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.

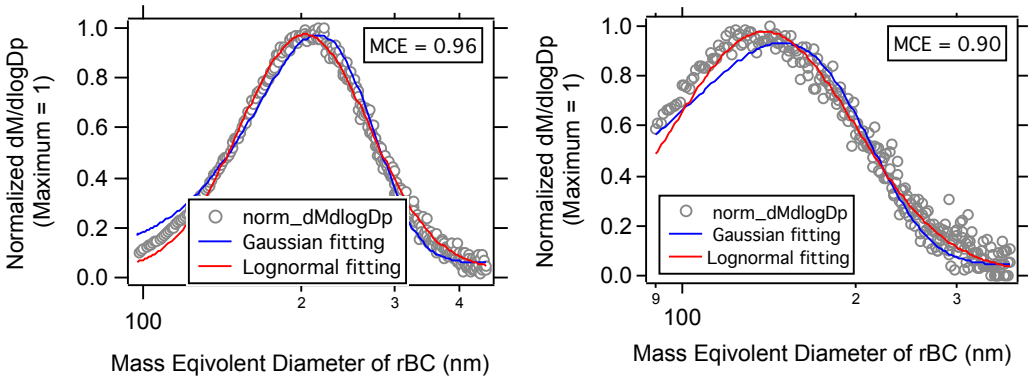

Figure 1 Gaussian and lognormal fitting for normalized mass size distribution of rBC for flaming- (left) and smoldering- dominant case (right).

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.

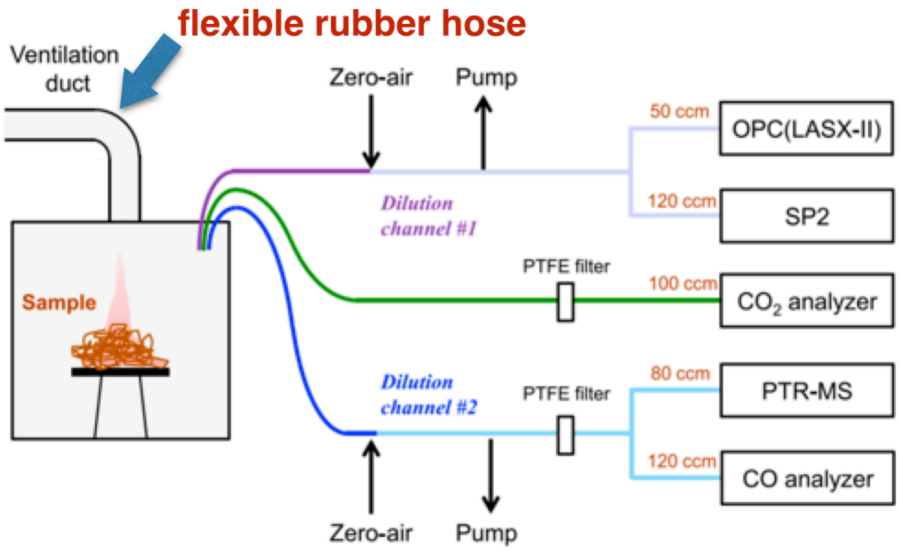

Figure 3. A schematic diagram of the laboratory biomass burning experiment

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.

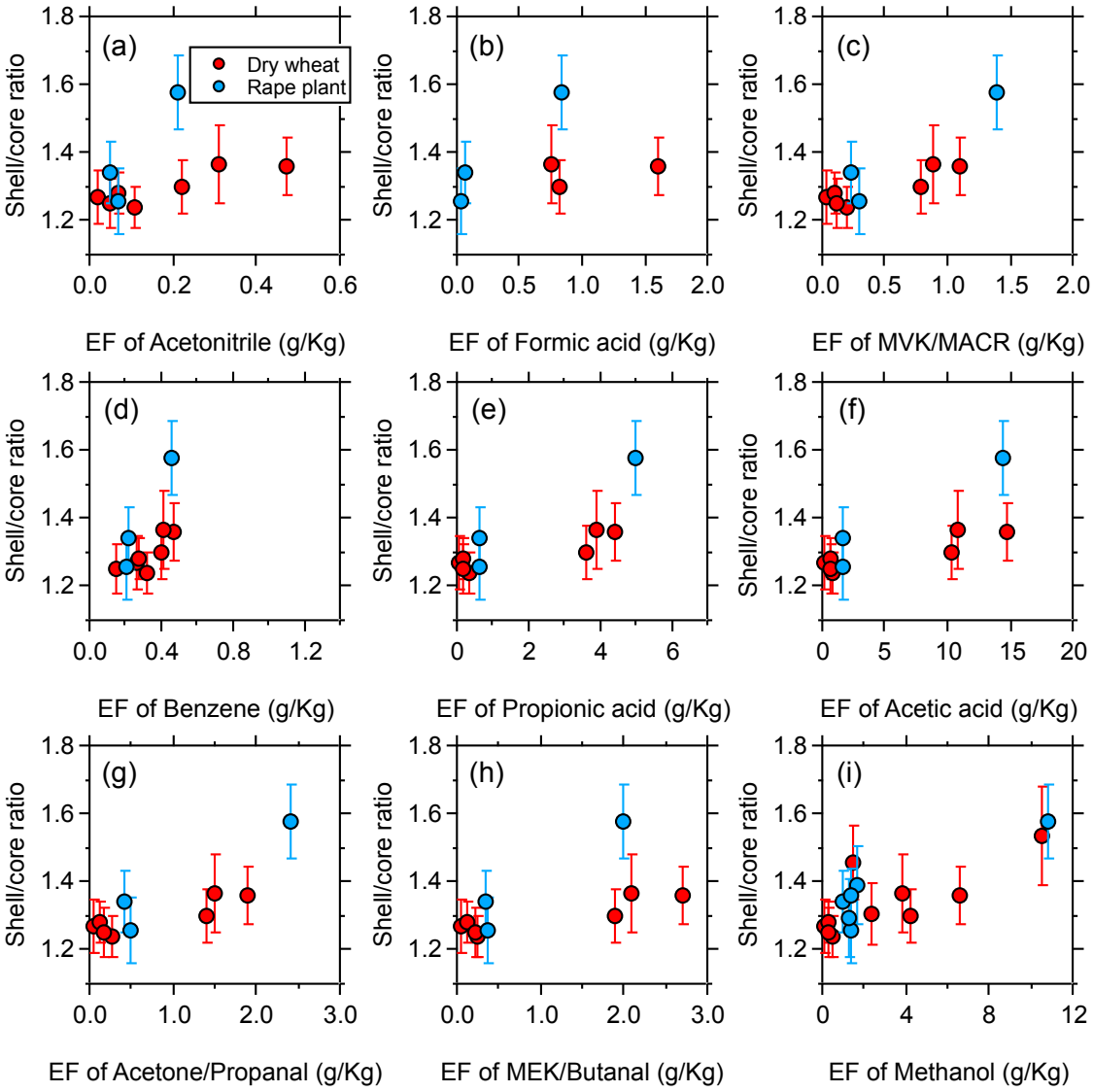

Figure 6. Variations in the shell/core ratios of rBC particles with MED = 200 ±10 nm as a function of the emission factor of each experiment. Here, EF is defined as the amount of each compound released per unit amount of dry fuel consumed. The red, green and blue colors indicate the dry wheat straw,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