m^3/ppbv) corresponding to dry wheat straw. This result implies that the wet biomass was unfavorable for the production of rBC particles. This phenomenon is consistent with the experimental results described by Chen et al., (2010) who reported an evident decrease in the emission factor of elemental carbon and a moderate increase in the emission factor of CO for burning of moist wildland biomass.

In this study, the average ΔrBC/ΔCO ratio was 13.9 ± 10.1 ng/m^3/ppbv for the burning cases with a fire-integrated MCE > 0.95. This value was probably a low estimation since both flaming and smoldering combustions were included in the calculation. However, by selecting the cases with both the 10th and 90th percentiles MCE value > 0.90, we found that the average ΔrBC/ΔCO ratio was 23.1 ± 11.4 ng/m^3/ppbv, higher than the value reported from airborne measurements (8.5 ± 5.4 ng/m^3/ppbv) for the outflowing aged OBB plumes observed in Asia during ARCTAS-A (Kondo et al., 2011) and the value (10 ± 5 ng/m^3/ppbv) for agricultural fires in Kazakhstan during ARCPAC (Warneke et al., 2009). In these studies, the OBB plumes were sampled after they had undergone a week of transport. In-cloud scavenging may take effect at these relatively low values, although precipitation had not occurred. The ΔrBC/ΔCO ratios derived from the FLAME-I and II experiments (McMeeking et al., 2009) are smaller (8.3 ± 9.7 ng/m^3/ppbv as converted from emission factors, expressed as g species kg^{-1} dry fuel), probably because the combustion was inclined to smoldering (average MCE = 0.92). *In situ* measurements of OBB plumes at the location where our samples for burning were collected (Pan et al., 2012) indicated that the ΔEC/ΔCO ratio from flaming-dominant burning was 17.4 ± 5.2 ng/m^3/ppbv. This result approximates those obtained in the laboratory. Measurements of OBB plumes in the North China Plain found that the ΔEC/ΔCO ratios from wheat straw burning ranged from 15 to 17 ng/m^3/ppbv (Pan et al., 2013). Kondo *et al*. (2011) reported ΔrBC/ΔCO ratios as low as 2.86 ± 0.35 ng/m^3/ppbv (MCE = 0.96) for a fresh OBB plume in North America. These large discrepancies might result from significant rBC losses during transport. The yellow shading in Fig. 3 indicates the variability of ΔrBC/ΔCO ratios used in emission inventories. Comprehensive analyses including all kinds of OBB showed that the ΔrBC/ΔCO ratios were 8.6 ± 1.2 ng/m^3/ppbv (as converted from emission factors, assuming a molar volume of 22.4 L at standard temperature and pressure conditions for CO) (Andreae and Merlet, 2001), 7.5 ± 1.3 ng/m^3/ppbv (Akagi et al., 2011), and 9.0 ± 1.6 ng/m^3/ppbv using the bottom-up method (Yan et al., 2006). Synoptically speaking, a relatively high rBC emission ratio was suggested for estimating emission inventories of OBB because the majority of rBC emissions normally occur during the flaming combustion stage, despite the longer duration of the smoldering stage.

The emissions of rBC relative to ΔCO_2 were also calculated for each burning case (see Table 2). In general, the $\Delta rBC/\Delta CO_2$ ratios did not show a clear increase with increasing MCE values, and they varied from 149 to 1541 ng/m^3/ppmv, with a mean value of 592.5 ± 364.1 ng/m^3/ppmv. Schwarz et al. (2008) reported a high $\Delta rBC/\Delta CO_2$ ratio of 1770 ± 400 ng/m^3/ppmv, much higher than the values obtained in this study. Small values were also reported for OBB plumes observed in North America (100–357 ng/m^3/ppmv), Siberia (167 ng/m^3/ppmv) (Kondo et al., 2011), and China (245 ng/m^3/ppmv)

(Pan et al., 2012). Despite the differences among these values, the $\Delta rBC/\Delta CO_2$ ratio remains a useful parameter in constraining the uncertainty of emissions of rBC from OBB to within an order of magnitude in models.

3.4 Delay time of incandescence

For the rBC-containing particles, the delay time (Δt) of the peak of the incandescent signal *after* that of the scattering signal is widely accepted as a proxy for the coating thickness of rBC particles. Particular caution should be employed when this concept was applied in data exploration. First, SP2 cannot detect particles with shell diameters less than 166 nm (the lower detection limit of SP2) owing to their weak scattering signal. A systematic bias always occurs for investigating the coating of rBC-containing particles with small rBC cores (i.e., MED less than 100 nm) because only very thickly coated rBC particles can be counted. To avoid this bias, we report only the rBC-containing particles with relatively large rBC cores (MED = 200 ± 10 nm). Second, only the rBC-containing particles with positive Δt values were technically deemed as having a core-shell structure, to which the delay time-based method and LEO fitting method could be appropriately applied. In general, the scattering profile of rBC particles in the core-shell structure contained a main peak with a shoulder peak, which resulted from the coating material and the rBC core, respectively. If there was only one predominant scattering peak with a quasi-Gaussian shape, it suggested that the evaporation of non-rBC coatings was insignificant, and the rBC-containing particle likely belonged to the attached type, as demonstrated in the literature (Moteki et al., 2014). In this study, the shell diameters of rBC-containing particles with the core-shell structure were estimated using the LEO fitting method (described in section 2.2.2). We found that the shell diameters of rBC-containing particles with rBC cores having MED = 200 nm ranged from 210 to 400 nm, with a 5^{th} percentile value of 218 nm and a 95^{th} percentile value of 330 nm. The corresponding shell/core (S/C) ratios were between 1.09 and 1.7.

The dependencies of Δt on the derived S/C ratios of all of the coated rBC particles for all of the burning experiments are shown in Fig. 4. The color in the plot represents the total number count of particles in each bin. In general, Δt increases as the S/C ratio increases, reflecting that the rBC particles must spend a longer period of time absorbing energy to evaporate thicker coatings. Histogram analysis showed that both the S/C ratio and Δt displayed neither simple Gaussian nor lognormal distributions. Instead, a multiple-peak Gaussian provided a good fit to their number distributions (Fig. 4). For the distribution of the S/C ratio, there were two modes. One mode (#1) occurs at an S/C ratio = 1.18, and another mode (#2) occurs at an S/C ratio = 1.34, indicating that the rBC particles had different levels of coatings. The differences in coating thickness were most likely related to the combustion state of biomass burning. As mentioned, although flaming combustion emitted a substantial amount of semi-volatile organic carbons, the production of rBC particles was also significant at high temperatures. The competing condensing processes under nuclei-rich conditions resulted in relatively thin coatings on the rBC particles, instead of direct formation of particulate organic matter. Previous studies (Kudo et al., 2014;Inomata et al., 2015) also found that the emission factor of NMVOCs during the flaming stage was lower by an order of magnitude than that during the smoldering stage. It also supported our conclusion that the thinly coated rBC particles associated with mode #1 and mode #2 were primarily related to the flaming combustion and smoldering combustion stages, respectively. In the

present study, the integrated area ratio between mode #1 and mode #2 was 0.76. This result suggested that the thinly and thickly coated rBC particles were almost the same. It was worth noting that the histogram of the delay times of rBC-containing particles also had two modes, with one mode occurring at $\Delta t = 1.74$ μs and another peak occurring at $\Delta t = 3.18$ μs. The integrated area ratio between these two modes was 0.78, almost the same as the ratio derived from the S/C mode. This result demonstrates that the rBC-containing particles with rBC cores of 200 nm and S/C ratios = 1.18 and 1.34 corresponded to delay times of 1.74 μs and 3.18 μs, respectively, at least in this study. Moteki et al., (2007) investigated the relationship between delay time and coating thickness for ambient rBC particles with MED = 200 nm, and they reported that the delay time increased linearly from 0-1 μs to ~4 μs as the coating thickness increased up to 200 nm (S/C ratio = 2), consistent with our study. It should be noted that the delay time for uncoated rBC particles (S/C = 1) was not necessarily zero because of intrinsic differences among SP2 instrumentations. For instance, a shift of $\Delta t^* = 0 \sim 0.6$ μs was found for uncoated rBC particles among studies (Moteki et al., 2007;Sedlacek et al., 2012). By subtracting the Δt^* value (0.8 μs) in this study, the Δt was found to be 0.9 ~ 2.4 μs for coated rBC particles in the biomass burning plumes.

3.5 Coating thickness of rBC as a function of MCE

Fig. 5a depicts the variations in modal Δt values for rBC particles with MED = 200 nm as a function of MCE value. As shown, the Δt clearly decreased as the MCE value increased ($r^2 = 0.63$), the decreasing trend was statistically significant at a level of 5%. S/C ratios of rBC particles (Fig. 5b) were found to be 1.4 at MCE < 0.9 (smoldering combustion) and 1.2 at MCE > 0.95 (flaming combustion). Such tendency was mostly due to formation of organic matter at different combustion phase. Collier et al., (2016) reported that organic aerosol emissions had negative correlations with MCE, implying that coating processes of semi-volatile organics played a key role in the increase of S/C ratio. Variations in both the Δt values and the S/C ratios as a function of MCE showed similar tendencies for particles with MED of the rBC cores ranging between 190 nm to 250 nm. Airborne measurements during the ARCTAS campaign (Kondo et al., 2011) showed an increasing tendency for the values of the S/C ratio (1.3 ~ 1.66) with increase of MCE, and the authors explained that this phenomena was because flaming phase plumes were more aged than the smoldering plumes, a 205 ± 40% increase of the volume of the coating materials resulted in a larger S/C ratio than that of rBC particles in smoldering plume.

Statistically, the modal coating thickness of rBC particles was found to be ~20 nm (Fig. S5). In fact, discrepancies exist among studies due to differences in biomass types, burning conditions and sampling locations. For example, ambient measurements in Europe indicated a coating thickness of rBC particles of 15 nm on average, and more than half of the rBC particles had a coating thinner than 10 nm (Laborde et al., 2013). Airborne measurements reported a thicker coating (65 ± 12 nm) for rBC particles from brush fires (Schwarz et al., 2008).

Table 3 summarizes recent studies that report the coating thicknesses and S/C ratios of rBC particles. Among studies, the coating thickness of freshly emitted rBC particles from burning of wheat residues was smallest with a mean value of ~ 20 nm. Coating thickness of rBC particle from brush fire (Schwarz et al., 2008) and boreal forest (Talyor et al., 2014) were 65 ±

12 nm and 50 ~ 100 nm, respectively. We noticed that there were large difference in the age of OBB plumes, and coating thickness of rBC seemed to increase as they experienced longer transport period. It implied that aging of particles was also play important role in determining the coating thickness of rBC particles. Further observational investigation on the evolution of OBB process is also need to explicate contribution to the total variability. The coating thickness of rBC particles from traffic emissions varied significantly, depending on the urban emission and photochemical processes. The transport pattern and meteorological parameters (such as RH) also play a role in changing the morphology of rBC-containing particles. Fan et al., (2016) reported that the hygroscopic shrinkage effect under high RH conditions led aggregated soot particles to become more tightly clustered, which resulted in an increase in the shell/core ratios. Such phenomena have also been observed under ambient conditions (Adachi et al., 2010). It has also been reported that condensation and coagulation processes cause the voids of rBC aggregates to be filled or cause the particles to collapse into a compact shell-core structure (Zhang et al., 2008).

3.6 Relationship between the S/C ratio and NMVOCs

Scatter plots of the S/C ratios of rBC particles with core MED = 200 nm plotted against the emission factor (EF, in unit of g/kg) of each condensable NMVOC are shown in Fig. 6. It is obvious that the S/C ratio increases with the EF for the burning of both dry wheat straw and dry rapeseed plants. As discussed in a previous study (Inomata et al., 2015), the high EF values of the NMVOCs are related to smoldering combustion, in which the production of rBC particles is less effective due to the low-temperature conditions. The condensation of semi-volatile organics was evident under rBC nucleus-limited conditions, resulting in higher S/C ratios. We also found that the S/C ratio from the laboratory burning of rapeseed plants was apparently higher than that of wheat straw under the same NMVOC emissions conditions. This difference is likely attributable to the physical formation processes of rBC particles under high-temperature conditions for different combustion types. For instance, intensive fires tend to produce non-spherical rBC particles with chain-like structures, which display uneven coatings of semi-volatile organics on the rBC particles; however, for compact, quasi-spherical rBC particles, it is much easier to form evenly distributed, thicker coatings. For wheat residues, the S/C ratios (~1.4) of rBC for wet samples was apparently higher than those (12~ 1.3) of dry samples at the same EF. This result indicates that the microphysical properties of the rBC particles varied under different biomass burning conditions. To answer these questions, further analysis of individual particles using electro-microscopy is needed.

4 Conclusions

In present study, biomass burning experiments were conducted in the laboratory using wheat straw and rapeseed plants, two major agriculture crop residues, which were obtained from the Yangtze River Delta Region (YRDR) during the Rudong field campaign. The combustion state of each biomass burning experiment was assessed using the modified combustion efficiency (MCE) that was calculated on the basis of fire-integrated excess CO and CO_2 mixing ratios, relative to their background values. A full calibration of the single particle soot photometer (SP2) was performed using commercial

calibrating particles (fullerene spheres and polystyrene latex particles) following the standard procedures that were proposed by Moteki and Kondo (2007). The mass equivalent diameter (MED) values of the rBC particles were calculated on the basis of the measured incandescence signals and a presumed rBC density of 1.8 g/cm^3. The major findings are as follows. (1) The emission ratio of rBC, defined as ΔrBC/ΔCO, increased from 0.2 μg/m^3/ppbv to 40 μg/m^3/ppbv as MCE increased from 0.84 to 0.98. The increasing trend was in accordance with previous laboratory studies, and this result was largely insensitive to the type of biomass considered. (2) The mass mode diameter of the rBC particles ranged from 152 to 215 nm. It was found that the rBC particles produced during flaming combustion had larger MMD values than those produced during smoldering combustion. This result indicated that the rBC coagulation/growth process was intensive during flaming combustion as a result of substantial production of rBC precursor particles, such as PAHs, under the high-temperature and oxygen-deprived conditions that occurred within intense flames. (3) For rBC-containing particles, the delay time of the occurrence of the incandescent peak *after* the scattering peak clearly increased as the S/C ratio increased, and smoldering combustion tends to produce more thickly coated rBC particles than flaming combustion. (4) The condensation of semi-volatile organics co-emitted by the thermal pyrolysis of biomass plays a key role in the formation of coatings on the surface of rBC particles, though the mixing/coating processes of condensable NMVOCs may vary significantly, probably due to the distinct physical characteristics of rBC particles produced by the burning of wheat straw and rapeseed plants.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (Grant No. 41675128 and No. 41225019).

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Tables

Table 1 Abbreviations and symbols used in this paper.

Symbol/acronym	Full name/explanation
rBC	Refractory black carbon, as derived using the LII method at a temperature of ~ 4000K.
Δt	The delay in the time of occurrence of the incandescence peak *after* that of the peak of the scattering signal
APM	Aerosol particle mass analyzer (Kanomax Inc.)
S/C ratio	Shell/core ratio
CO	Carbon monoxide
CO_2	Carbon dioxide
C_S	Scattering cross-section
DMA	Differential mobility analyzer (TSI Inc.)
FS	Fullerene soot (C60)
LEO fitting	Leading-edge-only fitting method proposed by Gao et al., (2007)
LSP	Light scattering particle
MCE	Modified combustion efficiency
MED	Mass equivalent diameter
MMD	Mass mode diameter
non-rBC	Non-refractory black carbon matter that evaporates as rBC absorbs energy
OBB	Open biomass burning
SP2	Single particle soot photometer (DMT Technologies)

Table 2 Description of sample types; overall combustion states; CO, CO_2, and rBC concentrations; MMD and geometric standard deviation (g_σ) of rBC; and emission ratios for the burning experiments. The ordering of these quantities is the same as in previous studies (Inomata et al., 2015).

No.	Sample* type	MCE [10th, 90th]	Duration Second	CO** ppbv	CO_2 ppmv	rBC*** ng/m^3	rBC/CO $ng/m^3/ppbv$	rBC/CO_2 $ng/m^3/ppmv$	MMD**** nm	g_σ
1	A	0.964 [0.941,0.991]	164	1,181	695	13983	24.2	904.8	215	1.32
2	A	0.930 [0.909,0.982]	122	311	91	2366	15.6	1171.5	188	1.46
3	A	0.952 [0.884,0.973]	94	261	114	1446	11.3	570.4	152	1.44
4	A	0.949 [0.913,0.999]	150	343	141	4812	28.7	1541.0	187	1.44
7	A	0.953 [0.830,0.987]	123	256	114	1408	11.2	554.6	160	1.42
8	A	0.976 [0.960,0.994]	184	380	340	6290	33.9	832.6	191	1.37
9	A	0.917 [0.900,0.987]	121	189	46	168	1.8	165.3	187	1.47
10	A	0.944 [0.911,0.979]	120	274	101	787	5.9	348.9	148	1.43
11	A	0.862 [0.828,0.920]	125	464	64	470	2.1	331.8	152	1.44
12	A	0.937 [0.853,0.988]	151	230	75	429	3.8	256.5	148	1.42
13	A	0.950 [0.896,0.976]	143	282	118	1790	13.0	682.8	163	1.46
14	A	0.952 [0.837,0.964]	158	290	126	1295	9.1	461.1	160	1.50
15	B	0.909 [0.881,0.999]	220	4,757	1,045	11255	4.8	484.5	196	1.33
16	B	0.904 [0.857,0.999]	207	1,339	277	8658	13.2	-	177	1.36
17	B	0.961 [0.840,0.988]	97	75	41	250	6.8	276.2	148	1.45
18	B	0.884 [0.730,0.999]	230	1,373	230	5350	8.0	1045.7	181	1.41
19	C	0.943 [0.902,0.999]	244	2,702	983	19802	15.0	906.0	204	1.29
20	C	0.923 [0.891,0.999]	226	3,512	926	13402	7.8	651.2	189	1.33
21	C	0.909 [0.839,0.947]	258	286	63	209	1.5	149.6	137	1.39
22	C	0.951 [0.895,0.976]	188	956	408	3052	6.5	336.4	155	1.41
23	C	0.960 [0.874,0.985]	172	457	241	1259	5.6	234.9	142	1.44
24	C	0.954 [0.944,0.994]	191	846	386	4609	11.1	537.4	144	1.47

*: Sample type: Wheat straw/dry (A), Wheat straw/wet (B), Rapeseed plant/dry(C)

**: the mixing ratio of CO was diluted by 22 times.

***: the mass concentration of rBC was diluted by 46 times.

****: mode diameter in mass size distribution of rBC, abbreviated as Mass Mode Diameter

Table 3 Brief summary of the coating thickness and shell/core (S/C) ratios for rBC emissions from different sources collected from recent studies.

rBC source		Coating thickness	S/C ratio	rBC core size	Age	Sampling description	Study
Biomass burning	Brush fires	65 ± 12 nm	-	*190~210 nm	0.5~1.5 hour	Airborne SP2 measurements during 2006 Texas Air Quality Study	(Schwarz et al., 2008)
		~ 15 nm		200 nm	-	Field measurements using SP2 in the agglomeration of Paris as part of MEGAPOLI European project	(Laborde et al., 2013)
	Boreal forest	50 ~ 100 nm	2.0 ~ 2.5	152~196 nm	1~2 days	Airborne SP2 measurement during the second phase of the BORTAS project over Eastern Canada and the North Atlantic during July-August 2011.	(Taylor et al., 2014)
	Agriculture	-	1.3 ~ 1.6	**120 ~ 140 nm	1~2 hours	Airborne SP2 measurements during ARCTAS in spring and summer	(Kondo et al., 2011)
	Wheat, rapeseed plant	20 nm (11 ~ 54 nm)	1.2 ~ 1.4	200 ±10 nm	< 10 s	Burning experiments in combustion chamber in laboratory environment	This study
Asia continental Free troposphere		- -	1.6 1.3 ~ 1.4	200 nm 200 nm	2~3 days 12 hours	Ground-based SP2 measurements at Fukue Island, Japan	(Shiraiwa et al., 2008)
Aged air mass Traffic influence		44 nm 2 ±10 nm	-	200 nm 200 nm		Field measurement using SP2 in the agglomeration of Paris as part of MEGAPOLI European project	(Laborde et al., 2013)
Traffic emission		110~300 nm		80~130	Highly aged	Ground-based SP2 measurement at Urban site at Shanghai, China	(Gong et al., 2016)
Traffic emission Solid fuel burning Europe continental		- - -	1.6 ~ 2.4 <1.2 1.45 ~ 1.6	- - -	- - -	Clean Air for London (ClearfLo) experimental campaign in winter, 2012	(Liu et al., 2014)
Urban emission		20 ~ 30 nm		> 200 nm	1~2 days	Airborne SP2 measurement during MILAGRO campaign	(Subramanian et al., 2010)

*: Volume equivalent diameter; ** Count Median Diameter

Figures

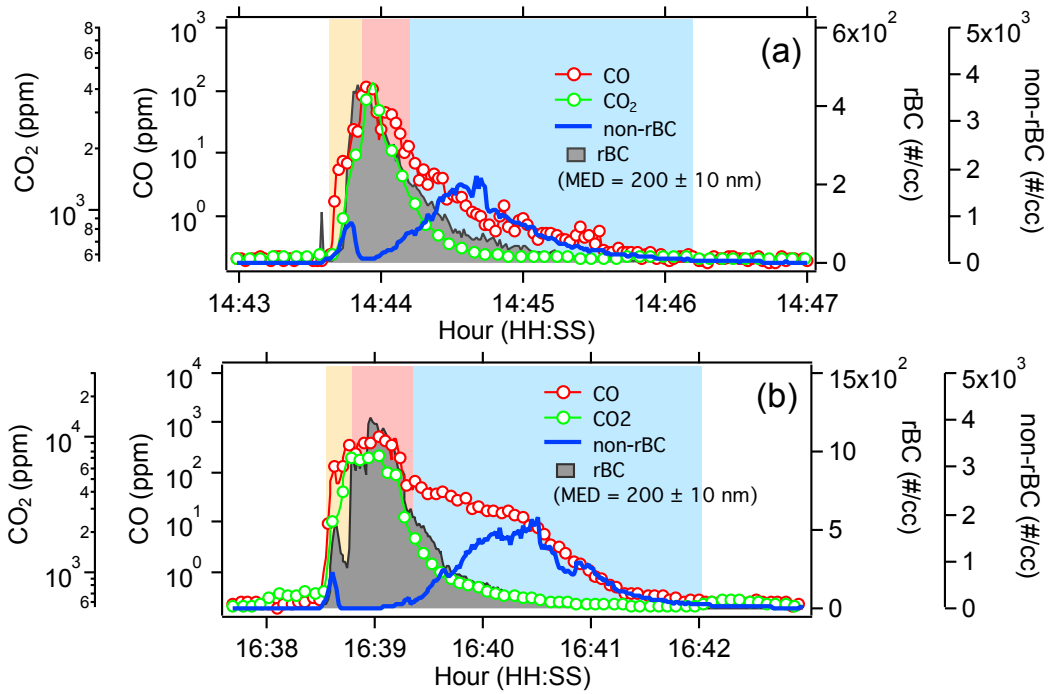

Figure 1: Temporal variations in the mixing ratios of CO, CO_2, the number concentrations of rBC and non-rBC particles for the burning of wheat straw (a) and rapeseed plants (b). The yellow (dry distillation step of the biomass), red (flaming-dominant combustion) and blue (smoldering-dominant combustion) shaded areas in the plot represent the different burning states.

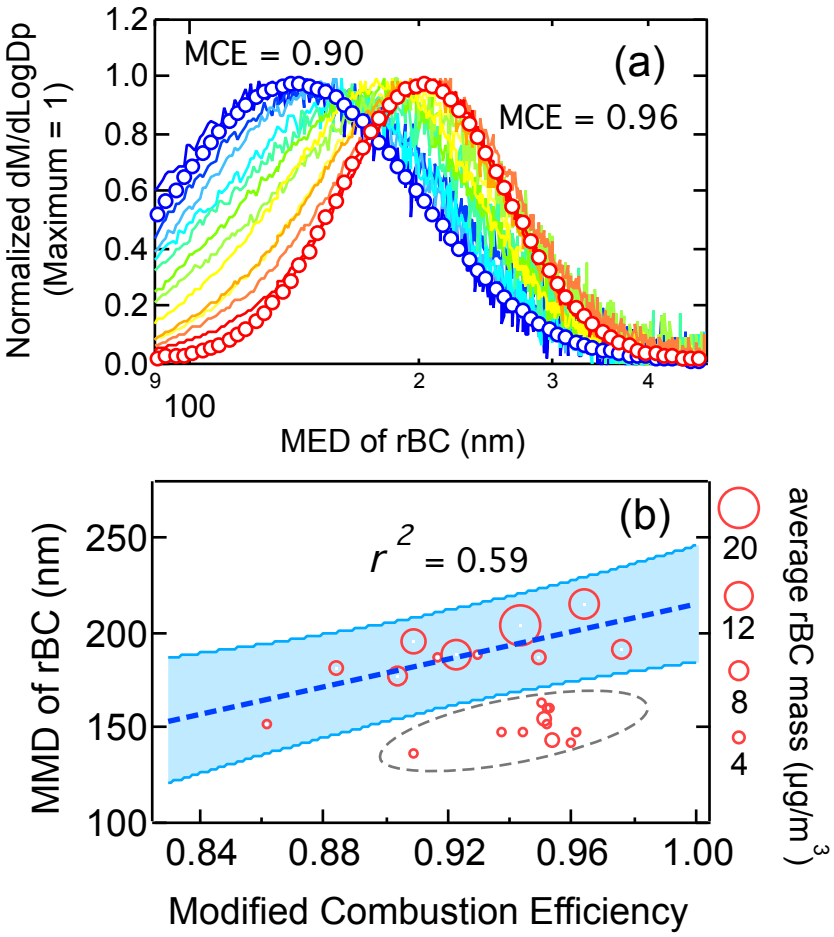

Figure 2. Normalized mass size distribution (maximum value = 1) of rBC particles for each burning experiments (a). For better understanding, lognormal curve fittings are shown for a flaming-dominant combustion case (red circle) and a smoldering combustion-dominant case (blue circle). Variation of mode mass equivalent diameter (MMD) as a function of the modified combustion efficiency (b). The size of circle indicates the average rBC mass concentration for each burning case. Blue dashed line and blue shaded area are the linear fitting and confidence interval for fit coefficients. The data in the gray dashed circle is excluded in the linear fitting because of their low rBC mass concentrations.

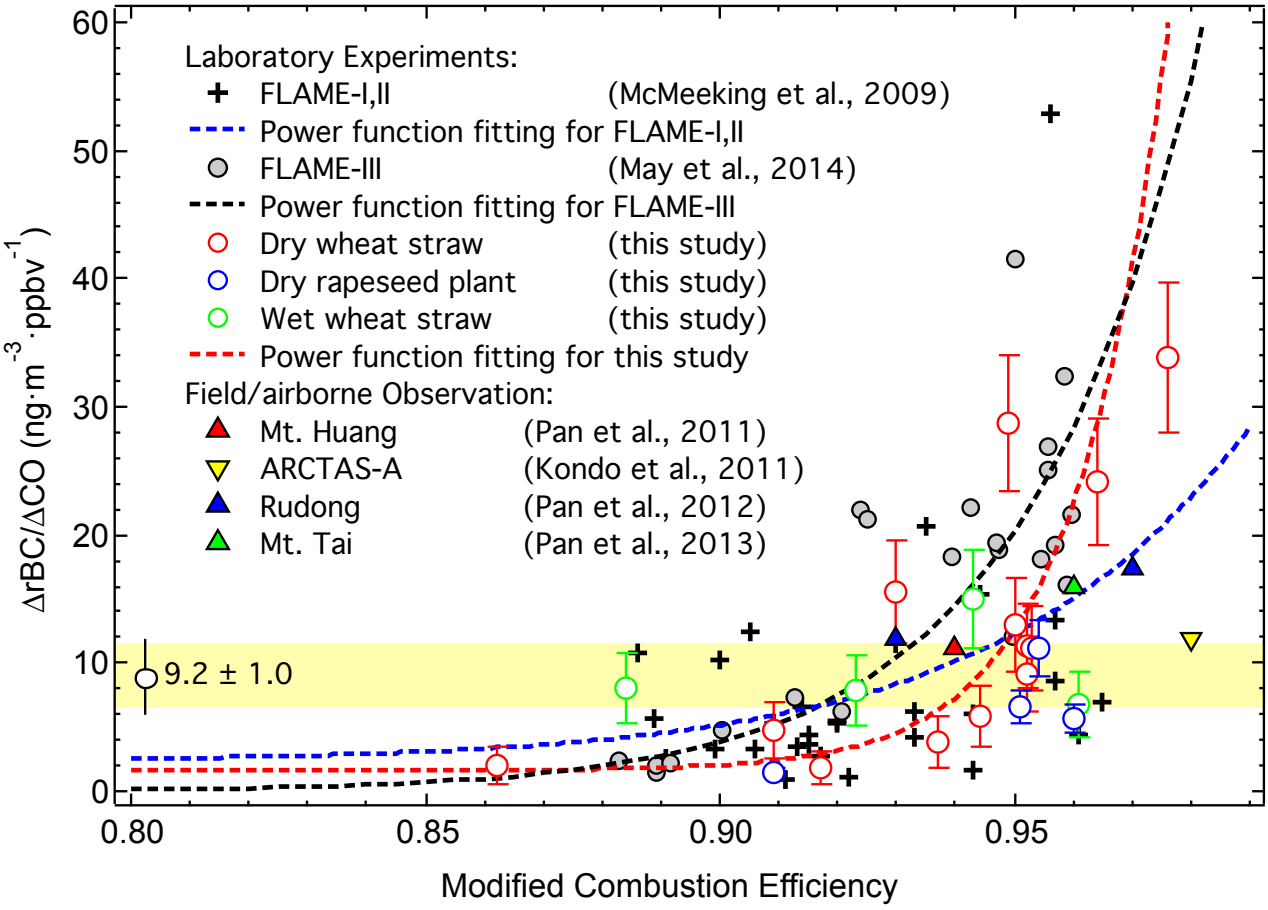

Figure 3. The variations in the emission ratio of rBC and ΔrBC/ΔCO, as a function of averaged MCE for all burning cases. Previous observations and the results of laboratory burning experiments are displayed in the plot.

5

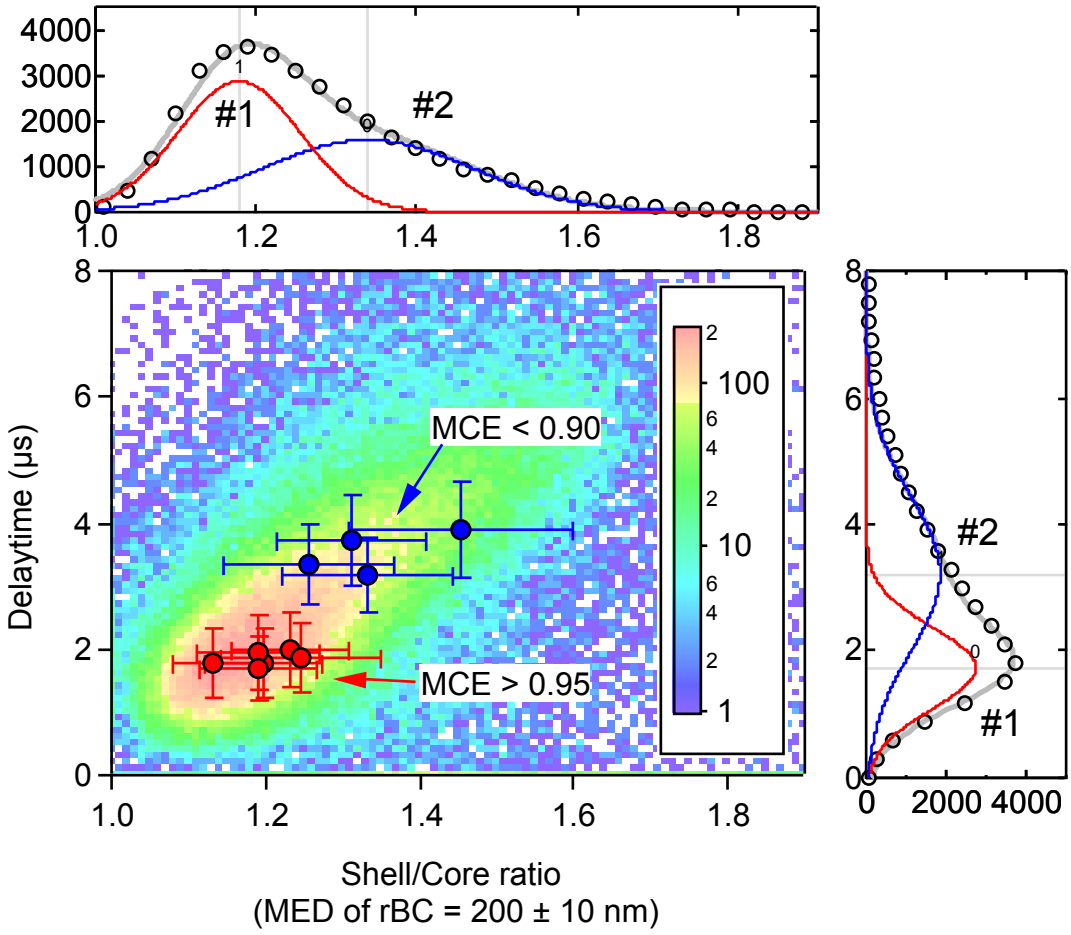

Figure 4. The dependence of delay time of the peak of incandescence signal *after* that of the scattering signal as a function of the shell/core ratio for the rBC particles with MED = 200 ± 10 nm for all the burning cases, and the multiple Gaussian fitting for all the data of cross-sections along the x-axis and y-axis. For comparison with the curve fitting results, observational data of flaming-dominant (MCE > 0.95, red circle) and smoldering-dominant (MCE < 0.9, blue circle) cases are also shown in the figure.

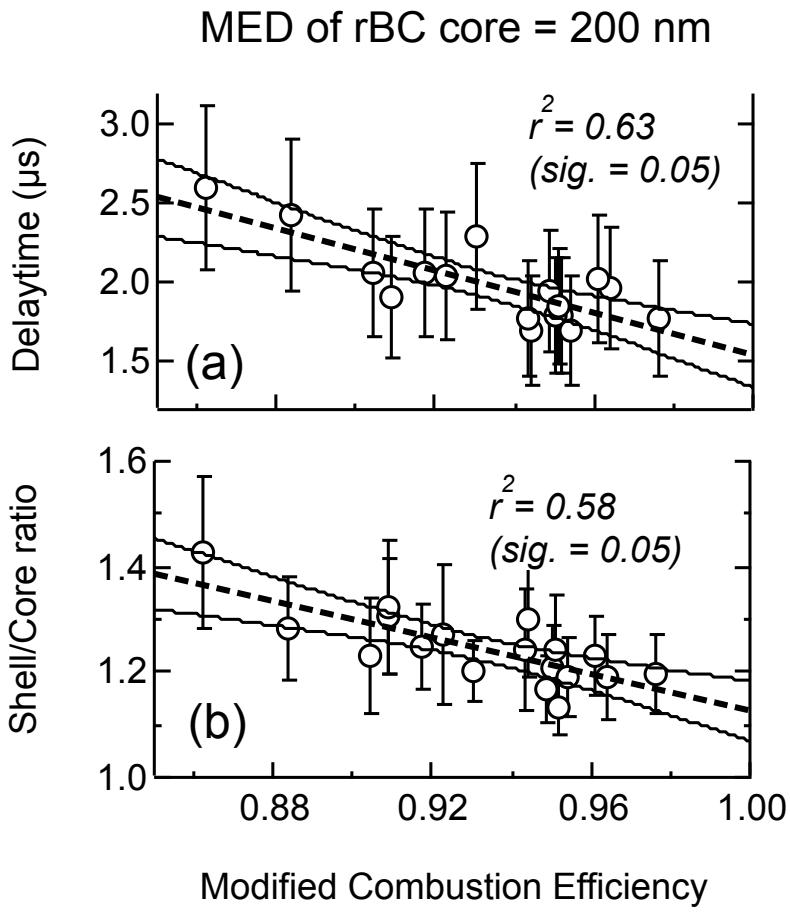

Figure 5. Variations in the delay time (a) and the shell/core ratio (b) as a function of MCE values for rBC particles with MED = 200 ± 10 nm.

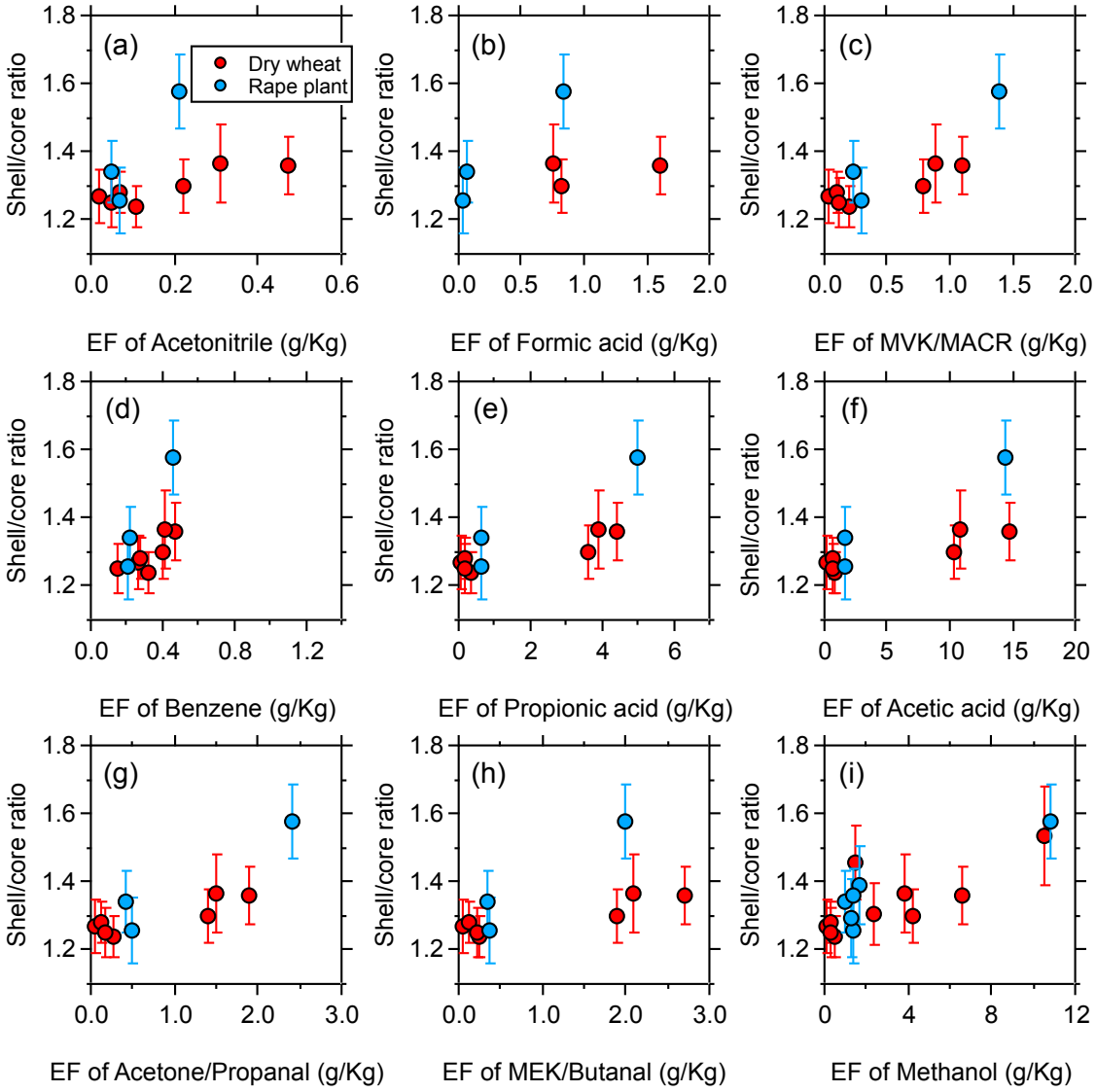

Figure 6. Variations in the shell/core ratios of rBC particles with MED = 200 ±10 nm as a function of the emission factor of each experiment. Here, EF is defined as the amount of each compound released per unit amount of dry fuel consumed. The red, green and blue colors indicate the dry wheat straw, wet wheat straw and rapeseed plant samples, respectively.

5